RESULTS AND DISCUSSION

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Evaluation of the Three Base Lube Oils:

1- Physico-chemical characteristics of the three base-lube oils:

The physico-chemical characteristics of the three base oils used in this work were determined using standard method of analysis. The results, are represented in table 1 . The three base lube oils are characterized by their low pour points (-6.0 to -8.0). It is clear that the viscosity and viscosity index, aniline point, ash content and carbon residue increase with increasing the molecular weight, while the reverse occur for nitrogen content. Results obtained in tables 1 and 2 indicate that base lube oil No. 2 has the highest total nitrogen content, while it has the lowest mean molecular weight.

2- Component and Hydrocarbon Types In The Three Base Lube oils.

The three base oils were separated into their hydrocarbon types using silica gel column chromatography. Results are shown in table 1 .

The saturated hydrocarbons represent the major type, being (70 %) and (66 %) in the base lube oil No. 1 and base lube oil No. 2 respectively, while the monocyclic aromatic hydrocarbons being (52 %) constitute more than half of the base lube oil No. 3.

The base lube oil No. 2 has a higher percent of bicyclic aromatic hydrocarbons than the other two base lube oils, while base lube oil No. 3 has a lower percent of polycyclic aromatics than the other two base lube oils.

3- Nitrogen Types In The Three Base Lube Oils:

Results given in table 2 , indicate that the percentage of total nitrogen content increases with decreasing of molecular weight. The percent distribution indicates that the strongly basic nitrogen decreases with decreasing of molecular weight and the reverse is true for weakly basic and non-basic nitrogen type.

It is clear that the strongly basic nitrogen represent the major content in the three base lube oils.

4- Sulphur Tpes In The Three Base Lube Oils:

Inspecting the results of sulphur type analysis as shown in table 2 , it can be deduced that the three base lube oils are characterized by their low sulphur content (0.30 - 0.77 %). Mercaptans are absent in all base lube oils. Base lube oil No. 3 has a higher percent of aliphatic monosulphide while base lube oil No. 1 has a higher percent of aromatics monosulphide and higher percent of disulphides.

5- Structural Group Analysis of The Three Base Lube Oils:

The structural group analysis of the three base lube oils were determined using the n-d-M method. Results are shown in table 3. The three base lube oils are characterized by their high paraffinic carbon percent (57 - 61%). The aromatic carbon percentage is more or less the same in the three base lube oils (9 - 10.g %). Oil No. 2 has a lower aromatic rings (0.62 %) and higher naphthenic ring (2.01 %).

Evaluation Effect of Metal Catalysts On Oxidation of The Three Base Lube Oils.

The oxidation of lubricating oils means oxidation reaction between gaseous oxygen and lubricants. Oxidation test have been devised involving metallic catalysts. Copper, iron and cobalt have been selected for this study as well recognized catalyst whose occurence in engines is almost invariables. The effect of these metals has been investigated by determining the rate of accumulation of oxidation of reaction products, or by determining the change of certain physical constants of the oxidized oils as increase in kinematic viscosity, total acid number, carbonyl groups and insoluble materials.

Results listed in tables 4-15 and represented graphically in figures 1-36 show the effect of these catalysts on the oxidation properties of the three tested base oil samples.

1- Effect Of Copper Catalyst On Oxidation of The Three Base Lube Oils:

a- Effect of dissolved and solid copper catalyst on Kinematic Viscosity of The Three Base Lube Oils.

Figures 1-4 indicate that the kinematic viscosity increases with increase the duration time of

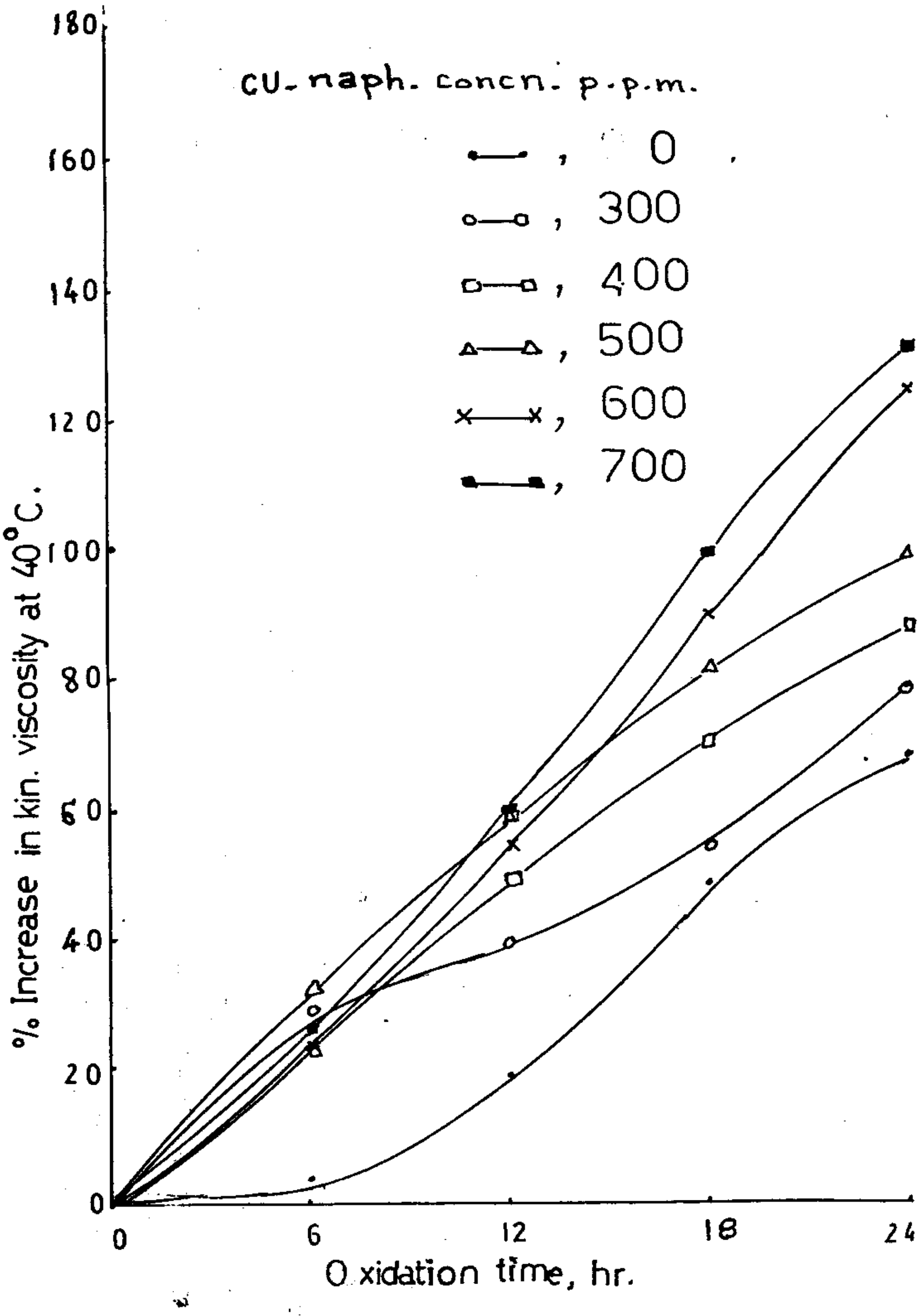


Fig.(1): Effect of oxidation of base oil No I on percent increase in kinematic viscosity at 40°c using copper naphthenate as catalyst and temperature 150°c.

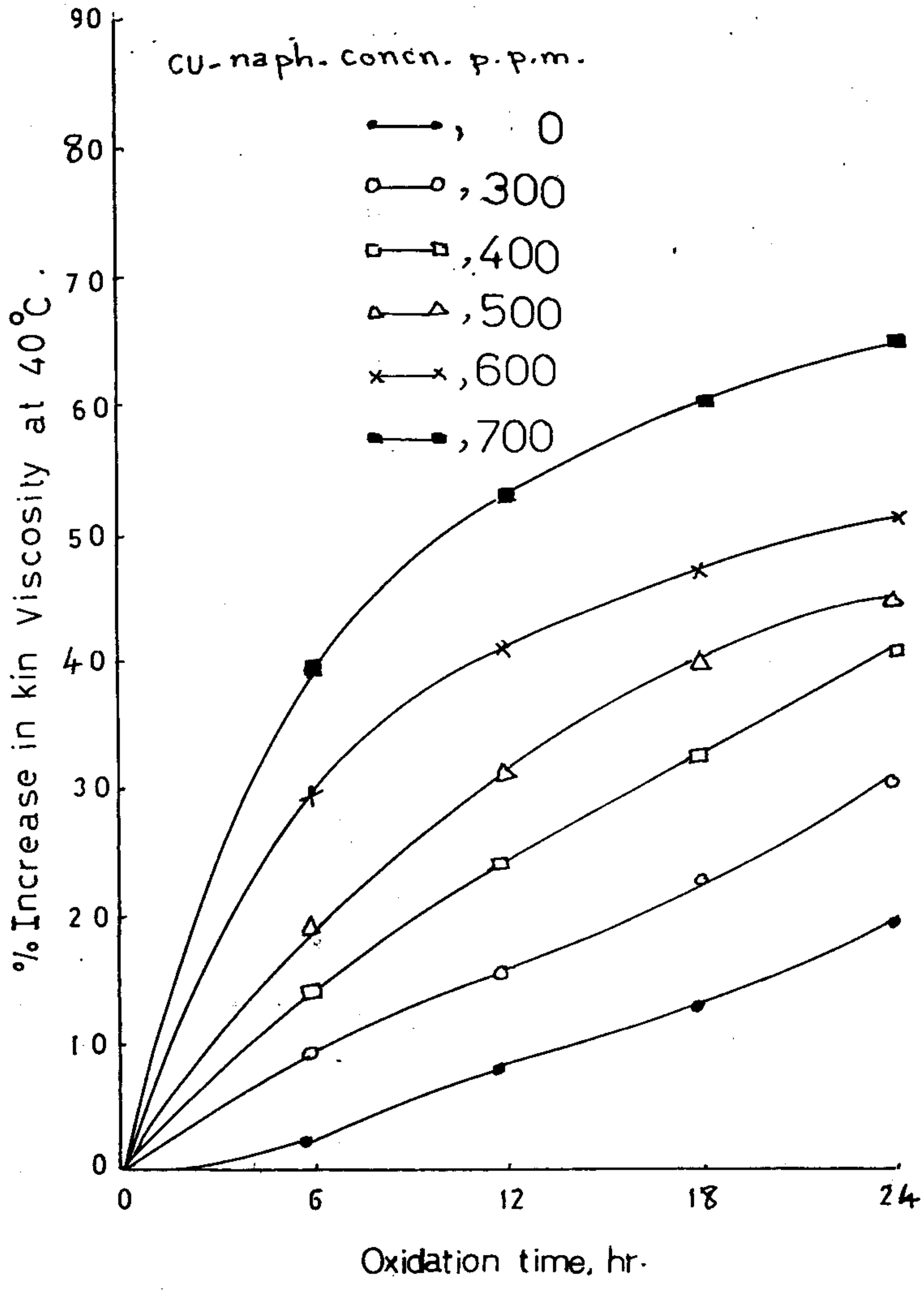


Fig.(2): Effect of oxidation of base oil No-2. percent increase in Kinematic Viscosity at 40 °C using copper naphthenate as catalyst and temperature 150 °C.

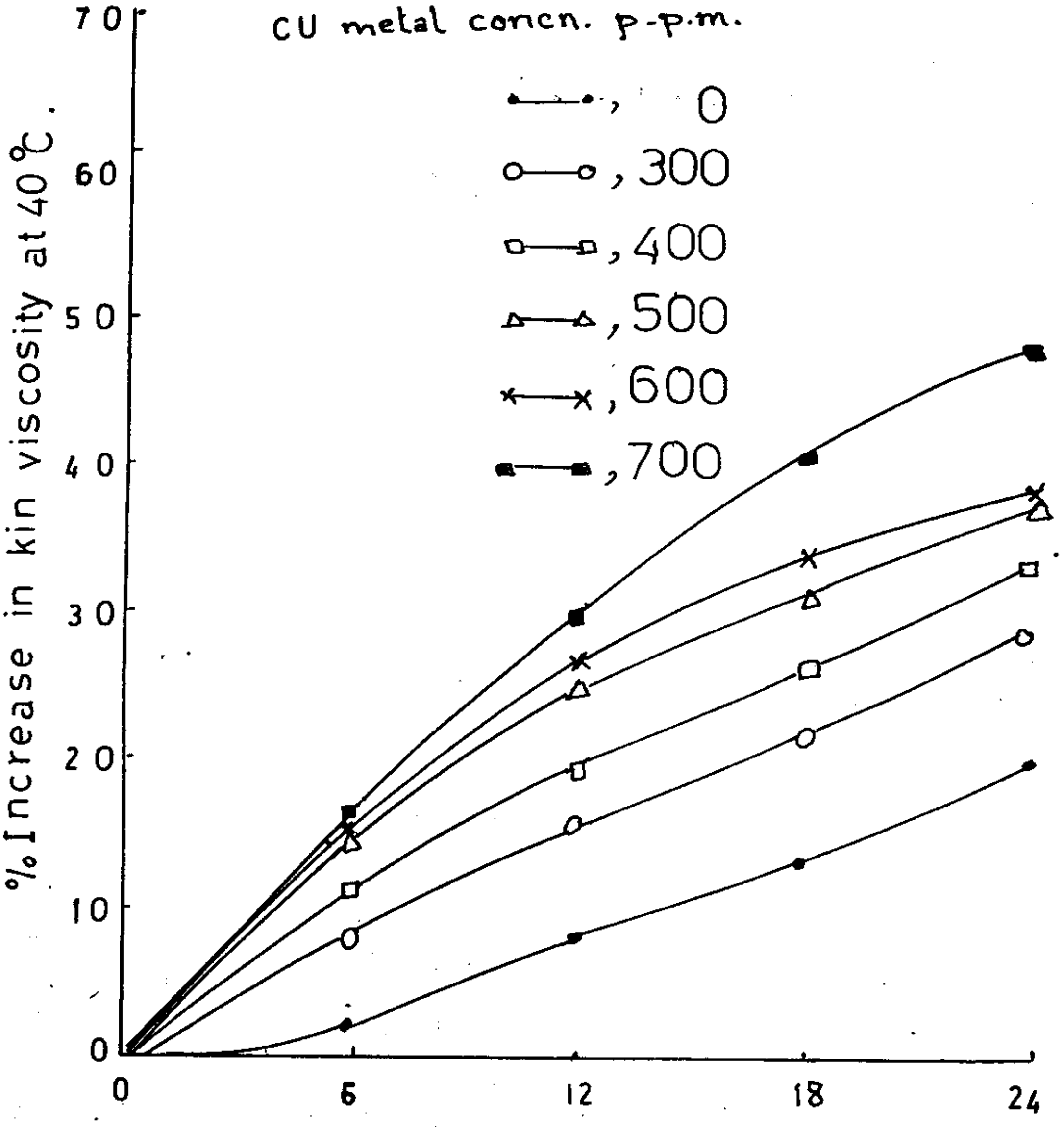


Fig.(3). Effect of oxidation of base oil No-2-on percent increase in Kinematic Viscocity at 40°C using copper metal as catalyst and temperature 150°C.

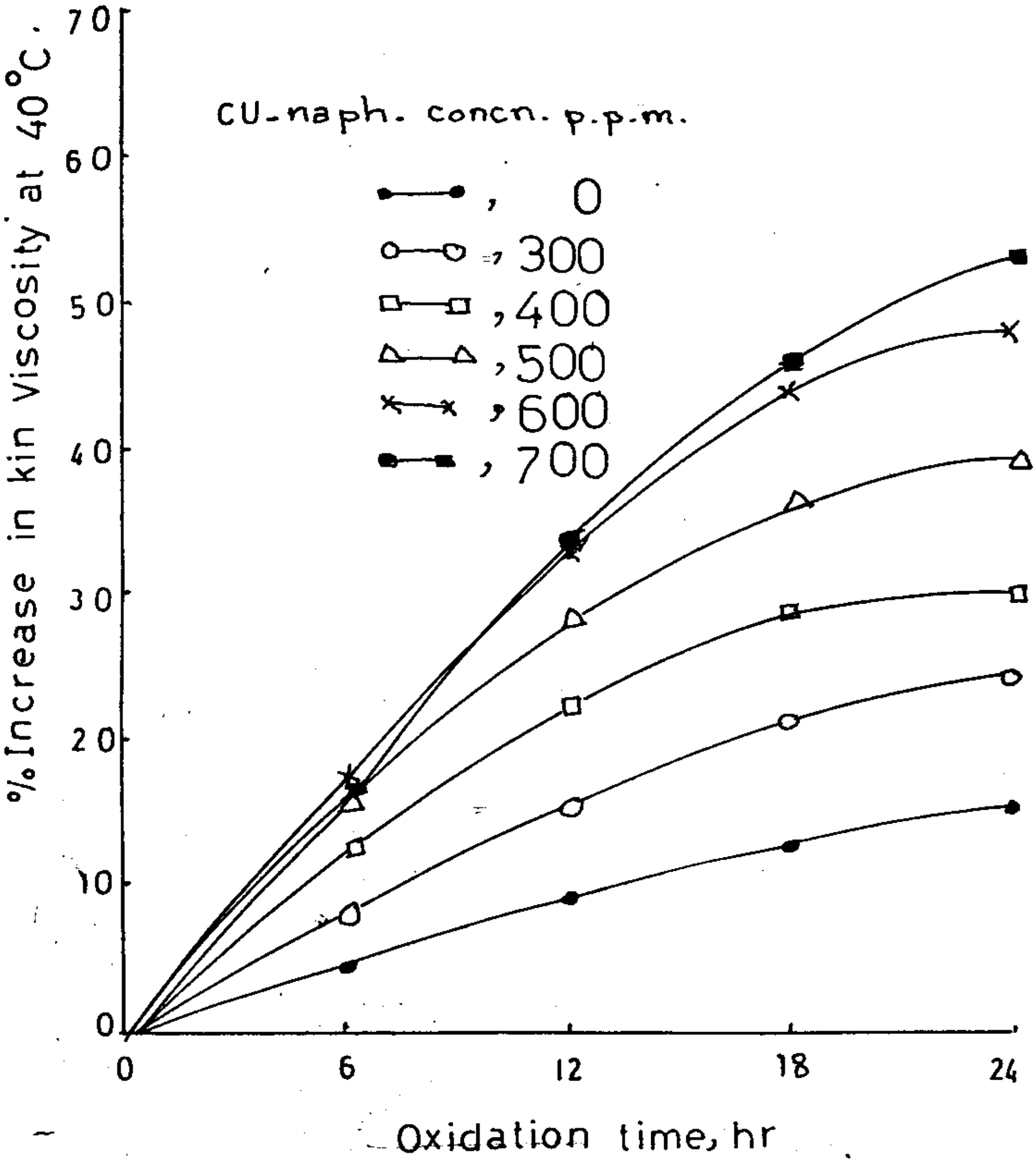


Fig.(4) **Effect of oxidation of base oil No. 3 on percent increase in kinematic viscosity at 40°c using copper naphthenate as catalyst and temperature 150°c.**

the test in all stage of oxidation for the three base lube oils. It is found that the presence of copper as catalyst reduce the induction periods (during which the rate of oxidation is relatively low) from 4 and 2 hrs reduced to zero hr. in the three base lube oils respectively as shown in Figs. 1-4.

In the lower stage of oxidation, the kinematic viscosity increased rapidly and the rate is higher in base lube oil No. 1 than the other two base lube oils, but at higher concentration of copper catalyst the rate of increase in kinematic viscosity is higher in base lube oil No. 2, Fig. 2.

At higher stage of oxidation the rate of increase in kinematic viscosity decreases with time and it is higher in base lube oil No. 1 than the other two base lube oils because it contains a higher percent of paraffinic constituents about 70 %, table 1, Fig. 1.

This is mainly depends on the chemical composition of the three base lube oils, and the activity and concentration of the catalysts.

Copper is the most active catalyst at low ratios of surface to oil volume and at low temperature below 180°C(111).

During oxidation of lubricating oils in presence of catalyst, peroxides and acids are formed.

The relative proportion of different products depends obviously on the oxidation conditions. The acids formed during the oxidation are condensed forming resins and sludge and at high temperature asphaltenes are formed.

Some of these products are soluble or partially soluble in the oil and increase the thicking of the oil, therefore, the viscosity increases and it is generally accompanied by increase in total acid number and **insolubles.**

Figs. 2 and 3 which represent the percent increase in kinematic viscosity using copper naphthenate and copper metal as catalyst for base lube oil No. 2, indicates that the percent increase in kinematic viscosity using copper naphthenate is higher than in case of using copper metal in the different stage of oxidation. This is mainly due to the effect of soluble metals because their ions react directly with oxidation products forming soaps. But solid metal catalyst is first transformed into oxides before becoming reactive toward the organic acids, or whether the metals are first carried into solution by the free radicals from peroxide decomposition is still undecided. This would means that the acceleration of oxidation is directly caused by the dissolved metals.

Also, this is probably a function of the ability of the oil either to remove it from solution by precipitation or to render it inactive by the formation of inert metal complexes.

b- Effect of Dissolved and Solid Copper Catalyst on Total Acid Number of The Three Base Lube Oils.

The effects of copper as catalyst on total acid number are listed in tables 7-9. The percent increase in total acid number is represented in Figs. 5-8.

All figures indicate that total acid number has increased with time in all stage of oxidation and the induction periods reduced from (6, 3 and 1 hrs.) to zero for three base lube oils respectively. In the early stage of oxidation the rate of increase in total acid number is higher than in the higher stage of oxidation. This may be attributed to the fact that the copper catalyst easily soluble in the oil in the initial stage of oxidation and therefore, oxygenated products increased by increase copper solubility.

