PREPARATION AND EVALUATION OF SOME COPOLYMERS AS POUR POINT DEPRESSANTS.

T. T. Khidr

Department of Petroleum Applications, Egyptian Petroleum Research Institute.

Nasr City, Cairo, Egypt.

Abstract

α-Olefin maleic anhydride copolymers were prepared by reacting C_8 or C_{14} olefin with maleic anhydride, then esterified with dodecyl or NAFOL 1822B alcohol, purified and characterized through average molecular weight, polydispersity index and infrared spectroscopy. A waxy crude oil (pour point =21°C and wax content = 18.9 wt %) was treated with the four synthesized additives as pour point depressants and determined using x-ray diffractometer. It is found that the X-ray diffraction patterns of waxes with additives are remarkably different from those without additives. The NAFOL 1822B ester of 1-tetradecene maleic anhydride copolymer also show stronger interaction with the wax than NAFOL 1822B ester of 1-octene copolymer, dodecyl ester of 1-tetradecene maleic anhydride copolymer and dodecyl ester of 1-octene maleic anhydride copolymer. These effects can be attributed to the chain length of side hydrocarbon. The wax solubilization is a function of copolymer.

Key words: α-Olefin-maleic anhydride copolymers, pour point depressants, waxy crude oil, x-ray diffraction.

Introduction

Crude oil and its many down stream fractions products are comprised of a complex and wide range of hydrocarbon components. A major constituent of these hydrocarbon stream is generally described as paraffin waxes. In some crude oils, waxes can represent up to 20

wt% of the total mixture. On cooling, the n-paraffins separate out as plate–like crystals which interact together to form three dimensional network in which still liquid oil becomes trapped as the results, in an increase of viscosity and a decrease of oil flowability [1]. Several options are available to countract the problems by paraffin waxes. These include heating the stream, blending with gasoline or kerosene and using a chemical additive treatment[2,3] . These additives function by modifying wax crystal size and shape during their growth. There are various laboratory and field tests for evaluating the performance of flow improver/pour point depressant in improving the cold flow properties of waxy petroleum fluids[4,5]. Flow improvers of different polymeric structures have been published in patent reviews such as polysaccharides [6] long alkyl chain fatty acid esters[7], polyacrylates[8] , polymethacrylate[9] , α-olefin-maleate copolymers[10], alkylfumarate-vinyl acetate copolymers[11], dendramines, dendramides[12], and star-shaped alkylcarbamates[13]. The paraffin deposition could be inhibited by trichlorethylene-xylene binary system which exhibit also a substantial effect as pour point depressant[14] These additives function by one or more of several postulated mechanisms, viz. nucleation, adsorption, co-crystallization and improved wax solubility, that result in the formation of smaller wax crystals with more regular shape[15]. Various analytical tools have been used to elucidate the mechanism of interaction of flow improver/pour point depressant with wax crystallization in petroleum fluids such as scanning electron microscopes[16], differential thermal analysis[17], differential scanning calorimeters[18] and x-ray diffraction [19,20] .

The present work deals with the synthesis and evaluation of some type of α- olefin maleic anhydride copolymers as wax dispersants was disperssion for waxy crude oil, also we intend to study the interaction between four synthesized additives and the wax constituent

in waxy crude oil through wide-angle x-ray diffraction in order to elucidate this phenomenon at typical field conditions.

Experimental

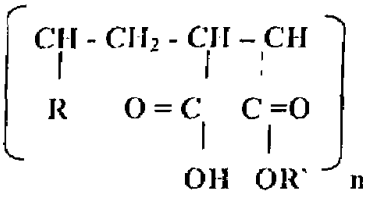
Materials used:

Linear long- chain alcohol blend (NAFOL 1822 B)were supplied by CONDEA chemical co. with the typical analysis listed in Table 1. Dodecyl alcohol, 1-octene, 1-tetradecene and maleic anhydride the other used chemicals are of technical grade. A sample of Umbarka waxy crude oil were used for evaluating the performance of the synthesized polymeric additives. The physico chemical characteristics of the crude oil are given in Table 2.