So the presence of copper catalysts increases the harmful effect on the deterioration of the oil properties, and also increases the total acid number.

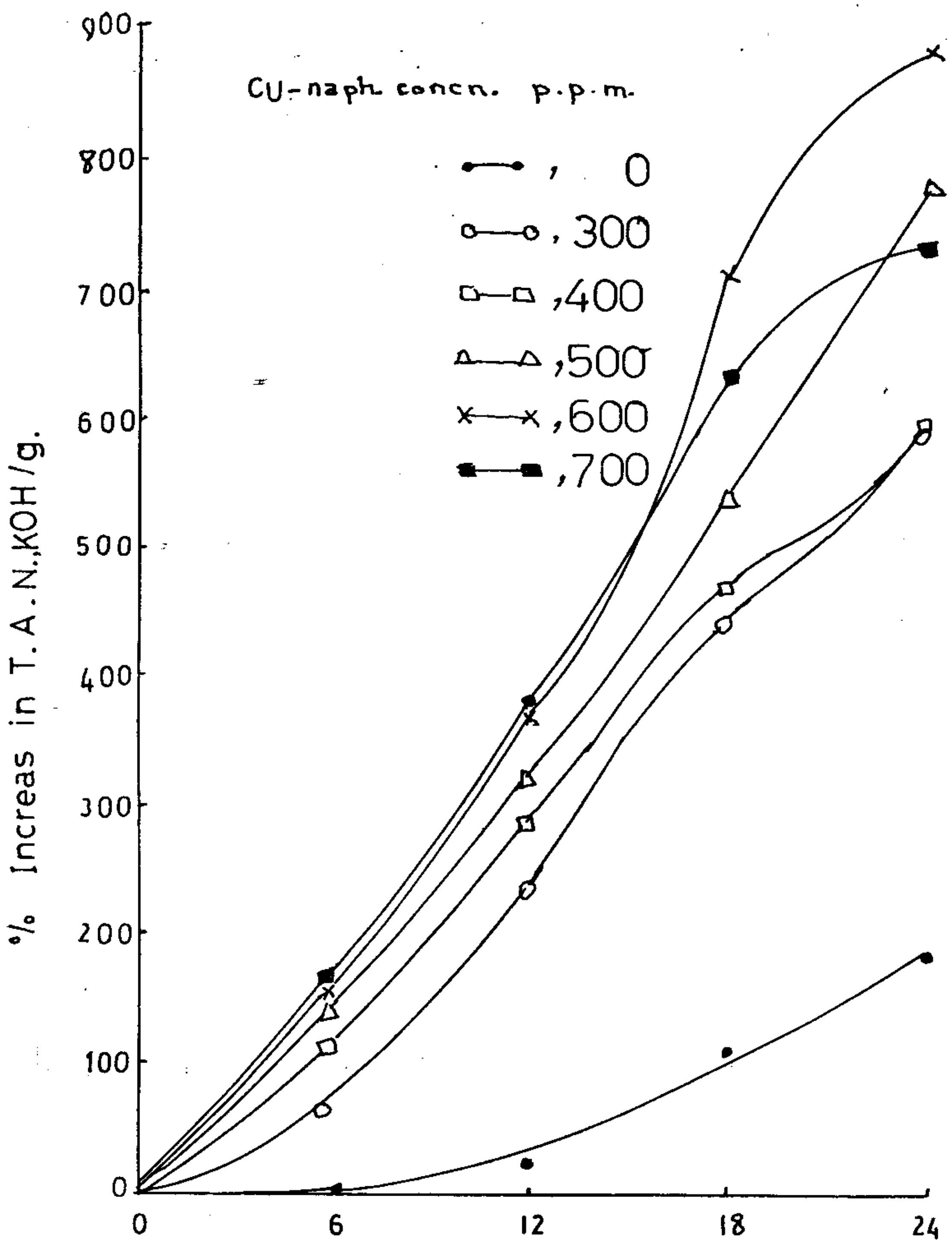


Fig. (5). Effect of oxidatin of base oil No-1- on percent increase in total acid number using copper naphthenate as catalyst and temperature 150°c.

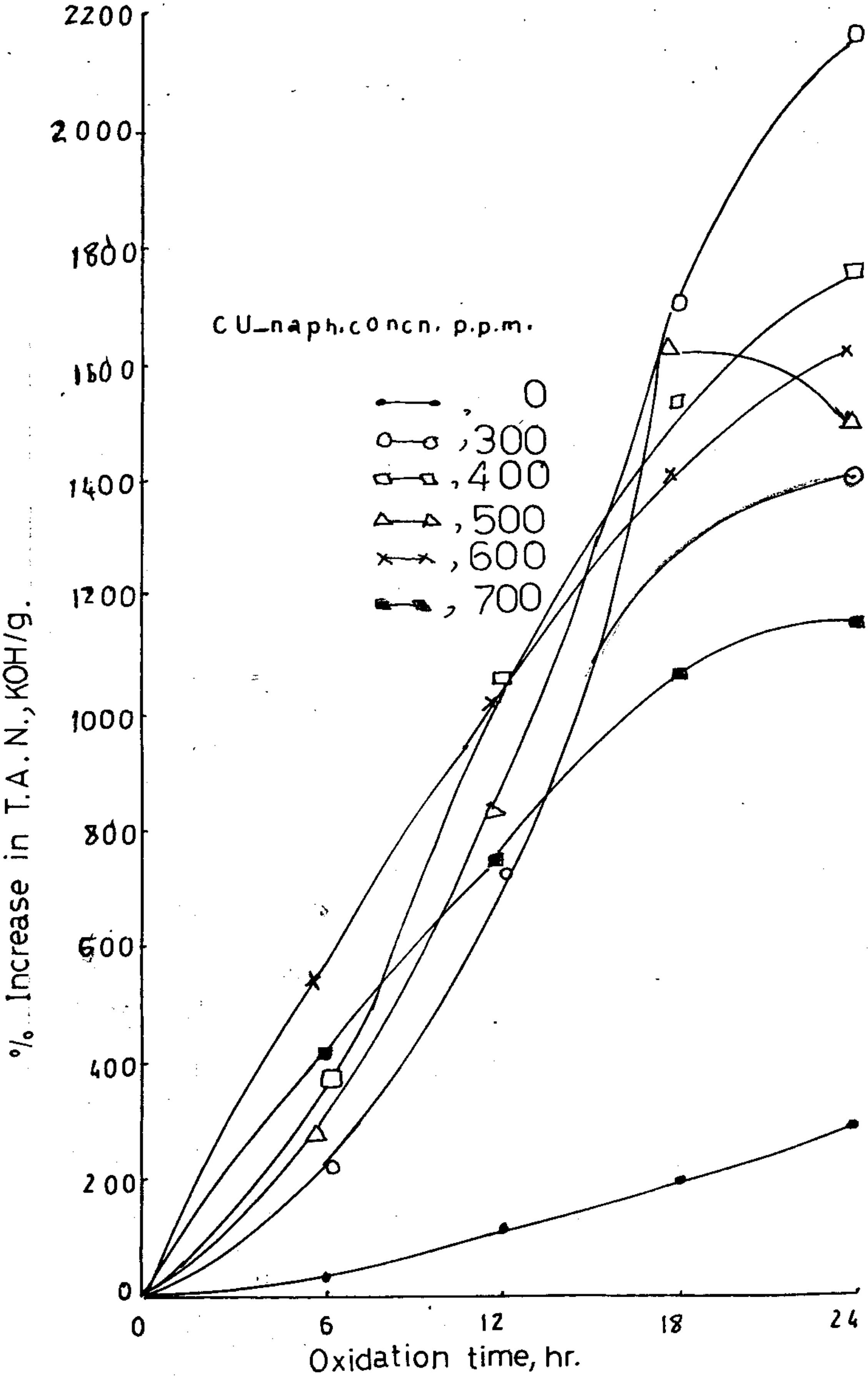


Fig.(6). Effect of oxidation of base oil No 2 on Percent increase in total acid number using copper naphthenate as catalyst and temperature 150 °C

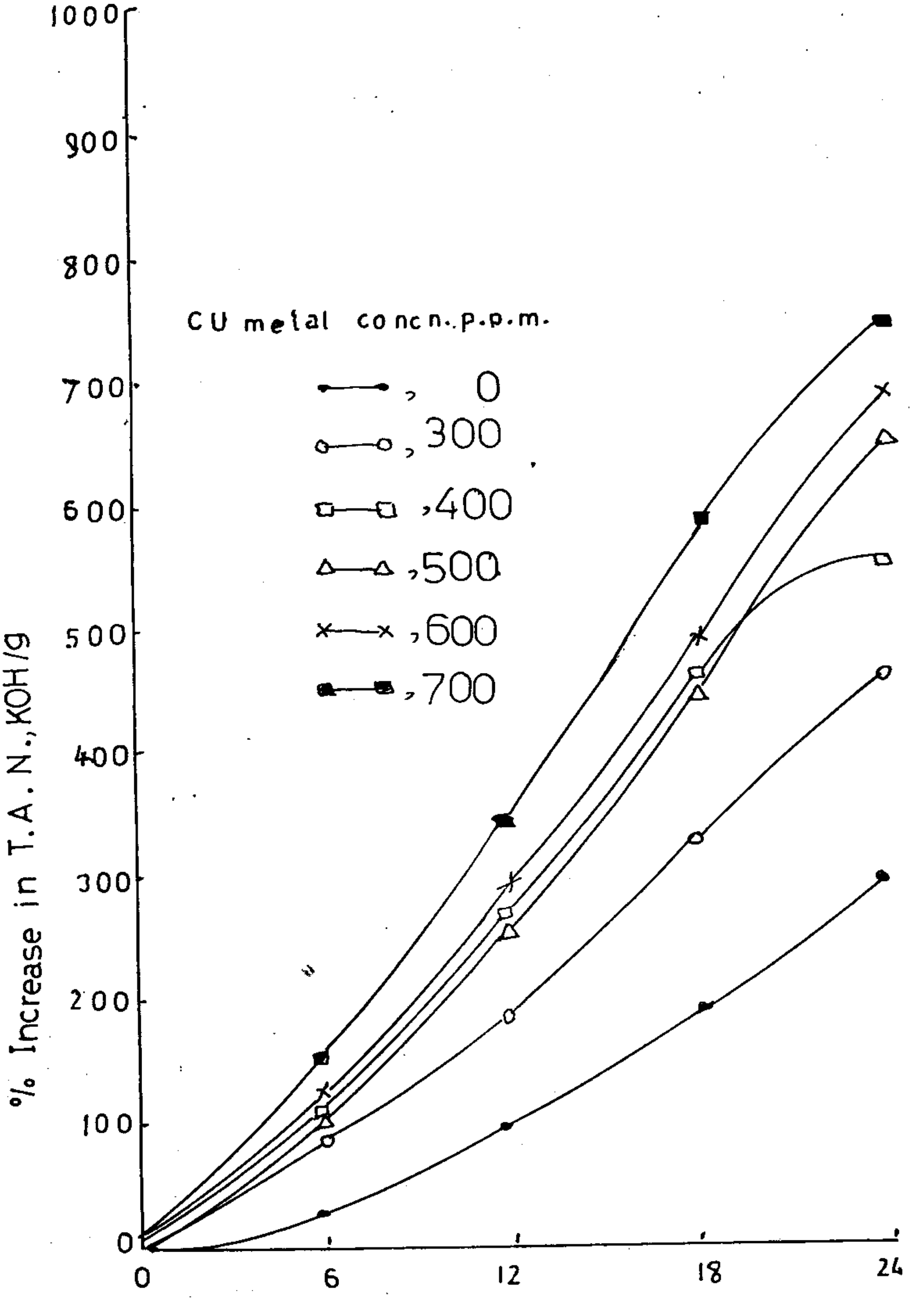


Fig.(7). Effect of oxidation of base oil No-2-on percent increase in total acid number using copper metal as catalyst and temperature 150 °C

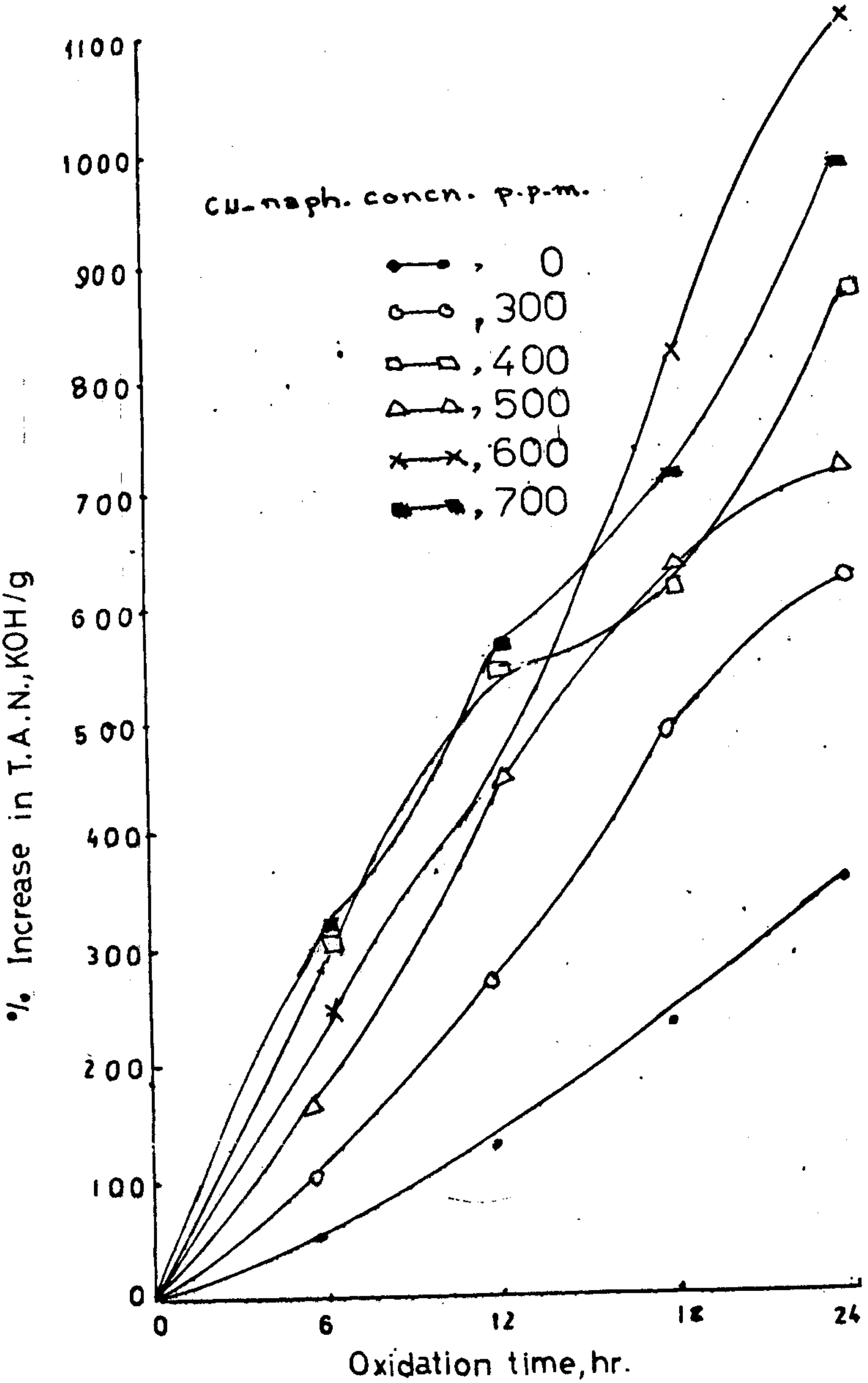


Fig.(8). Effect of oxidation of base oil No-3-on percent increase in total acid number using copper naphthenate as catalyst and temperature 150

In the early stage of oxidation Figs. 5-8 indicate that the percent increase in total acid number is lower in base lube oil No. 1 (75-175 %) than the other two base lube oils No. 2 and 3 (220-550, 9-160 and 100-225 %) respectively. This is mainly due to the change in chemical composition of the different base lube oils. Base lube oil No. 1 has lower percent of aromatics, which readily oxidized in the initial stage of oxidation than the other two base lube oils.

The increase in total acid number is either an indication with acidic combustion products or the result of oil oxidation.

The acids included in this determination may result in copper bearing corrosion.

Figs. 6 and 7 indicate that the percent of increase in total acid number is more in presence of copper naphthenate than copper metal (220 - 550 % and 90 - 160%) respectively.

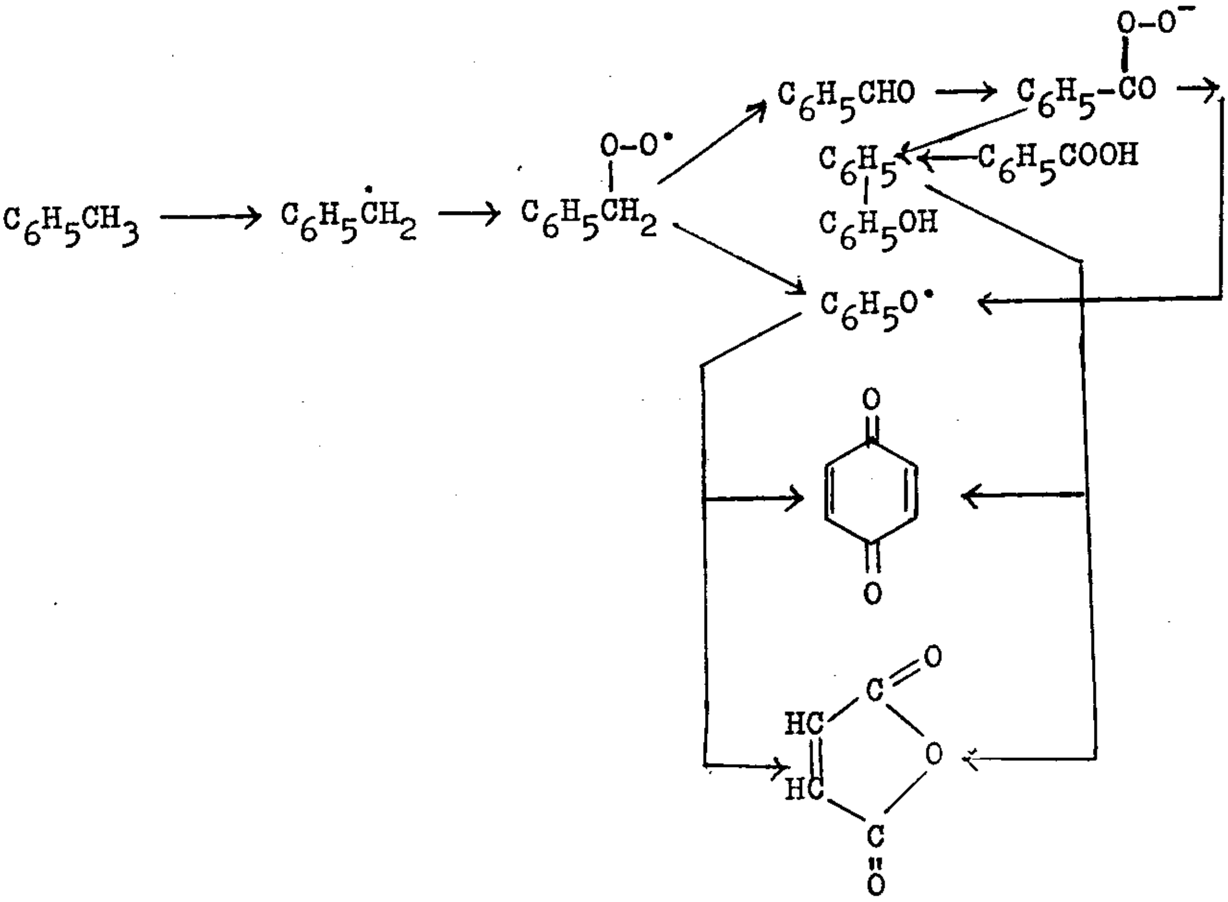
This is mainly due to the action of the metal in solution as salts which could be quite different from that of the bulk and massive metals.

Solid metal could has been coated very effectively or otherwise deactivated by some means (presence of nitrogen and sulphur compounds).

Fig. 6 indicates that at higher stage of oxidation, base lube oil No. 2 shows that the percent increase in total acid number is more at low concentration of catalyst (2150 %). This probably due to the dissociation of oxidation products and the presence of some copper ions.

During the oxidation reaction the catalyst do not remain unaltered, but pass through a cycle of valency changes, being converted initially to the higher valency state and after a short period of time reduced to the lower valency. The effect of these catalyst on the reaction rate may be explained by their capacity to initiate free radical formation, particularly by reaction with the hydroperoxides formed during the oxidation of hydrocarbons and the acid formed.

The following scheme for oxidation of toluene over a metal catalyst may serve as an example for oxidation of alkyl aromatics and aromatics.



c- Effect of Dissolved and Solid Copper Catalyst On Carbonyl Groups Content of The Three Base Lube Oils.

Figs. 9-12 which represent the rate of increase of carbonyl groups during oxidation for three base lube oils indicate that the presence of copper catalyst increases the rate of formation of carbonyl groups and the induction periods have been reduced from 4 and 2 to zero hrs. as given in figures.

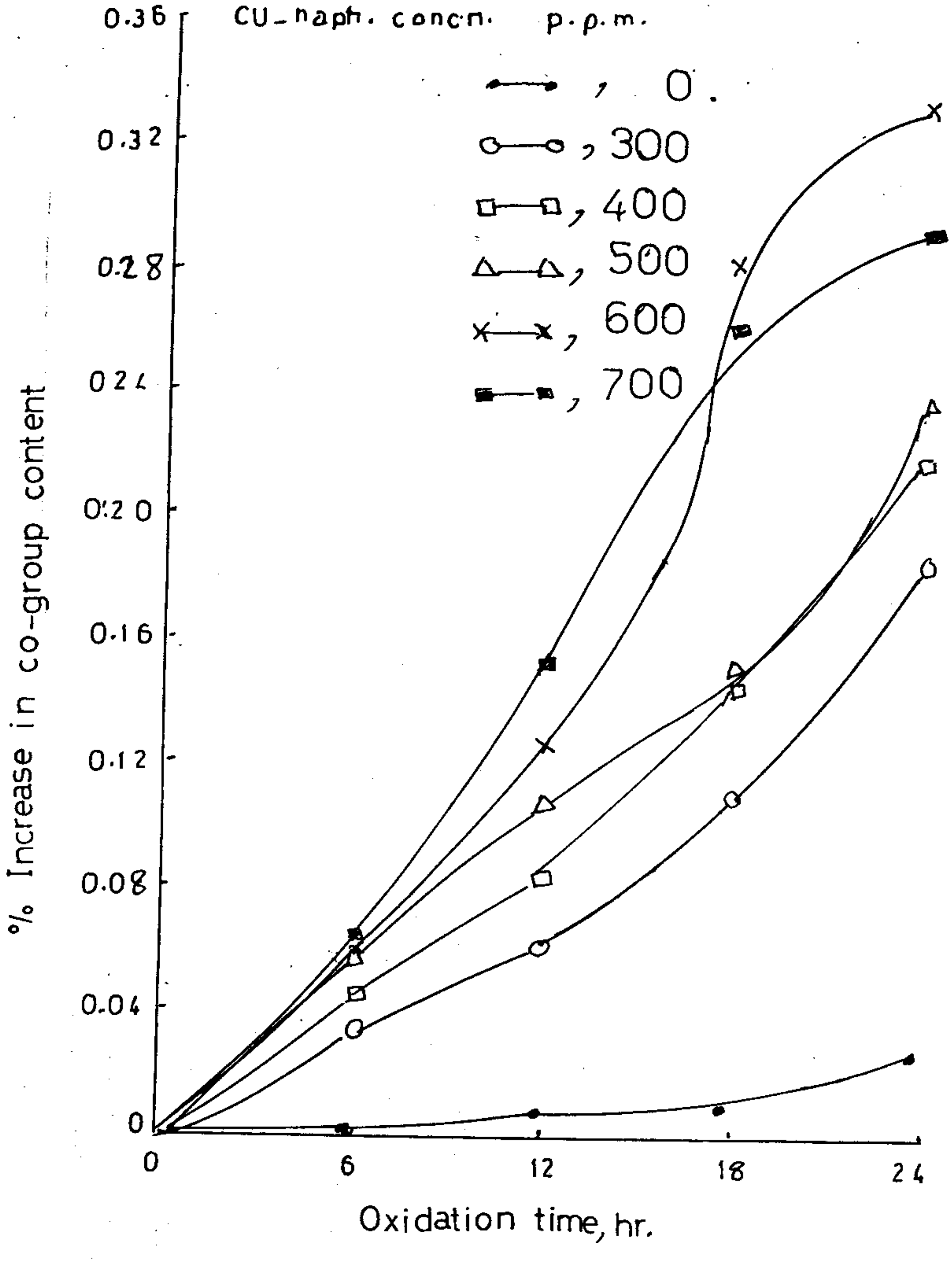


Fig.(9). Effect of oxidation of base oil No-1- on percent increase in carbonyl group content using copper naphthenate as catalyst and temperature 150 °C

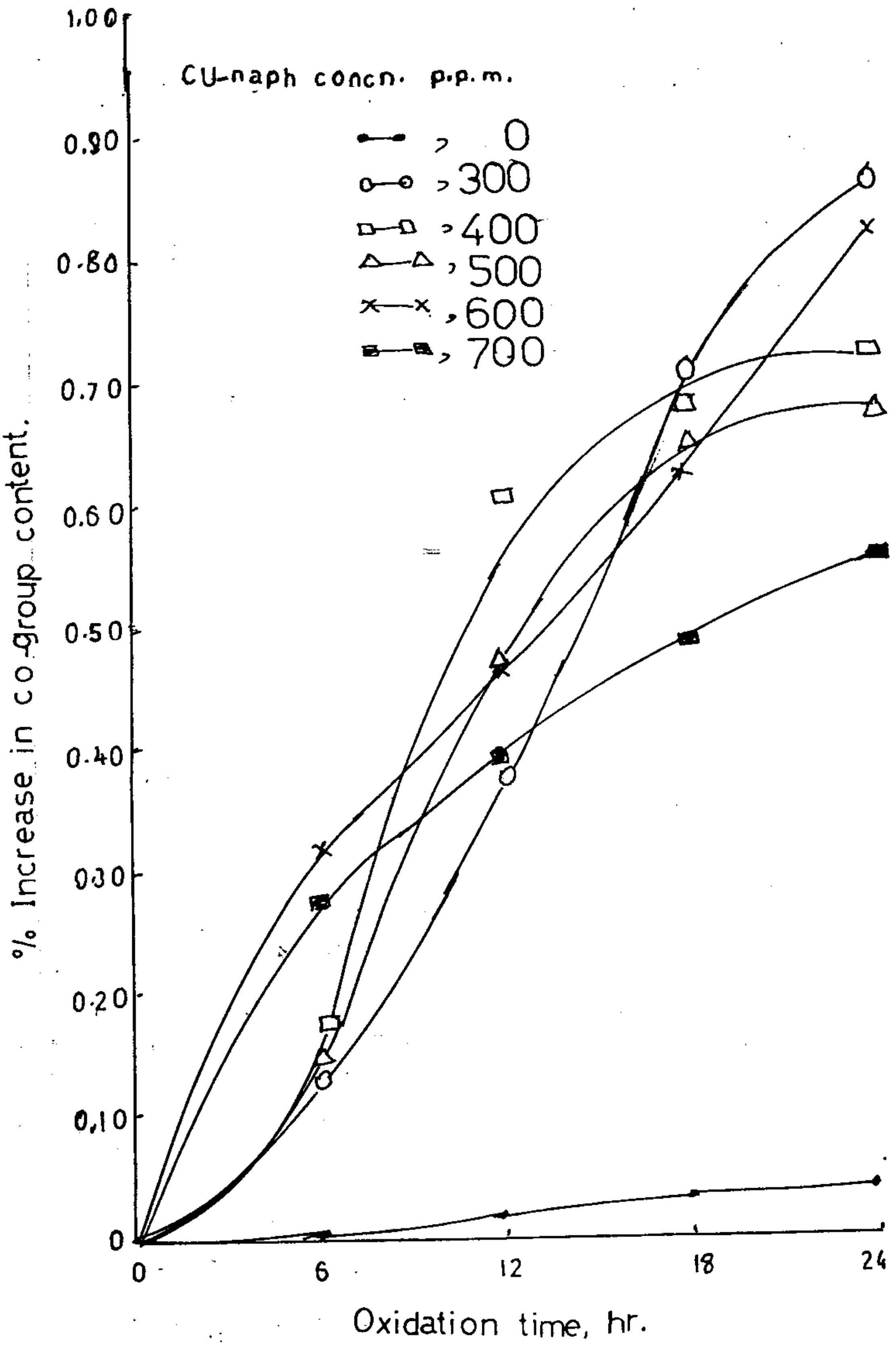


Fig.(10). Effect of oxidation of base oil No-2-on percent increase in carbonyl group content using copper naphthenate as catalyst and temperature 150 °C

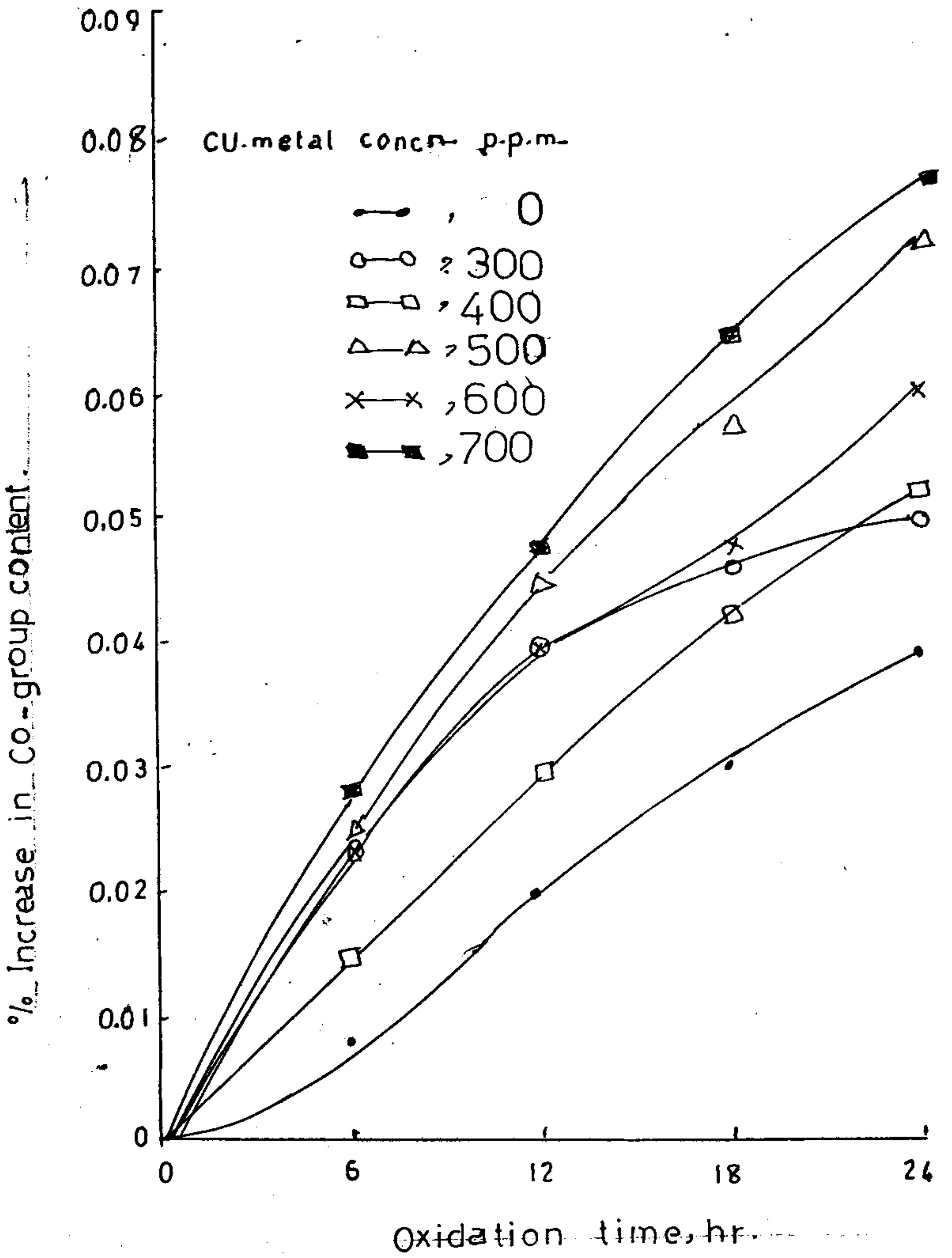


Fig.(11). Effect of oxidation of base oil No. 2 on percent increase in carbonyl group content using copper metal as catalyst and temperature 150°c.

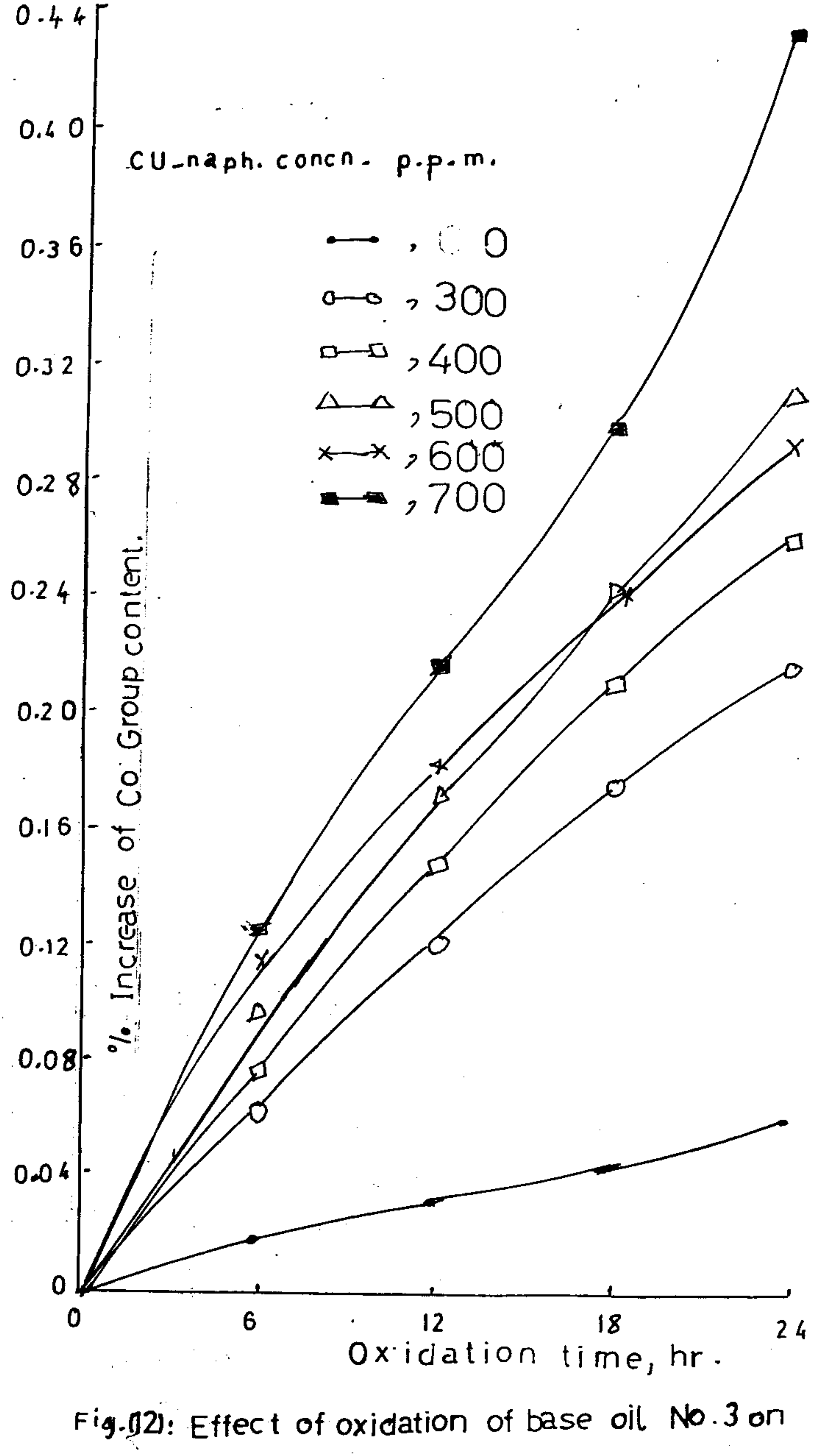


Fig.(12): Effect of oxidation of base oil No.3 on percent increase in carbonyl-group content using copper naphthenate as catalyst and temperature 150°c.

In base oil No. 1, Fig. 9, at lower concentration of copper catalyst the increase in the rate of formation of carbonyl groups is slowly in the early stage of oxidation and rapidly in the higher stage of oxidation and the reverse occurs at higher concentrations due to thedissociation of the oxidation products.

Results obtained indicate that metal catalyst reduce the induction period for initiation of hydrocarbon and in certain cases accelerate the decomposition of certain intermediate hydroperoxides. These reactions indicate that the metal catalyst undergoes a change in valence state, i.e. one electron transfer reactions.

$$ROOH + M^{2+} \longrightarrow RO^{\bullet} + OH^{-} + M^{3+} \quad \ldots\ldots\ldots \quad (1)$$

$$ROOH + M^{2+} \longrightarrow RO^{-} + \dot{O}H + M^{3+} \quad \ldots\ldots\ldots\ldots \quad (2)$$

The metal catalyst is usually placed in the system in its lower state, and the hydroperoxide converts it to the higher oxidation state. So that the rate of increase in the carbonyl groups in the higher stage of oxidation is higher as given in Figs. 9-12.

Bawn(112,113) has suggested that the metal catalyst in its higher oxidation state functions as an oxidation initiators:

$$CH_3-CH_2-CH_2-CH_3 + M^{3+} \longrightarrow \dot{C}H_2-CH_2-CH_2-CH_3 + M^{2+} + H^+ \quad (3)$$

$$CH_3-CH_2-CH_2-CH_3 + M^{3+} \longrightarrow CH_3-\dot{C}H-CH_2-CH_3 + M^{2+} + H^+ \quad (4)$$

The system is not, of course as simple as pictured in these equations (3,4). The reactivity of the catalyst ion will be determined by the nature of the compounds present in the base lube oil.

There is considerable controversy in the literature(114,115). It has been suggested that the catalyst functions by placing radicals in the system which initiate chains by hydrogen abstraction.

$$ROOH + M^{3+} \longrightarrow RO_2^{\bullet} + M^{2+} + H^+ \; .... \; (5)$$

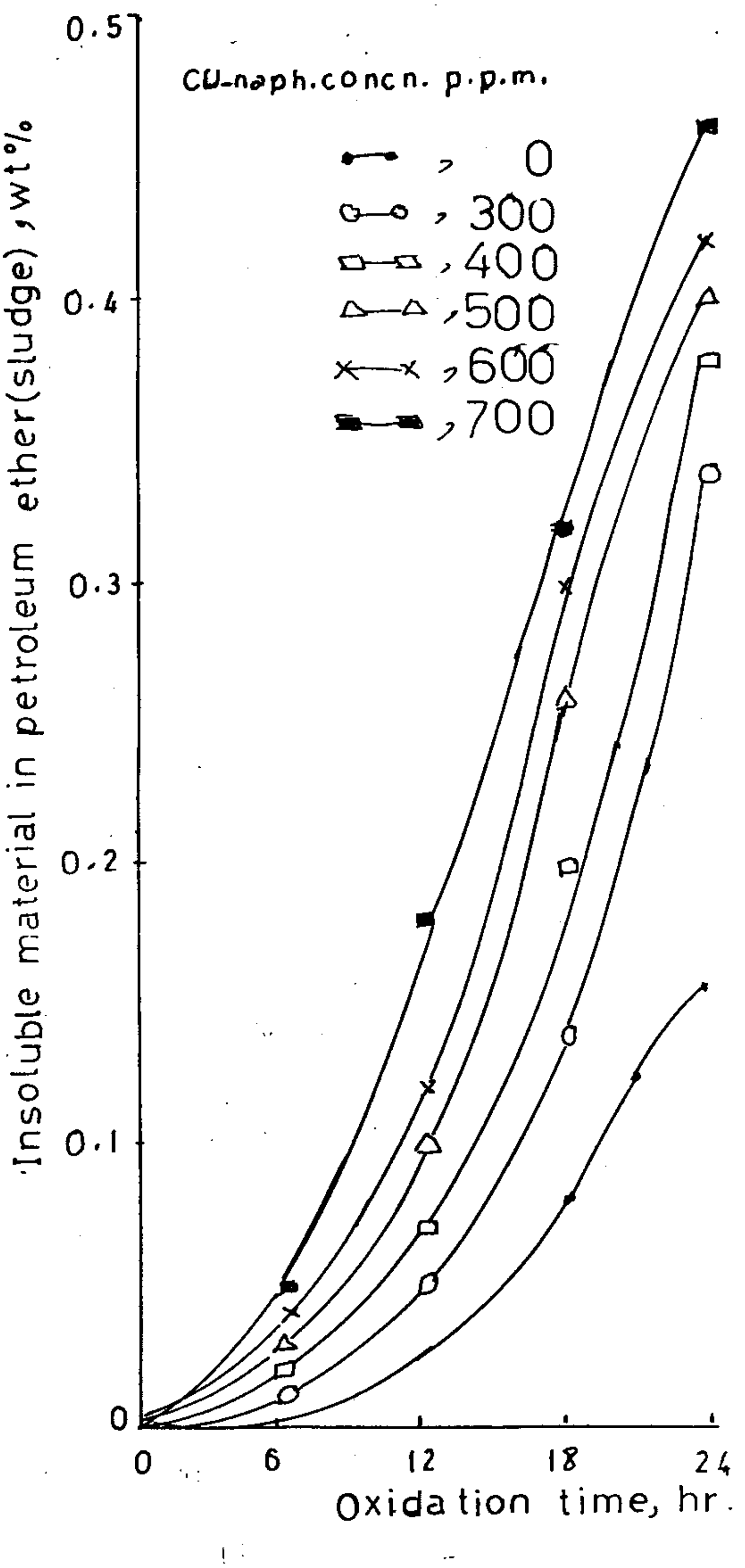
$$ROOH + M^{2+} \longrightarrow RO^{\bullet} + M^{3+} + OH^- \; .... \; (1)$$

It is evidence that metal catalysts transfer between its two oxidation state as given in Fig. 9, in which the rate of increase of carbonyl groups at higher concentrations of copper catalyst increases rapidly in the initial stage of oxidation and decreased in the higher stage of oxidation.

d- Effect of Dissolved and Solid Copper Catalyst on Insoluble Materials of The Three Base Lube Oils.

The petroleum ether insolubles include the insoluble materials in the oil and some oil soluble resinous materials (oxidized products) originating from external contamination. The effect of presence of copper catalyst on the insoluble in petroleum ether are listed in tables 13-15. The weight percent of insolubles with different concentration of copper catalyst against oxidation time is represented in Figs. 13-16. These Figs. indicate that the insoluble content increased with increase in oxidation time in all stage of oxidation. The three base lube oils are quite susceptible to catalyst. The catalytic susceptibility of the oils varies from catalyst to catalyst. Fig. 16 shows that the base lube oil No. 3 is more susceptible to catalyst and the percent of insolubles is higher in all stage of oxidation as compaired with the other two base lube oils (0.56 %). It is found that there is a relation between the amount of metal dissolved and the reactivity of the oil(111).

Results obtained from table 14 and graphically represented in Figs. 33 and 34 indicate that the increase in the quantity of soluble copper helps to increase the insoluble content and form a large quantity of deposits



Fig(13). Effect of oxidation of base lube oil No.1 on insoluble materials using different concentrations of copper naphthenate as catalyst and temperature 150°C.

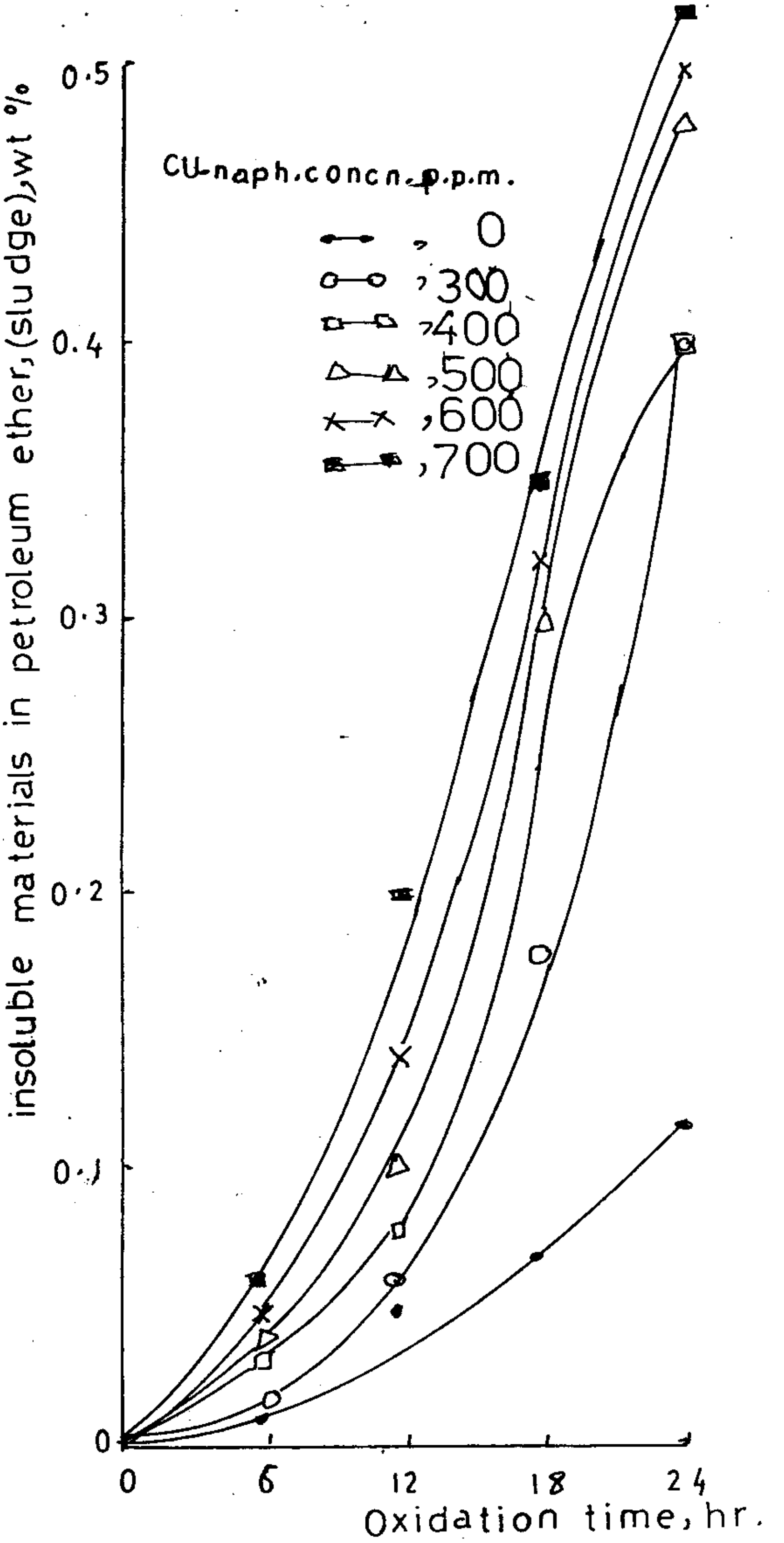


Fig.(14). Effect of oxidation of base lube oil No-2-on insoluble materials using different concentrations of copper naphthenate as catalyst and temperature 150°C .

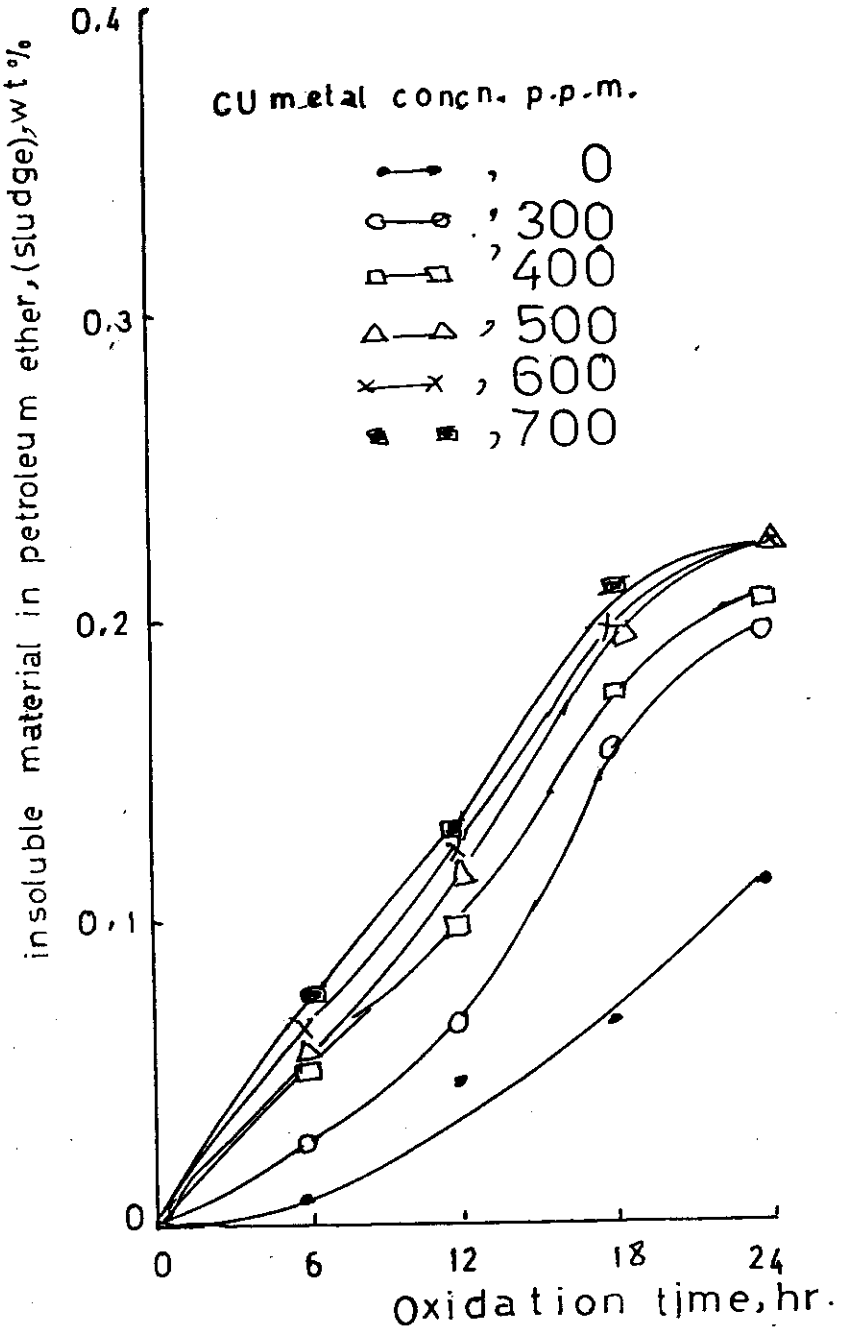


Fig.(15): Effect of oxidation of base lube oil No.2 on insoluble materials using diffecent concentrations of copper metal as catalyst and temperature 150°C

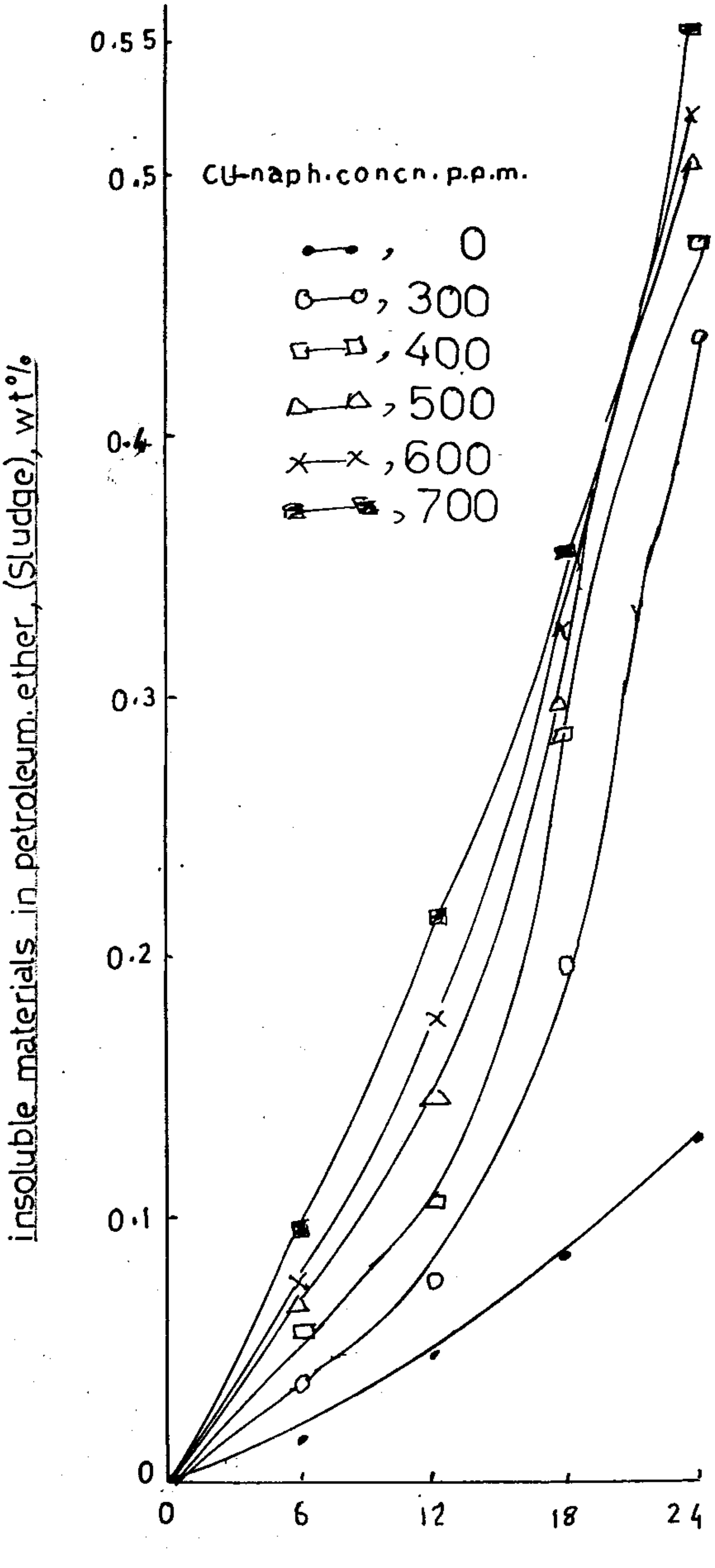


Fig.(16). Effect of oxidation of base lube oil No. on insoluble materials using different concentrations of copper naphthenate as catalyst and temperature 150°c .

and resins in short time.

This may be attributed to the fact that its cuprous oxide is more soluble in the oxidized oil, or, high ability of its ion to be soluble in oxidizing oil and its solubility increases with the increase in the time.

Fig. 15 in which copper metal is used as catalyst indicate that the rate of formation of insolubles increases slowly as compared with using copper naphthenate at given in Fig. 14, and the rate decreased in the higher stage of oxidation. This is mainly due to the fact that the naphthenic salts generally show a maximum catalytic activity which is particularly pronounced in the case of copper. The decreasing effectiveness of the metal catalyst with time is probably a function of the ability of the oil either to remove it from solution by precipitation as inactive sludge (lacquered) or to render it inactive by the formation of inert metal complexes.

Downing and co-workers(111) studied the problem of catalysis in an engine by successively selected metal parts, it is found that lacquered metal surfaces have little catalytic activity, and these surfaces freed of such surface film by rubbing.

2- Effect of Dissolved Cobalt Catalyst on Oxidation of The Three Base Lube Oils.

To study the evaluating effect of dissolved cobalt catalyst on the degree of oxidation of the three base lube oils, the change in physical properties such as kinematic viscosity, total acid number, carbonyl groups and insoluble materials are measured.

The results are listed in tables 4-15 and represented graphically in Figs. 17-28.

Cobalt naphthenate has a harmful effect on the oil properties but less than copper naphthenate because the latter more soluble than cobalt naphthenate.

1- Effect of Cobalt Naphthenate Catalyst on Kinematic Viscosity of The Three Base Lube Oils.

Figs. 17, 18 and 19 indicate that the kinematic viscosity increased with oxidation time in all stage of oxidation. The rate of oxidation is slowly in the early stage of oxidation than in the higher stage of oxidation.

The induction periods reduced from 4 and 3 to zero hrs. for base lube oils 1 and 2 respectively. This seems to depend on the solubility of the catalyst, and the catalyzed reaction can therefore be changed by varying

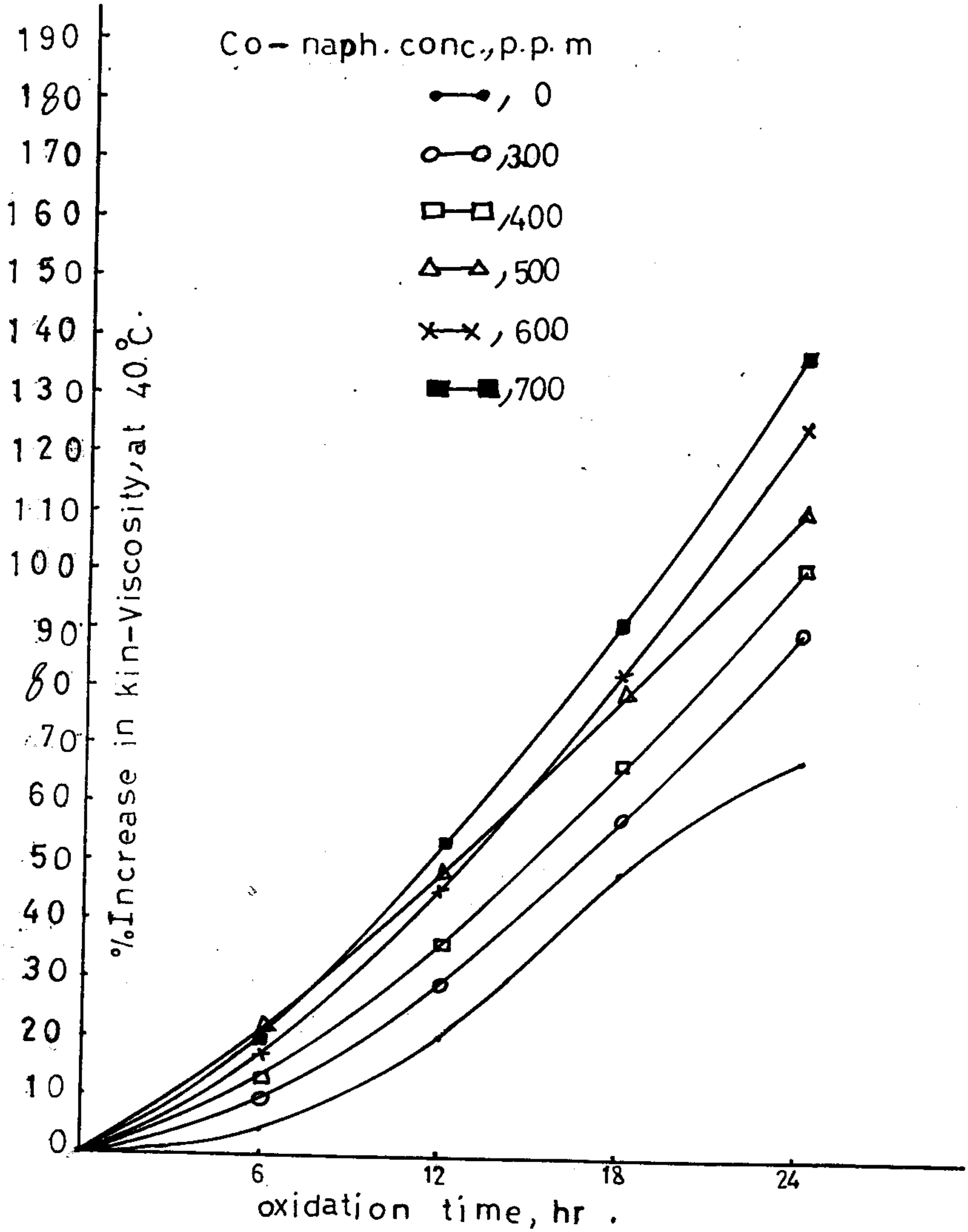


Fig (17) Effect of oxidation of base oil No.1 on percent increase in kinematic viscosity at 40°c using cobalt naphthenate as catalyst and temperature 150°c.

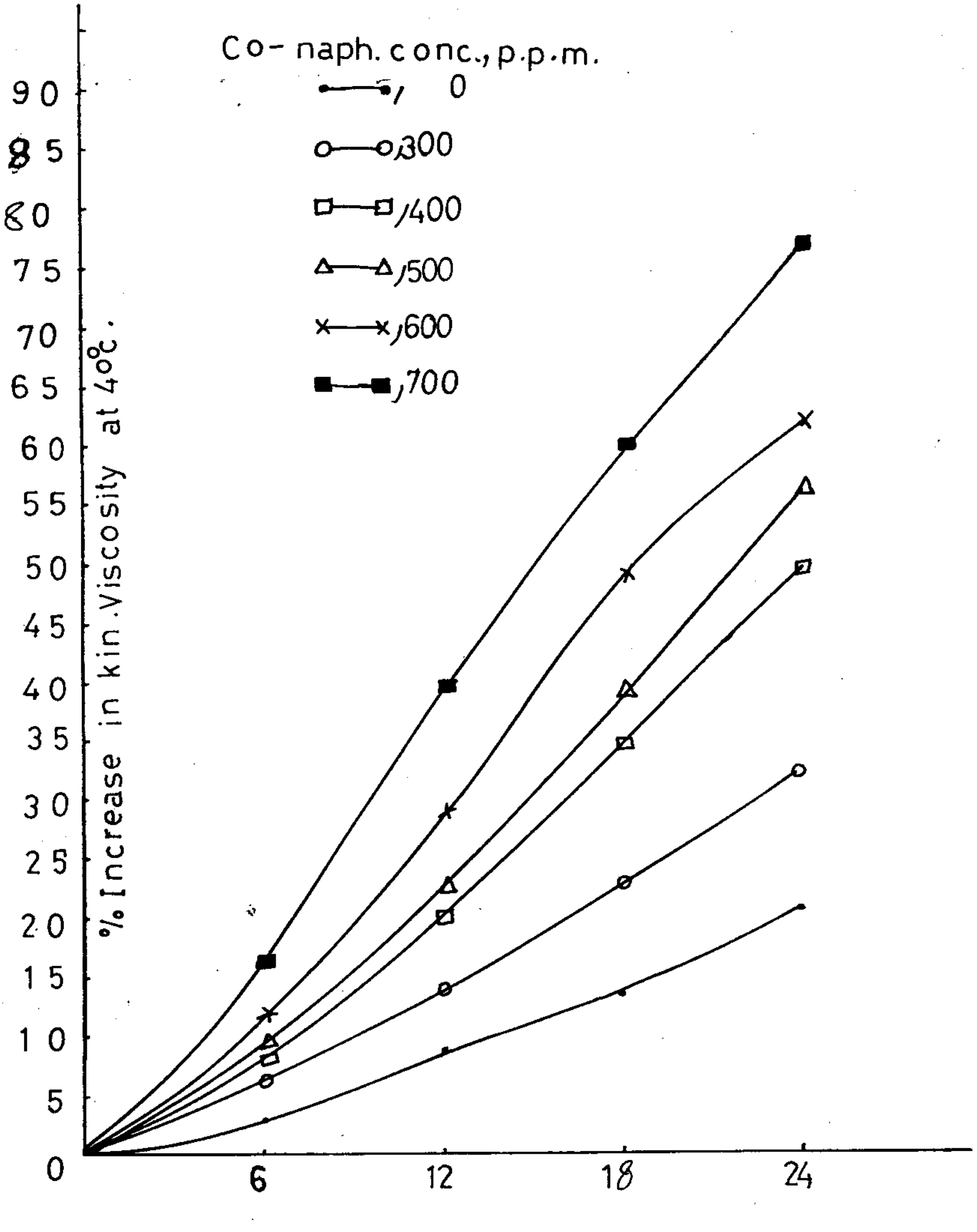


Fig (18) Effect of oxidation of base oil No. 2 on percent increase in kinematic viscosity at 40°c using cobalt naphthenate as catalys and temperature. 150°c.

concentration of reactant and products.

Figs. 17, 18 and 19 also indicate that the rate of increase in kinematic viscosity different from oil to oil which is attributed to difference in chemical composition of the three tested base lube oil samples. Base lube oil No. 1 has a higher percent of paraffinic constituents,(70 %) has a higher rate of increase at higher stage of oxidation (90-137 %) as given in Fig. 17. While base lube oil No. 3 (has a higher percent of aromatic components, 58 % and higher percent of sulphur content 0.77 %) has a lower rate of increase in the higher stage of oxidation, (24-64 %) as given in Fig.19.

2- Effect of Cobalt Naphthenate Catalyst on Total Acid Number of The Three Base Lube Oils.

Figs. 20, 21 and 22 indicate that the rate of oxidation increased with times. Fig. 20 indicates that the presence of cobalt naphthenate reduce the induction period from 6 to zero hrs., especially at higher concentrations. At higher stage of oxidation, the rate of increase in total acid number increased rapidly at lower concentrations. This means that the catalyst thus has a dual role during an oxidation reaction, namely an initiating function (which influences the rate of the

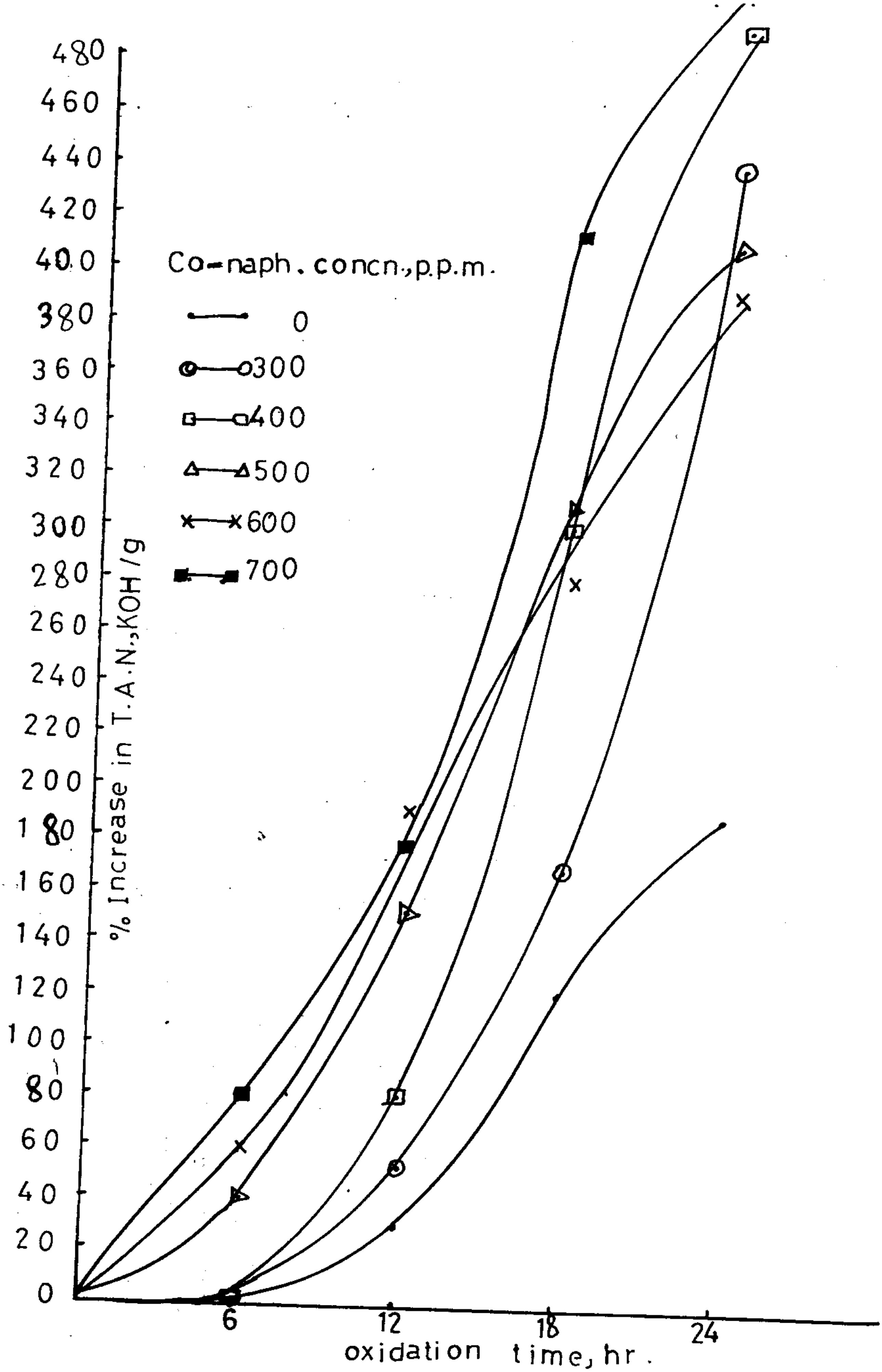


Fig (20): Effect of oxidation of base oil No. I on percent increase in total acid number using cobalt nephthenate as catalyst and

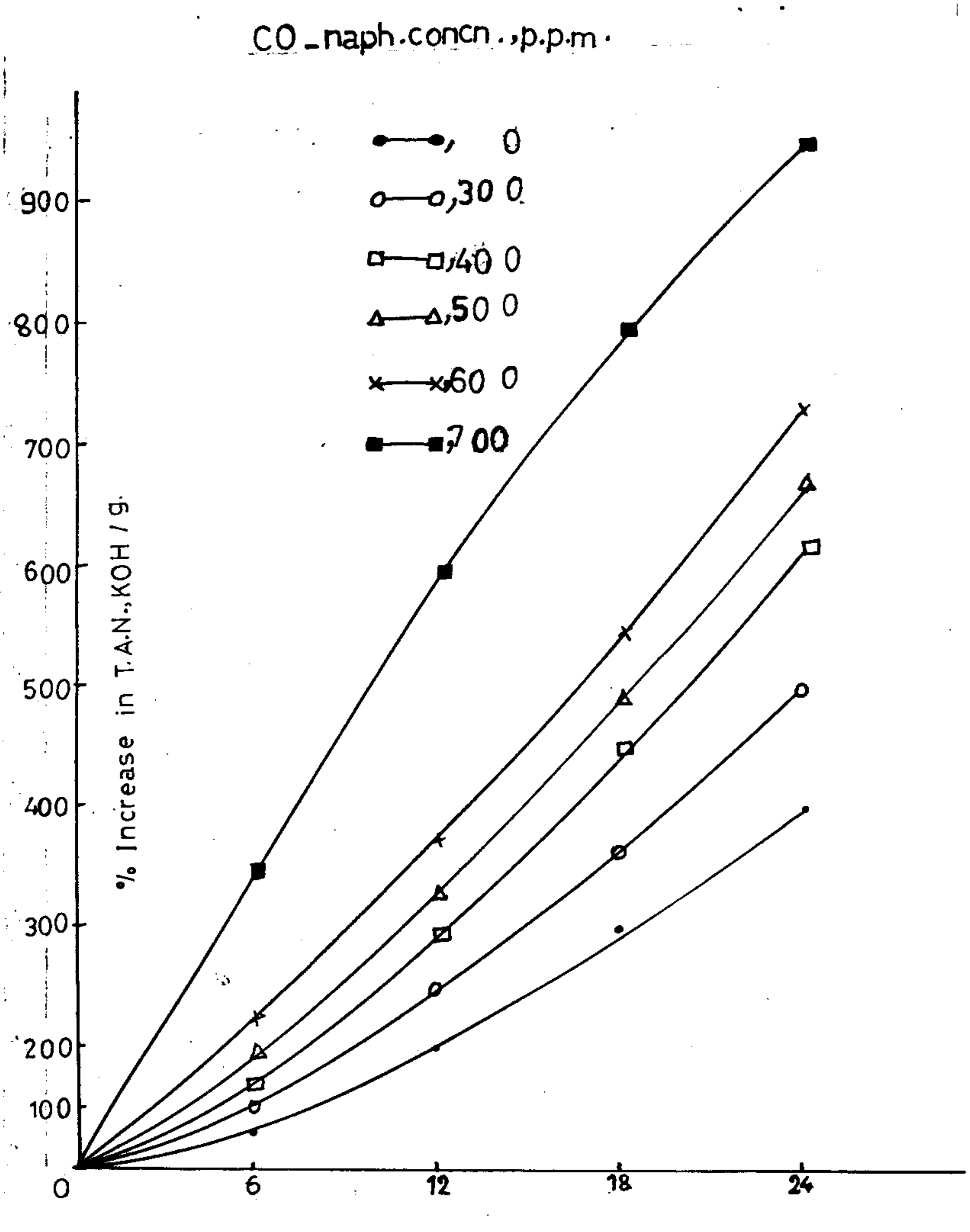
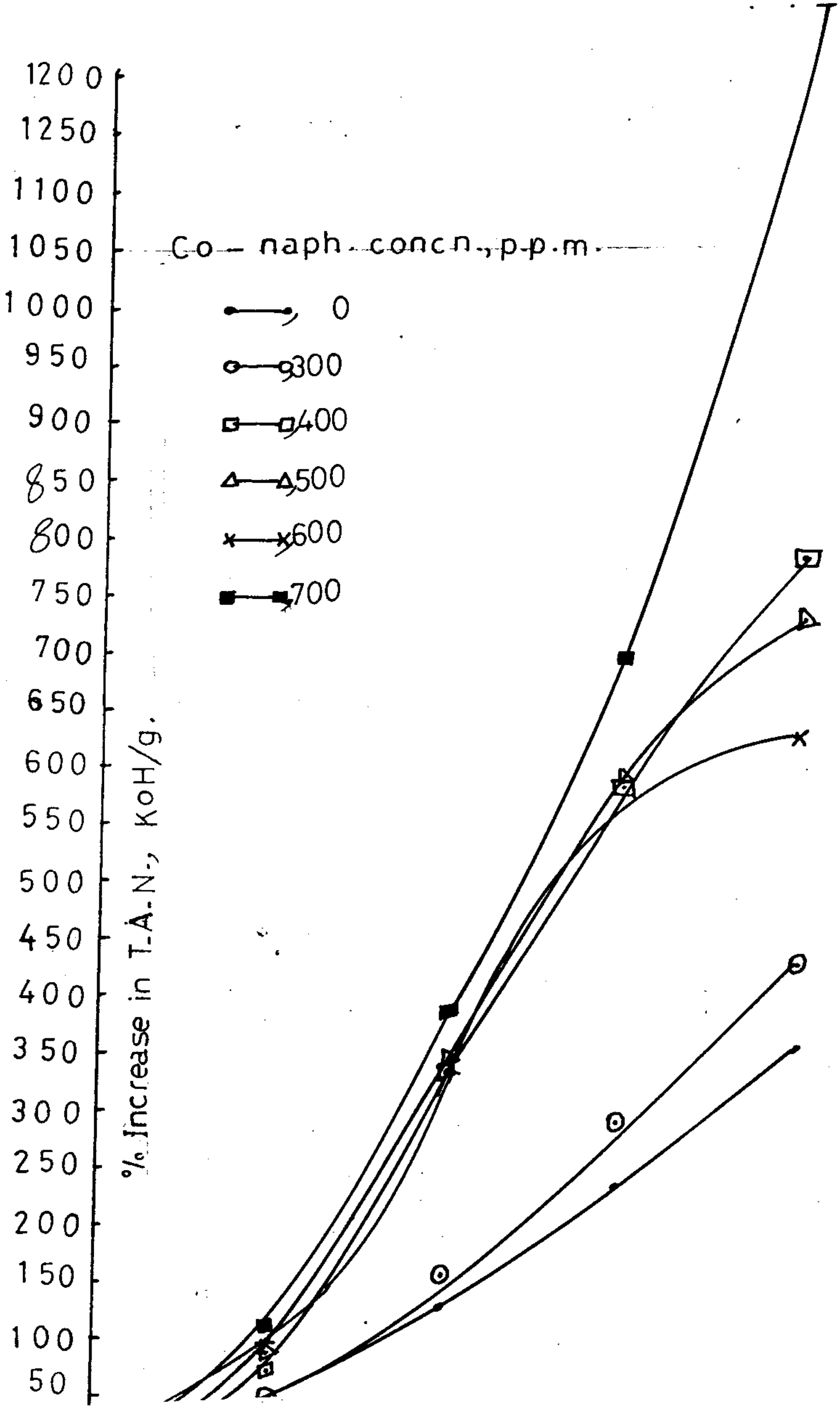


Fig (21) Effect of oxidation of base oil No. 2 on percent increase in total acid number using cobalt naphthenate as catalyst and temprature. 150°c.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100
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% Increase in T.A.N., KoH/g.
Co – naph. concn., p.p.m.
0
300
400
500
600
700

process) and a regulating function (which influences the reaction product composition).

Fig. 22 indicates that the presence of cobalt catalyst decrease the induction period (2 to 1 hrs.) and the rate of oxidation increased with the increase of concentration of cobalt naphthenate, while at the higher stage of oxidation it decreased at concentration of 400-600 p.p.m. of cobalt naphthenate. Since most of the catalyst precipitates and an acid is formed, it is possible that the catalytic action may be both homogeneous, on the precipitate.

The catalyst (cobalt naphthenate) undergoes a number of changes during the course of a reaction. Immediately after its introduction into the reaction the bivalent cobalt is partially converted to the tetravalent state and the concentration of the tetravalent cobalt becomes stationary and then begins to fall and all the cobalt is restored to the divalent state. As acid accumulates the cobalt precipitates as salt.

3- Effect of Cobalt Naphthenate Catalyst on Carbonyl - groups Content of The Three Base Lube Oils.

Figs. 23-25 indicate that the catalyst increases, the

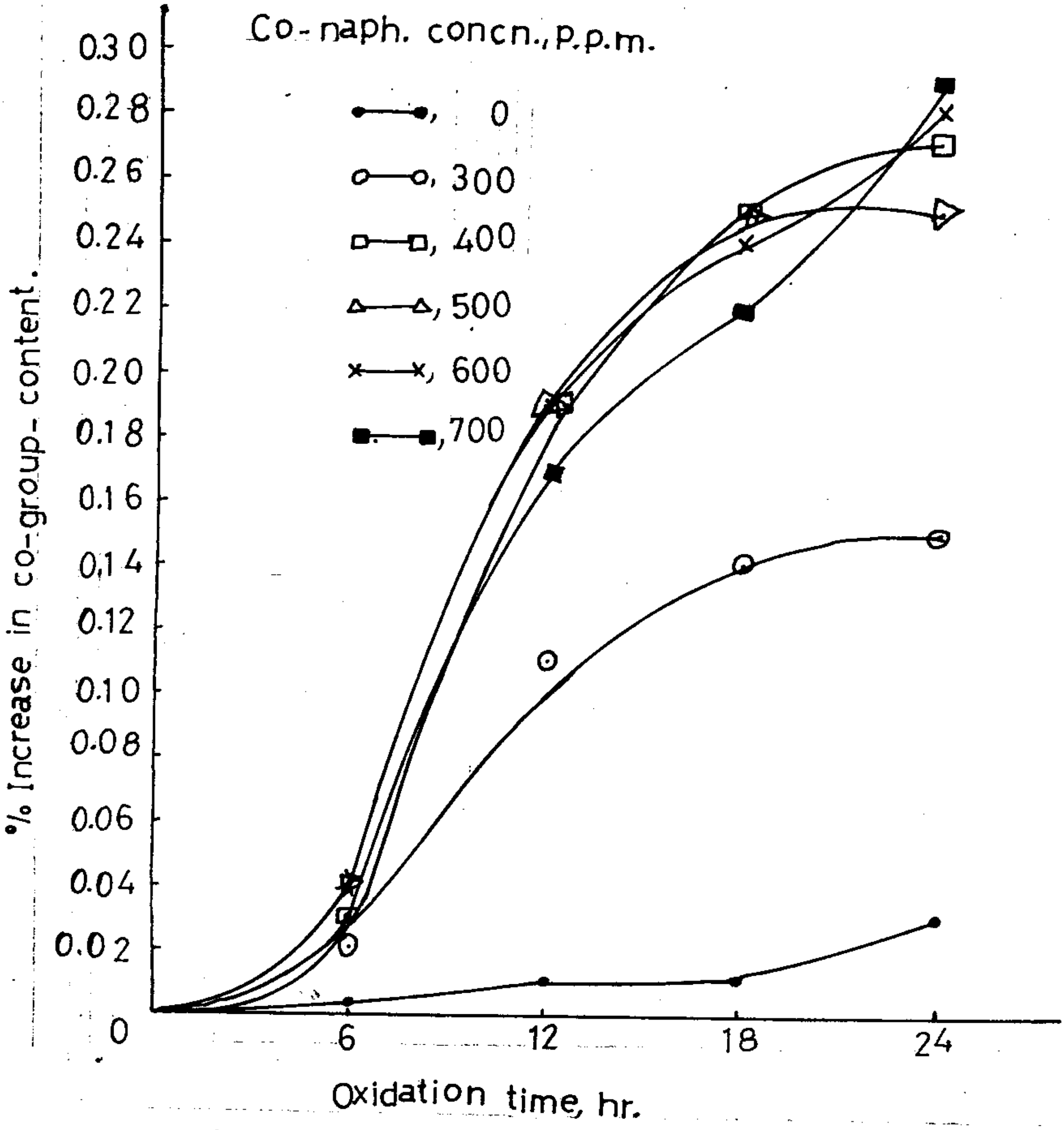


Fig. (23). Effect of oxidation of base oil No. 1 on percent increase in carbnyl group content using cobalt naphthenate as catalyst and temperature 150 °C.

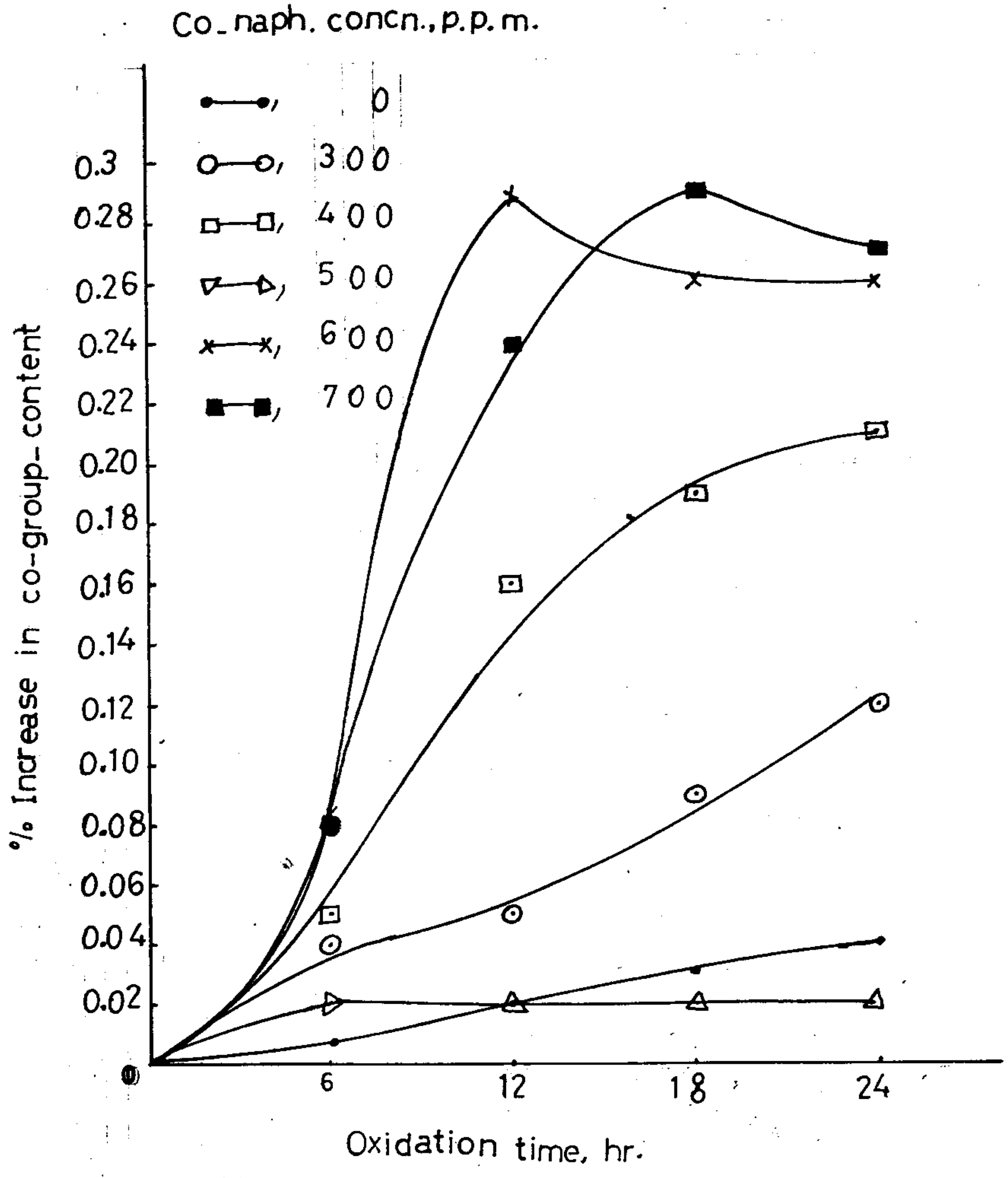


Fig. (24). Effect of oxidation of base oil No. 2. on Percent increase in carbonyl group content using cobalt naphthenate as catalyst and temperatur 150 °C.

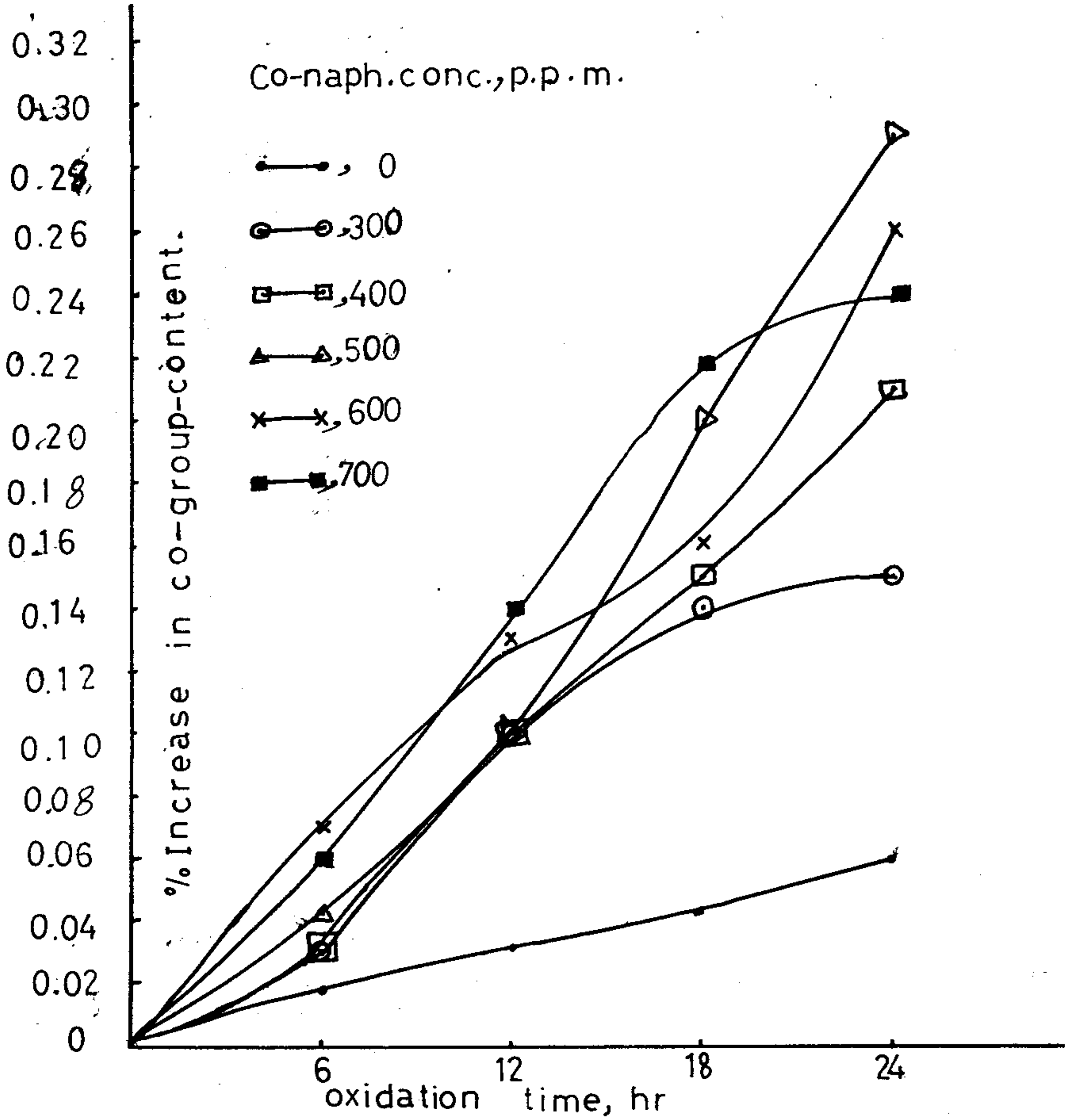


Fig: (25): Effect of oxidation of base oil No. 3 on percent increase in carbonyl group using cobalt naphthenate as catalyst and temperatur 150°C.

rate of development of oxidations and reduces the induction period from 3 to 1 hrs. as given in Fig. 23 and from one to zero hr. as shown in Fig. 24.

In the initial period of the oxidation, when the cobalt naphthenate is in solution and undergoes the valency change, the reaction may be considered as a rapidly accelerating one. During this stage the transition from bivalent to tetravalent cobalt occurs and this initiates the oxidation of the oils. The amount of ketone produced in this first stage is commensurate with amount of tetravalent formed.

Figs. 23-25 indicate that at higher concentrations of cobalt naphthenate the rate of formation of carbonyl groups decreased at the higher stage of oxidation.

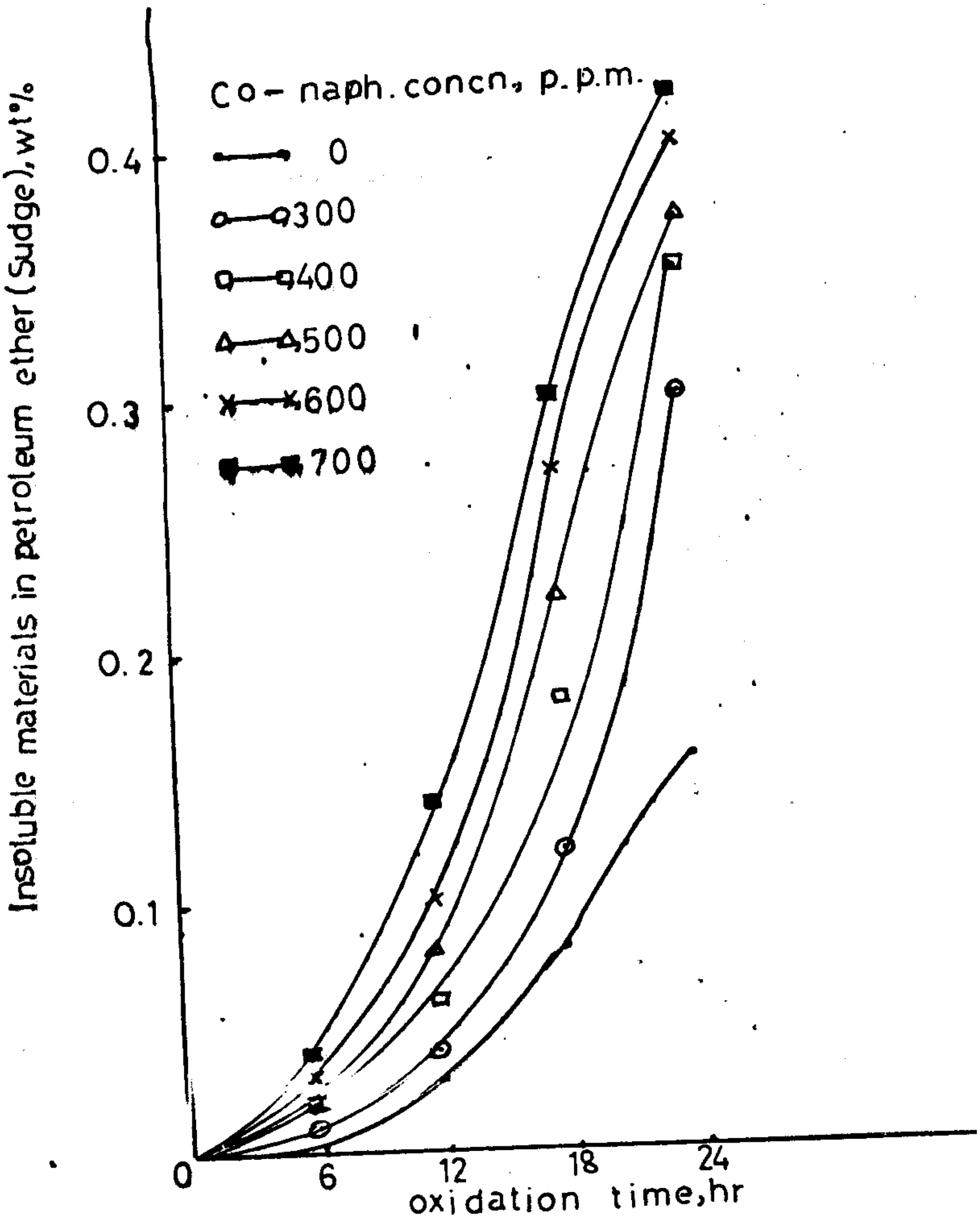
Fig. 24 indicates that at concentration of cobalt naphthenate (500 p.p.m.) the rate of formation of carbonyl groups decreased than that of the original oil itself. This may be attributed to the inhibition of the catalyst by water and alcohol which are formed during the oxidation and the hydrated cobalt naphthenate did not produce neiether ketone nor an initiated oxidation and the cobalt is very slowly converted into the tetravalent.

4- Effect of Cobalt Naphthenate Catalyst on Insolubles Materials of The Three Base Lube Oils.

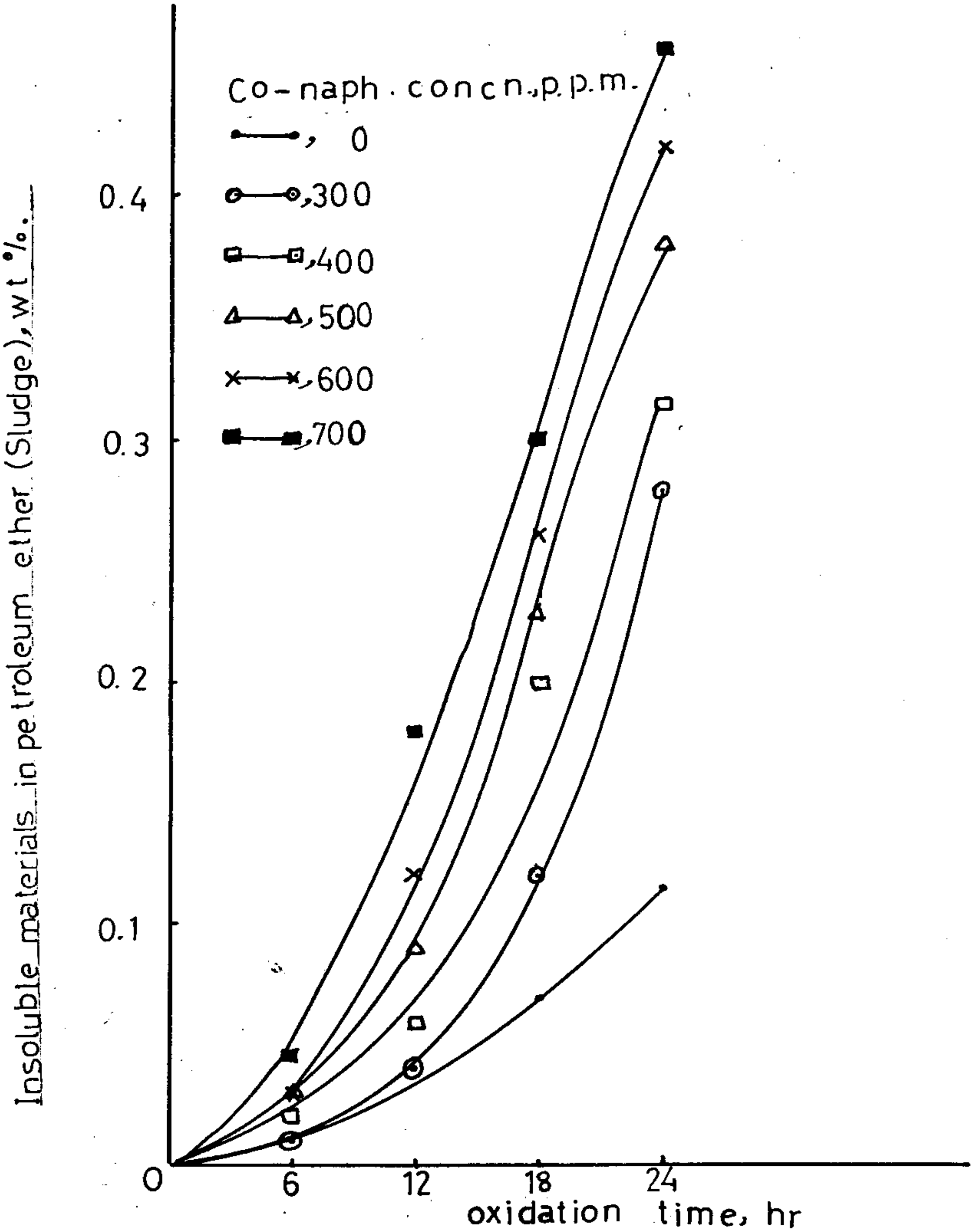
Figs. 26-28 indicate that the rate of formation of insoluble products increased with the increase in concentrations of dissolved catalyst and in all stage of oxidation. Base lube oil No. 3 has a higher percent of insolubles than the other two base lube oils, this is due to its chemical composition which is characterized by percent of aromatics (58 %) and sulphur content (0.77%) which are easily oxidized as shown in Fig. 28.

The catalyst increases the rate of formation of alcohols, carbonyl compounds, acids and esters. The catalyst always passed through the initial stage of valency transformation but was subsequently precipitated as a cobalt salt and deposit from the system. The catalyst influences the rates between the reaction products, as well as the reaction rate, by participating in chain propagation reactions. It was shown that as the concentration of catalyst was increased, the rate of development of the reaction increased.

The insoluble content deposits in short times because its ions initially have high ability to dissolve in the oxidized oils and latter on it agglomerates producing the insoluble gum.



Fig(26): Effect of oxidation of base lube oil No.1 on insoluble materials using different concentrations of cobalt naphthenate as catalyst and temperature 150°C.



Fig(27): Effect of oxidation of base lube oil No.2. on insoluble material using different consentrations of cobalt naphthenate as catalyst and temperature 150°C.

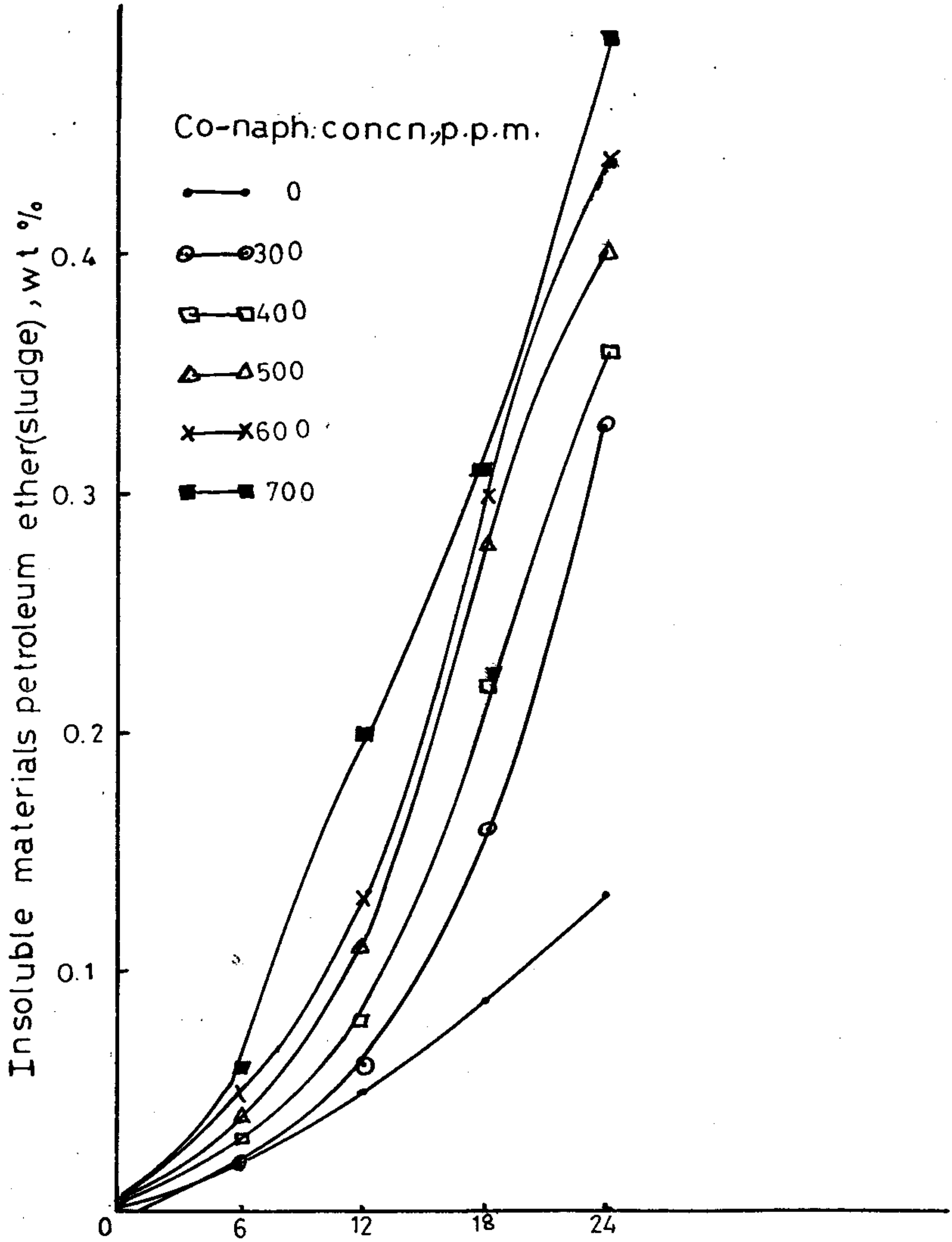


Fig (28): Effect of oxidation of base lube oil No. 3 on insoluble materials using different concentrations of cobalt naphthenate as catalyst and temperature 150°C .

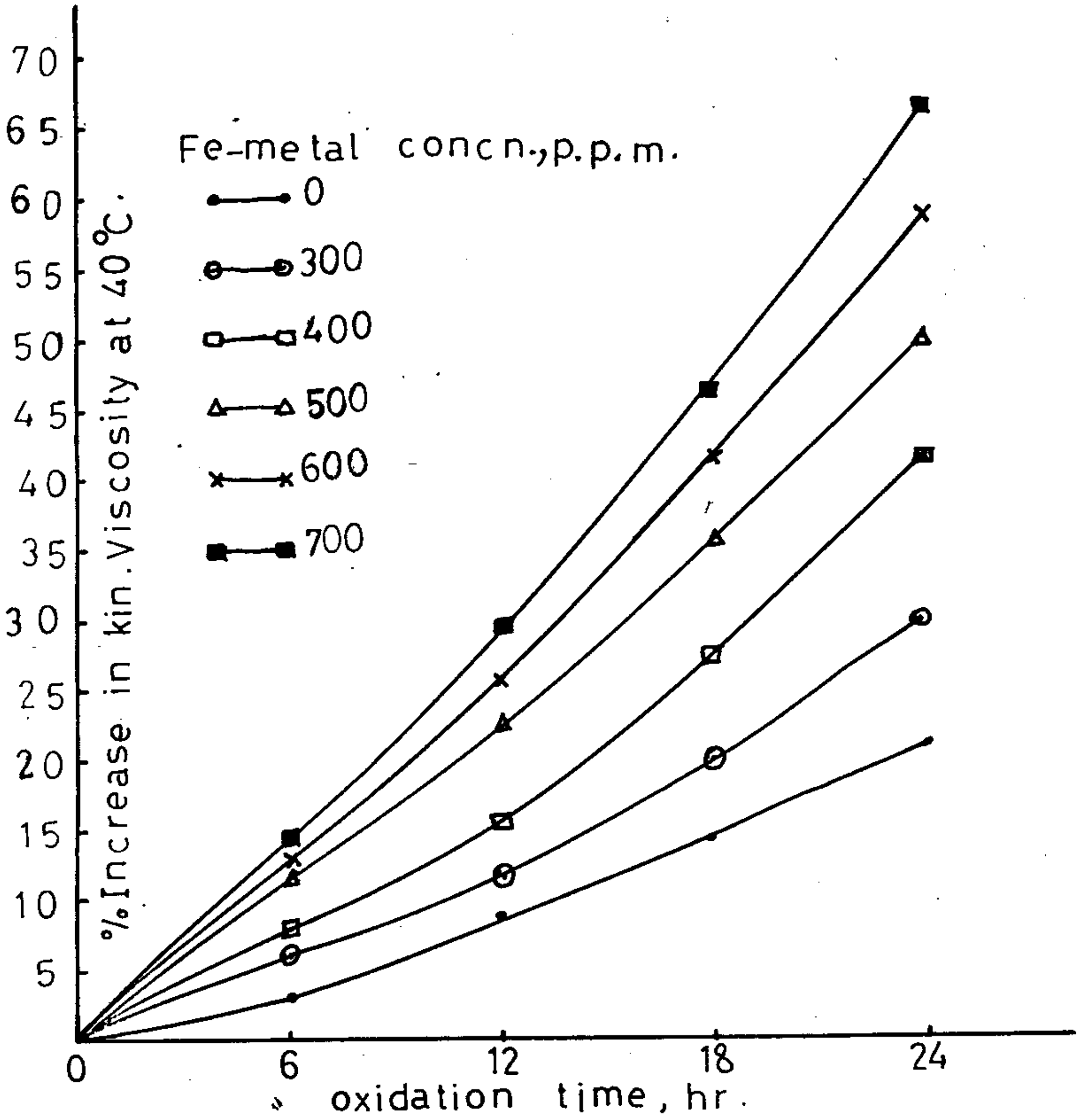
3- Effect of Iron Metal Catalyst on Oxidation of Base Lube Oil No. 2.

It was recognized that the action of metal in solution as salts (homogeneous catalyst) could be quite different from that of bulk or massive metals (heterogeneous catalyst), which offer only a limited amount of surface.

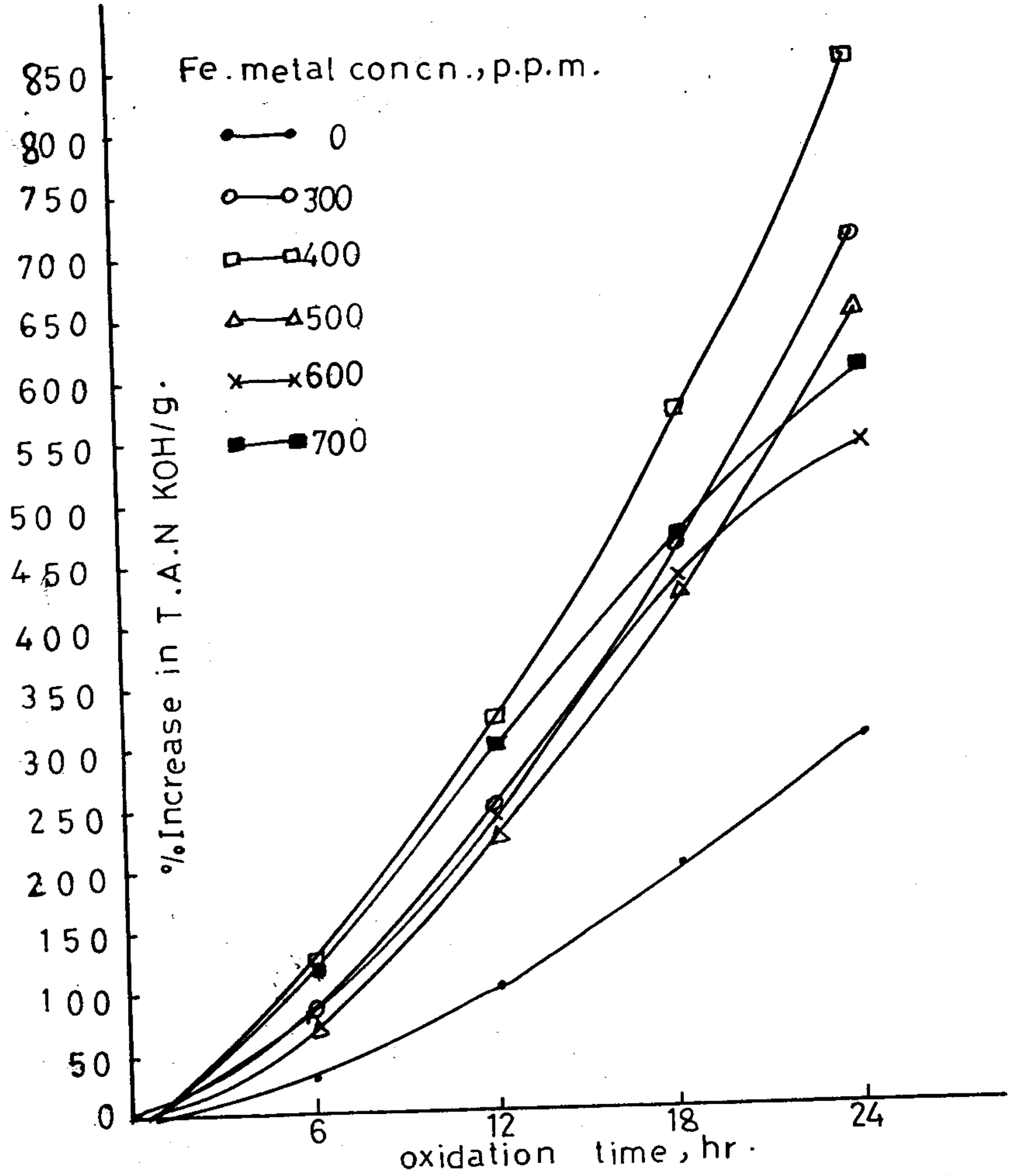
The effect of iron metal catalyst on the rate of oxidation of base lube oil No. 2 was traced by measuring the increase in kinematic viscosity, total acid number, carbonyl groups and insoluble materials. The results are listed in tables 5,8,11 and 14 and represented in Figs. 29-32.

Figures 29-32 indicate that iron catalyst has a deterioration effect on the properties of the oil. In the lower stage of oxidation the rate of increase in kinematic viscosity, total acid number, carbonyl groups and insolubles is lower as shown in figures while in the higher stage of oxidation the reverse is true.

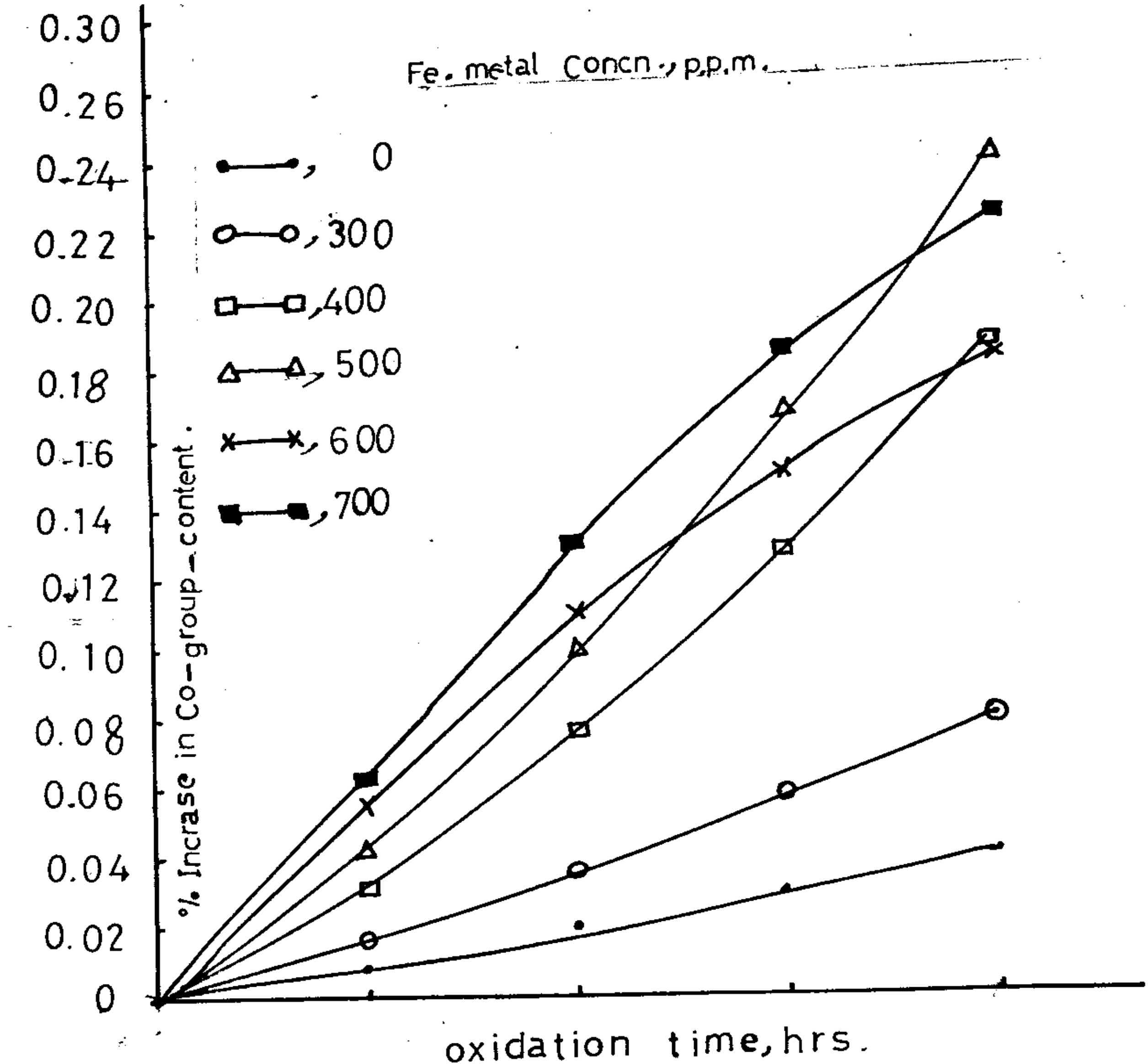
This is mainly due to the oxide catalyst which is changed in its ion valency induced by interaction with the environment, and in fact the reaction occurs on a partially reduced catalyst. There is a change in the



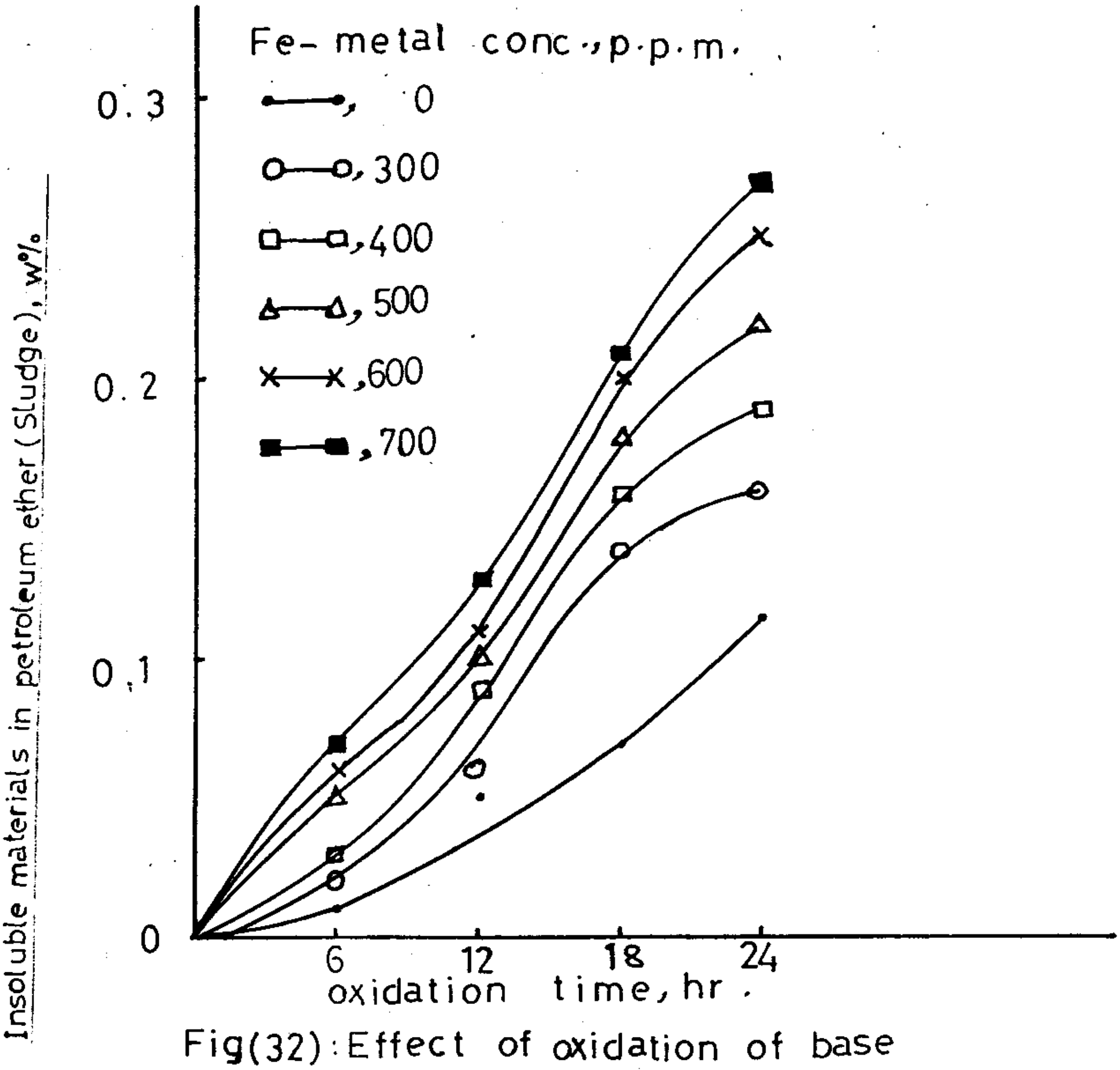
Fig(29): Effect of oxidation of base oil No. 2 on percent increase in kinematic viscosity at 40°c using Iron metal as catalyst and temperature 150°c.



Fig(30): Effect of oxidation of base oil No.2 on percent increase in total acid number using Iron metal as catalyst and temperature 150°C.



Fig(31): Effect of oxidation of base oil No. 2 on percent increase in carbonyl group content using Iron metal as catalyst and temperature 150°c.



Fig(32): Effect of oxidation of base lube oil No.2 on insoluble materials using different concentrations of Iron metal as catalyst and temperature 150°C.

M-O bond energy, anion vacancies and other deffects appear, and electron exchange between lattice ions becomes stronger or weaker(116). Such transfers are known for simple oxides:

Cu^{2+}— Cu^{+} for propene oxidation to acrolein and more complex oxide systems such as iron-molybdenum catalyst (Fe—Mo) in which electron transfer as $Fe^{3+} \longrightarrow Fe^{2+}$. The mechanism of liquid-phase oxidation catalyzed by a solid surface S involves the following steps(117,118):

$$S + O_2 \longrightarrow \left[S \ldots \overset{-\delta}{O_2}\right] \xrightarrow{RH} R^{\bullet} \quad \ldots\ldots\ldots \quad (6)$$

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \quad \ldots\ldots\ldots \quad (7)$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad \ldots\ldots\ldots \quad (8)$$

$$S + ROOH \longrightarrow \left[\overset{-\delta}{ROOH} \ldots S\right] \quad \ldots\ldots\ldots \quad (9)$$

$$\left[\overset{-\delta}{ROOH} \ldots . S\right] \longrightarrow RO^{\bullet} \quad \ldots\ldots\ldots \quad (9')$$

$$\left[\overset{-\delta}{ROOH} \ldots S\right] \longrightarrow RO_2^{\bullet} \quad \ldots\ldots\ldots \quad (9'')$$

$$ROOH \ldots S + RH \longrightarrow R^{\bullet} + RO^{\bullet} + H_2O \quad \ldots\ldots\ldots \quad (9''')$$

$$RO^{\bullet} + RH \longrightarrow R^{\bullet} + ROH \quad \ldots\ldots\ldots \quad (10)$$

$$RO^{\bullet} \xrightarrow{S} R'COCH_3 + \dot{C}H_3 \quad \ldots\ldots\ldots \quad (11)$$

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{S} ROOR + O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

$$2RO_2^{\bullet} \longrightarrow 2RO^{\bullet} + O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12')$$

$[\delta]$ is the effective charge $|\delta| < 1$, $\xrightarrow{S}$ means that the reaction can occur both in the liquid and on the catalyst surface. Three mechanisms of radical generation have been suggested: activation of a hydrocarbon (RH), oxygen activation (Reaction 6), and activation and decomposition of a hydroperoxide (Reaction 9, 9''').

The generation of radicals in liquid-phase oxidation can occur by competing reactions (7) and (9). The adsorption of electron donor molecules (H_2) on the catalyst favours electron transfer from the catalyst to the hydroperoxide molecule, and this enhances hydroperoxide decomposition. The decrease in electron density at active catalyst sites that is induced by adsorption of acceptor (O_2, CO_2 etc.) hinders electron transfer to the hydroperoxide molecule and its decomposition to radicals $RO^{\bullet}$ oxygen as an electron acceptor, obtains a negative charge, thus becoming active and initiation by Reaction (6) consequently becomes stronger.

Effect of Chemical Composition of The Three Base Lube Oils on Dissolved and Solid Metal Catalysts:

1- Effect of Chemical Composition of Base Lube Oil No.1.

Base lube oil No. 1 have a higher percent of saturated hydrocarbon about 70 % and higher percent of polycyclic aromatics (16 %) while have low percent of dicyclic aromatics (1.8 %) and less percent of nitrogen and sulphur content (0.01 and 0.3 % respectively) as shown in tables (1 and 2).

The initiation step in autoxidation is apparently dependent on the structure of the component. The ease of hydrocarbon autoxidation follows the general order, alkyl aromatic > diolefins > mono-olefins > paraffins(119-123).

In the absence of the catalyst, the autoxidation of hydrocarbon takes place by means of degenerate-branching chain reactions. In the pure hydrocarbon the free radicals may be formed by reaction with oxygen.

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots \quad (13)$$

$$2RH + O_2 \longrightarrow 2R^{\bullet} + H_2O_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (14)$$

Each radical causes a chain in which hydrocarbon and oxygen molecule form the hydroperoxides(124)

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

$$R\,O_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots \quad (16)$$

The peroxide formed of oxidation of paraffinic hydrocarbons decomposed forming alcohols, aldehydes and ketones which are soluble in the oil giving rise to on increase in the carbonyl group Figs. 9 and 23 and also increased its viscosity as shown in Figs. 1 and 17. The acidic compounds may be formed by chain breaking as shown in Figs. 5 and 20. Oxidation of paraffinic oils increase its viscosity and become acidic and corrosive in service. At higher stage of oxidation of paraffinic compounds insoluble product formed but give low deposits as shown in Figs. 13 and 26.

In this work we will cover the effect of metals on the initiation of autoxidation and the decomposition of hydroperoxides. Matals play an intricate role in instability. Thus, the effect of metals on the acceleration, of hydrocarbon autoxidation, hydroperoxide decomposition and the stability of other oil components is of prime importance in the general area of instability.

Figs. 1,5,9,13,17,20,23 and 26 which represents the rate of change in kinematic viscosity, total acid number, carbonyl groups and insoluble products with oxidation times, indicates that there is a so-called induction periods during which the rate of oxidation is relatively low, (3-6 hrs) as shown in Figs. At the end of this period there is a sharp increase in the rate of increase in kinematic viscosity, total acid number, carbonyl groups and insoluble materials which continues at a relatively uniform rate until the oil is highly oxidized where the oxidation rate declines. Induction periods reduced to zero by using dissolved catalysts as shown in all the above Figs.

Figs. 1,5 and 9 in which copper naphthenate used as catalyst indicate that during the initial stage of oxidation the rate of increase in kinematic viscosity, total acid number and carbonyl groups were relatively high while this rate decreased in the higher stage of oxidation. This is mainly due to the fact that the catalyst accelerates the reaction initially but is precipitated as the reaction progresses and does not further affect the course of the reaction.

Thus, hydrocarbon-metal interactions could initiate autoxidation by the following redox reaction:

$$RH + M^{n+} \longrightarrow R^{\cdot} + H^{+} + M^{n-1} \quad \ldots\ldots\ldots\ldots \quad (17)$$

A similar reaction has been postulated for the initiation of hydroperoxide decomposition.

$$ROOH + M^{3+} \longrightarrow RO_2^{\cdot} + M^{2+} + H^{+} \quad \ldots\ldots\ldots\ldots \quad (5)$$

$$ROOH + M^{3+} \longrightarrow RO^{\cdot} + M^{2+} + HO^{-} \quad \ldots\ldots\ldots\ldots \quad (18)$$

Since acids are oxidation products, they may solubilize the metal ions as shown in Figs. 5, and 20.

The reserve occurs in Figs. 17, 20 and 23, which represents the rate of change in kinematic viscosity, total acid number and carbonyl groups using cobalt naphthenate as catalyst. This is probably due to the difference in the activity and selectivity the two metals. Solubility of copper naphthenate is higher than that of cobalt naphthenate, so the copper is more active than cobalt in the initial stage of oxidation.

Copper melt at around 1000°C while cobalt at 1500°C. Therefore surface and bulk Tammann temperatures fall within the range 150-350°C and 300-600°C for each metal respectively. So the rate of development of the reaction increased for cobalt.

During the oxidation reaction, catalyst do not remain unaltered, but pass through a cycle of valency changes, being converted to the higher valency state **and** after a short period of time reduced to the lower valency.

$$ROOH + M^{2+} \longrightarrow RO^{\cdot} + \bar{O}H + M^{3+} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$ROOH + M^{3+} \longrightarrow RO_2^{\cdot} + M^{2+} + H^{+} \quad \ldots\ldots\ldots\ldots \quad (5)$$

The amount of oxidation products using cobalt naphthenate in the first stage is commensurate with the amount of tetravalent formed and the cobalt is very slowly converted into the tetravalent.

Also, copper more active in the decomposition of hydrogen peroxide than the other metals. Figs. 13 and 26 which represent the rate of formation of insoluble materials with oxidation times. The rate of increase is higher at the higher stage of oxidation. As the reaction progress, the metals are eventually precipitated from solution by acid formed during the oxidation reaction. Thus, metal contribute primarily to the initial stages of the reaction. The total conversion of the reactant and the composition of the products depend on the presence or absence of metals.

The rate of formation of sludge which are formed during oxidation of base lube oil No. 1 are lower than in the other two base lube oils as shown in Figs. 14, 15,16,26,27,28 and 32 . It reaches maximum about (4.2, 4.6) for base oil No. 1 to (2.3 - 5.2) and (4.9 - 5.6 wt %) for the other two base lube oils respectively. This is due to the lower percent in aromatic compounds in the base lube oil No. 1 than the other two base lube oils, as shown in table (1).

The base lube oil No. 1 have a higher rate of increase in kinematic viscosity reach (13 - 136%) as shown in Figs 1 and 17 than the other two base lube oils Figs. 3 and 8 because it have a higher percent of paraffinic compounds form soluble viscous products which increase its viscosity.

2- <u>Effect of chemical composition of base lube oil No. 2</u>.

Base lube oil No. 2 has a higher percent of saturates about 62 % as listed in table (1), and nearly equal percent of mono- and polycyclic aromatics (16.2 and 14.2 %) while has a lower percent of dicyclic aromatics about 7.20 %. Also, it has a higher percent of total nitrogen compounds about 0.02 % as shown in table 2 and has 50 % of strongly basic nitrogen content and it contains about 0.4 % sulphur content so shown in table 2.

Metal exert a substantial influence on the rate of oxidative processes in oils. The catalytic action of metals on the oxidation of oils are given in Figs. 2,3,6, 7,10,11,18,21,24,29,30 and 31 and 14,15,27 and 32 and the relative efficiency of the various means of preventing the acceleration of oxidation of oils in the presence of metals will be considered.

Metal catalyst to reduce the induction period for initiation of hydrocarbon autoxidation from (2 to zero hrs.) as shown in all the above Figs.

Figs. 2,3,6,7,10,11,14,15,18,21,24,27,29,30,31 and 32 which represent the rate of change in kinematic viscosity, total acid number, carbonyl groups and insoluble materials indicate that the values of these properties increased with increase of oxidation times.

Figs. 6,7,21 and 30 which represent the rate of increase the percent of total acid number with times using different catalysts.

All these figures indicate that the rate of increase in these values different from catalyst to catalyst. In higher stage of oxidation the rate of increase is higher in case of copper naphthenate than in presence of cobalt naphthenate and other metals. Copper is found to be more soluble if compared with other metals. Therefore, it seems to be more active than the other metals. Also the rate of oxidation is lower in presence of copper metal as shown in Figs. 3,7,11 and 15 than in case of dissolved copper as shown in Figs. 2,6,10 and 14. It is found that soluble catalyst accelerates more the rate of oxidation than solid catalyst because their ions react directly with oxidation products forming soaps, resins. But solid metals go into oil medium and initiate the rate of reaction. Also, the activity of metals is reduced or destroyed by adsorption or by forming complex compounds give rise to a less active or inactive surface. The very reactive electronegative species (oxygen, sulphur) and the electron-pair donors (water, carbon monoxide, sulphide, phosphine etc.) and their derivatives can be powerful poisons when present as adventitious impurities or as reactant, depending upon the facility of the catalyst reaction. These poisons may be adsorbed or they may react to form compounds in surface layers (oxides, sulphides, halides, etc.). If activity recovers on exclusion of the poison from the reactants, the poisoning is said to be reversible, otherwise it is permanent.

Fig. 10 which represents the rate of increase in carbonyl groups against time, indicate that the rate of increase in the carbonyl group at the lower concentration reaches 0.87 % at higher stage of oxidation in presence of copper naphthenate as catalyst. At the higher concentrations it reaches 0.57 % while in case of base lube oil No. 1, the rate of increase in carbonyl groups at the lower concentrations reaches 0.25 %. At higher concentration it reaches 0.29 % as shown in Fig.9.

The reverse is remarkable as shown in Figs. 23 and 24 in presence of cobalt naphthenate as catalyst. It was found that at higher stage of oxidation the percent increase in carbonyl groups reaches 0.15 and 0.29 % at lower and higher concentration respectively in case of base lube oil No. 1, while it reaches 0.12 and 0.27 % at lower and higher concentrations respectively in case of base lube oil No. 2. This difference is mainly due to the change in chemical composition of the base oils which have different sensitivities to the catalytic activity of metals.

High oxidation activity is confined to oxides such as CuO. In hydrocarbon oxidation an incomplete activity series is roughly Pt, Pd $>$ Ag $>$ MnO, Co_3O_4, CuO $>$ NiO $>$ Fe_2O_3. Oxidation activity decreases with increasing atomic number in each group of the periodic table (5).

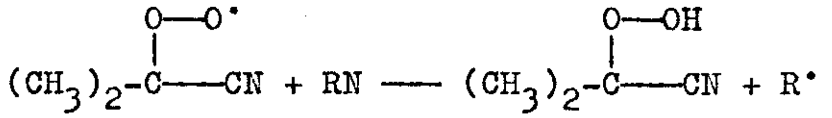
Base lube oil No. 2 has a higher percent of nitrogen compounds, 80 % of these is basic compounds and 50 % of these compounds is strongly basic compounds. The basic nitrogen constituents of base lube oils are stable species and would not be expected to autoxidize readily while the non-basic constituents are highly susceptible to autoxidation(125). Thus, it is quite likely that basic nitrogen compounds accelerate or catalyze the anion-radical autoxidation of these acidic base compounds(126-128). Basic nitrogen also form salts with hydroperoxides, which in the presence of thiols are unstable and decompose rapidly to disulphide, alcohols and water.

$$R_3NHSR \rightleftharpoons R_3N^+H + RS^- \quad \text{.........} \quad (19)$$

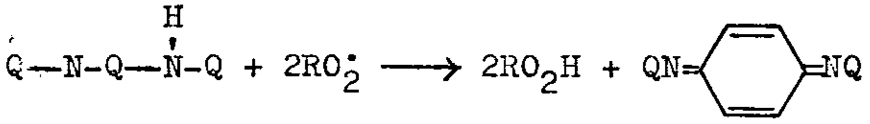
$$RS^- + O_2 \longrightarrow RS^\bullet + O_2^- \quad \text{.............} \quad (20)$$

The basic nitrogen compounds act as inhibitor, it eliminate the chain propagation step because it possess readily abstractable hydrogen atoms or it readily combine with peroxy radicals as shown in equations:

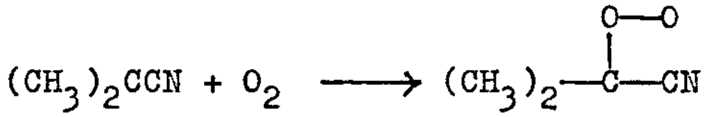
$$\left.\begin{array}{l} R^\bullet + O_2 \longrightarrow RO_2^\bullet \\ RO_2^\bullet + RH \longrightarrow ROOH + R^\bullet \end{array}\right\} \begin{array}{l}\text{chain} \\ \text{propagation} \\ \text{step}\end{array} \quad \begin{array}{r} \text{.....(15)} \\ \text{.....(21)} \end{array}$$



$$(CH_3)_2\text{-}\overset{O-O^{\bullet}}{C}\text{—}CN + RN \text{ —— } (CH_3)_2\text{-}\overset{O-OH}{C}\text{—}CN + R^{\bullet}$$ .... (22)

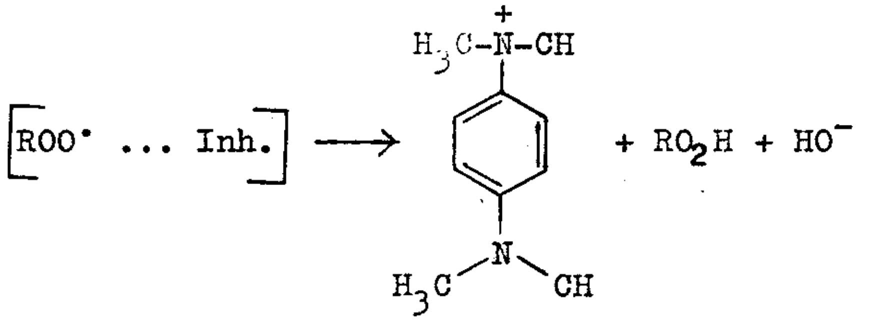


.... (23)



$$(CH_3)_2CCN + O_2 \longrightarrow (CH_3)_2\text{—}\overset{O-O}{C}\text{—}CN$$ .... (24)

Inhibitors of this type stop two radical chains per molecule. The rate determining step in the inhibition reaction appears to be formation of a charge - transfer complex between the peroxy radical and the inhibitor $[ROO^{\bullet} \ldots \text{inh.}]$.



..... (25)

Certain complexing agents deactivate certain metals but simultaneously can change the oxidation potential of the other metals so that they become more active oxidation in hydrocarbon media. The inhibitor can precipitate the metal or change its oxidation potential. Alkyl amine are employed as antioxidant by complex formation and in combination with base(129).

$$Cu^{2+} + RNH_2 \longrightarrow Cu^{+} + RN^{+}H_2 \ldots\ldots\ldots\ldots\quad (26)$$

Metals should be more active as initiators in polar media. It is found that in presence of basic nitrogen (such as pyridine) they form an oxygen complex which is reversible and is an excellent oxidation catalyst. Complexes of natural **porphyrins with nitrogen** compounds in hydrocarbons could supply active oxygen for the initiation of hydrocarbon oxidation.

Figs. 29,30,31, and 32 which represent the rate of oxidation of base lube oil No. 2 with times, using iron metal as catalyst, indicate that the rate of deterioration is more remarkable than in presence of copper metal at higher stage. The percent increase in kinematic viscosity at concentrations 500 p.p.m. of iron metal catalyst nearly equal that at concentration 700 p.p.m. of copper metal catalyst as shown in Figs. 3 and 29. Generally, we can say that there are few ions of iron in the oil, are more effective than the presence of high concentration of copprous ions. These ions (e.g. ferrous ions) form complex compounds with some polar groups and prevent them from giving good service.

It is well known that metal catalysts used in a variety of chemical processes are prone to deactivation by certain chemical species which are able to donate electrons into the unfilled d-orbitals of the metal. Small amounts of sulphur can have a significant effect on catalyst activity although the effect varies from catalyst to catalyst. Sulphur lowers the activity of the catalyst, the level of the activity decrease with the increase ofsulphur content of the oil. The poisoning effect of sulphur is reversible and at any given operating temperature there is a sulphur concentration below which no detectable poisoning occurs. A poisoned catalyst soon recovers its full activity when operated with oil containing sulphur in concentrations below that level. Sulphur compounds, such as H_2S or COS, in concentration below 200 p.p.m. have no effect on the normal activity of the catalyst. The catalyst can, however, absorb the sulphur compounds, and releases them is slowly. The sensitivity of the catalyst to poisoning is increased when operating temperatures are lowered. The activity of FeS is approximately half that of Fe_3O_4 and in these circumstances the calculated catalyst volume must be increased by a factor of two. The effects, which are reversible, are an indication that Fe_3O_4 absorbs sulphur even at low sulphur concentrations. The quantity of sulphur absorbed is related to the partial pressure of sulphur and that absorbed sulphur acts as a mild poison.

The catalyst can be oxidized with oxygen:

$$4\ Fe_3O_4 + O_2 \longrightarrow 6\ Fe_2O_3 \quad \Delta H = -111.0\ K.cal \quad ...(27)$$

The catalyst requires controlled oxidation with a limited supply of oxygen.

When the catalyst has been operated in the sulphided state (that is to say, part of the catalyst is in the form FeS) it would be damaged by allowing it to react with oxygen.

$$6\ FeS + 13.5\ O_2 \longrightarrow 2\ Fe_2(SO_4)_3 + Fe_2O_3 \quad ....(28)$$

$$\Delta H = -1344K.cal$$

Following this reaction the catalyst loses activity. The cause is not certain and it could be either that the ferric sulphate cannot be re-reduced to Fe_3O_4, or that the exothermic reaction lowers the surface area of the catalyst.

To explain the difference in behaviour between the presence of different metal catalysts, copper, iron and cobalt on the properties of the oxidized base lube oil the following mechanism(130-132) is represented into equations :

$$\text{ROOH} + \text{metal ion}^{n+} \longrightarrow \text{RO}^- + \text{M}^{(n+1)^+} + \text{OH}^- \text{......(29)}$$

$$\text{or} \longrightarrow \text{RO}^\bullet + \text{M}^{(n+1)^+} + \text{OH}^- \text{............(30)}$$

and for Cu^+

$$\text{ROOH} + \text{Cu}^+ \longrightarrow \text{RO}^\bullet + \text{Cu}^{2+} + \text{OH}^- \text{...............(31)}$$

$$\longrightarrow \text{RO}^- + \text{Cu}^{2+} + \text{OH}^\bullet \text{...............(32)}$$

Cu^{2+}

$$\text{ROO}^- + \text{Cu}^{2+} \longrightarrow \text{ROO}^\bullet + \text{Cu}^+ \text{.....................(33)}$$

and for Fe^{2+}

$$\text{ROOH} + \text{Fe}^{2+} \longrightarrow \text{RO}^\bullet + \text{Fe}^{3+} + \text{OH}^- \text{...............(34)}$$

$$\text{or} \longrightarrow \text{RO}^- + \text{Fe}^{3+} + \text{OH}^\bullet \text{...............(35)}$$

$$\text{ROO}^- + \text{Fe}^{3+} \longrightarrow \text{ROO}^\bullet + \text{Fe}^{2+} \text{.....................(36)}$$

and for CO^{2+}

$$\text{ROOH} + \text{CO}^{2+} \longrightarrow \text{RO}^\bullet + \text{CO}^{3+} + \text{OH}^- \text{...............(37)}$$

or $\longrightarrow RO^- + Co^{3+} + OH^\bullet$ ....(38)

and

$ROO^- + Co^{3+} \longrightarrow ROO^\bullet + Co^{2+}$ ....(39)

3- Effect of chemical composition at base lube oil No. 3.

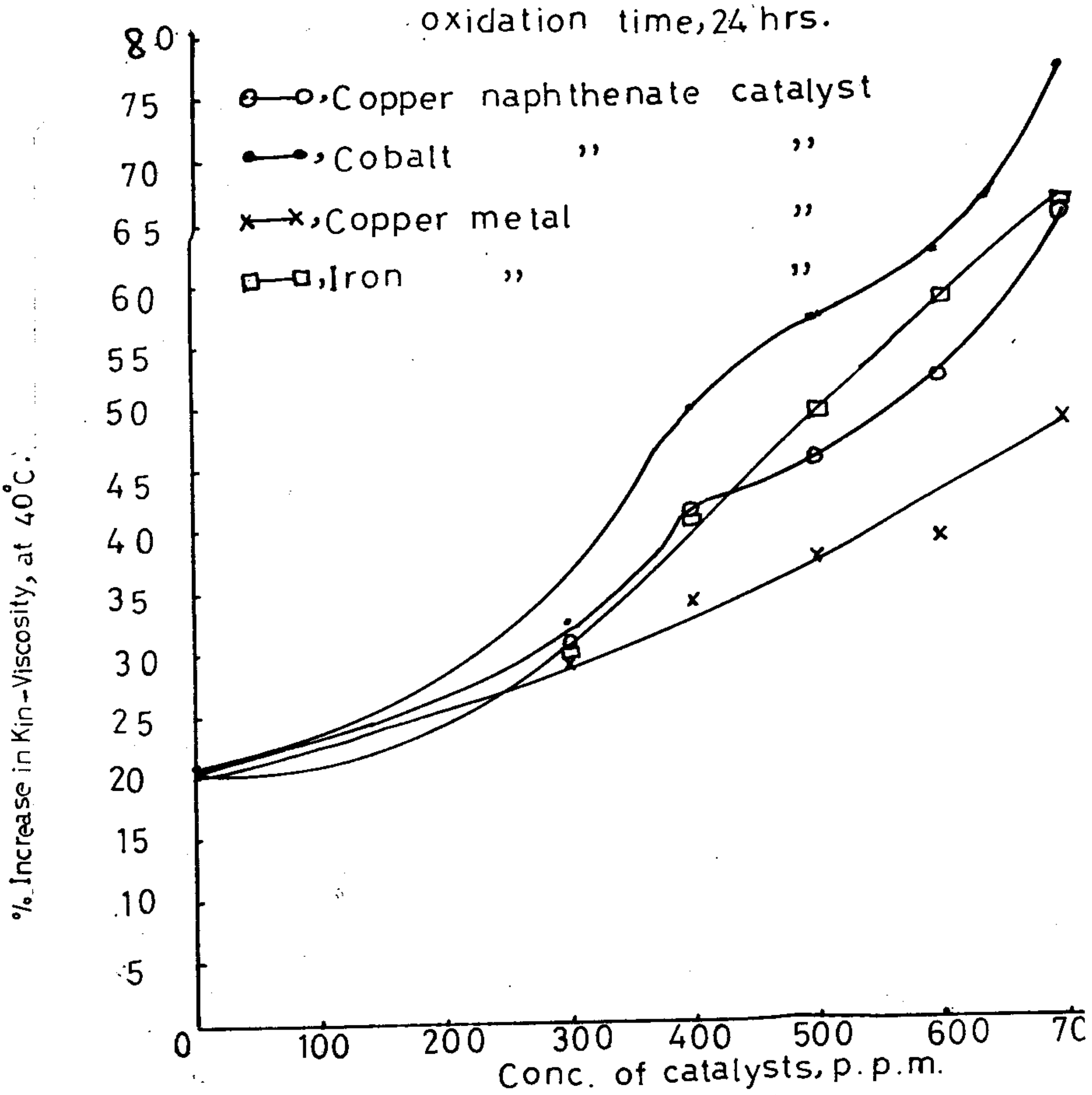
This base lube oil is characterized by having a lower percent of paraffinic hydrocarbon components about 40% and higher percent of aromatic hydrocarbon components about 58%, 51% of which Figs. 4,8,12,16,19,22,25 and 28 indicate that the oxidation curves are straight or almost straight lines which means that the rate of change in constant. The percent increase in total acid number, carbonyl groups and insoluble content are higher in base lube oil No. 3 than the other two. This may be due to the high aromatic content about 58% which are more easily oxidized than paraffins or naphthenes, probably due to the reactivity of hydrogen atoms situated near to the aromatics nucleus where the degree of oxidation is high it seems that oxygenated materials have apparently remained in soluble form resulting in high increase in acidity and carbonyl groups.

The relatively high concentration of sulphur in base lube oil No. 3 promotes the autoxidation process and leads to the formation of insoluble materials. This is mainly due to the disulphides (0.006 %) which are known to be active sludge formers. The settlement of this sludge out from the oil lowers the increase in the viscosity of the oil. This could explain the behaviour of base lube oil No. 3 regarding the percent increase in its kinematic viscosity with time which has the lowest rate although it is more liable to be oxidized.

Comparative Evaluation For The Effect of Metal Catalysts Through Oxidation of Base Lube Oil No. 2.

Fig. 33 represents the rate of increase in kinematic viscosity against concentrations of different metal catalysts after 6 hours oxidation of base lube oil No.2. It indicates that the rate of increase in kinematic viscosity using copper naphthenate is higher at all concentrations especially at concentrations (500-700 p.p.m.) if compared with the effect of different other metals. This is mainly due to the ability of copper ions to dissolve in the oil in large quantities than the other metals. It is found that the oxygenated products increased by increase of catalyst solubility. Therefore, it seems to be more active than the other metals as given in Figs. 33 and 35. Fig. 34 represents the change of kinematic viscosity with different metal catalyst at higher stage of oxidation of base lube oil No. 2.

It is found that as given in Fig. 34, the deterioration effect of oil with iron and cobalt ions is higher than that of oil with copper ions. This may be attributed to the formation of some complex compounds between these ions and some polar groups of some natural inhibitors and prevent them from giving good service. Also, it is found that their ions have a higher equivalent numbers



Fig(34): Correlation between the effect of different metal catalysts on the rate of increase in kinematic viscosity for base oil No.2 after 24 hrs oxidation time.

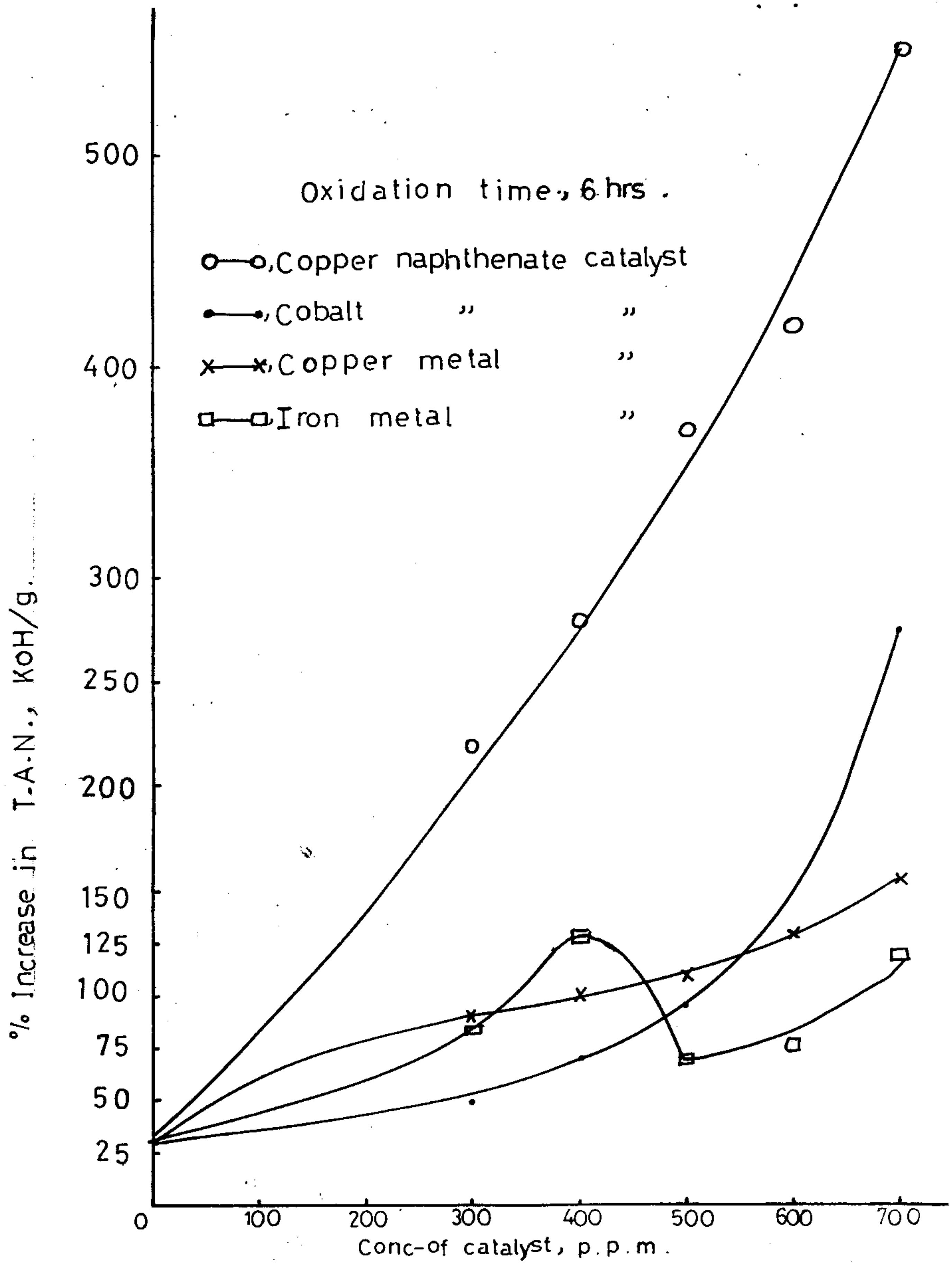


Fig (35): Correlation between the effect of different metal catalyst on the rate of increase in total acid number for base oil No. 2 after 6hrs oxidation time.