Synsthesis of the polymeric additives:

Esters of α-olefin maleic anhydride copolymers were prepared by reacting (1mol) of 1-octene or 1-tetradecene with 0.6 mol of maleic anhydride. Xylene (200 mL.) as a solvent and (0.01 mol) of benzyl peroxide dissolved in 20 mL xylene as an initiator were gradually added to the reactants .The reaction mixture was then refluxed with vigorous stirring in the temperature range 120-125°C for 6 hours,finally white powder copolymer (intermediate product) was obtained. The two polymeric products (1-octene or 1-tetradecene maleic anhydride) were then esterified successively with 1.6 mol of dodecyl alcohol or long chain alcohol blend NAFOL 1822B. P-Toluene sulphonic acid (2g) was added as a catalyst while heating to 140° C even no more water of reaction was collected to obtain four polymeric additives: dodedcyl ester of : 1-octene maleic anhydride copolymer (CP1), dodedcyl ester of 1-tetradecene maleic anhydride copolymer (CP2), NAFOL 1822B ester of 1-octene maleic anhydride copolymer (CP3) and NAFOL 1822B ester of 1-tetradecene maleic anhydride copolymer (CP4).

Purification of the reaction products (CP1 to CP4) was carried out by washing with distilled water for removing the acid catalyst, separation of the organic layer, drying over anhydrous $Na_2 SO_4$ and vacuum distillation for stripping of solvent and unreacted alcohol and maleic anhydride. Each product was precipitated in an excess volume of methanol and was then filtrated. Further purification by dissolution of the product in xylene and reprecipitating by pouring into methanol, filtration and vacuum drying, finally light yellow viscous liquid was obtained for test use.The products have purity of approximately 98 %. The general formula of the prepared additives is as follows :



Where R = $(CH_2)_5 CH_3$ or $(CH_2)_{11} CH_3$ and R` = $(CH_2)_{11} CH_3$ or NAFOL 1822B.

The chemical structure was confirmed by infrared spectroscopy and average molecular weight by high performance liquid chromatography.

Characterization of the prepared copolymers :

The four synthesized copolymers (CP1-CP4) were characterized in terms of their weight average molecular weights and polydispersity index using a gel permeation chromatography technique, against polystyrene molecular weight standards. The measurement was carried out by high performance liquid chromatography apparatus (HPLC) (Waters Model-510) under the following conditions: Solvent: Toluene HPLC grade; Column: Ultrastyragel 500, 1000, 10000,100000Å; Temperature: 25°C; Flow Speed:18 cm^3 min^{-1};

Results are given in Table 3. The prepared copolymers were also studied through infrared spectrophotometry by using a FTIR spectrometer, Model Mattson-infinity series bench top 961. Their spectra are shown in Fig.1, which indicate the presence of the characteristic bands at 3100- 3423cm^{-1} (OH stretch), 2915, 2846 cm^{-1}(CH stretch), 1726-1774 cm^{-1} (C=O stretching in aliphatic esters), 1718-1726 cm^{-1} (C=O stretching in aliphatic carboxylic acids),1464 cm^{-1} (CH_3 bending),1368 cm^{-1} (OH bending), 1176cm^{-1}(C-C stretching) and 740cm^{-1}(-$(CH_2)_n$-).

Evaluation of synthesized products.

Different concentrations (100,250,500,1000 and 2000 ppm) of each of the four polymers were incorporated in the waxy crude oil sample at 40°C, then the treated crude oil sample was subjected to pour point determination according to the ASTM D97 method. Identical portion from the surface layer of the pour point test sample was then transferred at the pour point test, immediately after the pour point determination, to the x-ray diffractometer (Shimadzu, Model DP-DI) where the diffraction pattern was recorded at 500 ppm of the CP1-CP4 additives.

Results And Discussion

The physico chemical characteristic of the tested waxy crude oil are given in Table 2. Average molecular weights of the prepared esters of α-olefin maleic anhydride copolymers are listed in Table 3. It is evident that their average molecular weights increase as the (carbon numbers) of the fatty alcohol increase. Changes in the pour point of the crude oil treated with different concentrations of the synthesized additives are also listed in Table 3 and represented graphically in Fig. 2. It can be seen from these results that the response of the crude oil towards the synthesized copolymers, as pour point depressants, is clearly varied. The waxy crude oil shows low response towards CP1 and CP2 additives, while its response towards CP3 and CP4 is good. Such differences in their activity can be attributed to the increase in their average molecular weight and polydispersity index.

The above results can be confirmed through x-ray diffractograms. The x-ray diffraction of the untreated waxy crude oil is displayed in Fig. 3 (a) and shows two sharp crystalline peaks that appear at 2θ =21.292°, interplanar spacing d =4.1694Å at high intensity I/I_o=100, and at 2θ =23.6710° , d = 3.7556 Å and I/I_o = 29. The x-diffraction patterns of interaction of the additives with the crude oil are shown in Fig. 3 (b-c). The diffraction of pattern CP1 shows two sharp crystalline peaks at 2θ = 22.671°, d = 3.4556 Å at I/I_o = 100, and at 2θ = 24.00°, d = 3.7032 Å, I/I_o = 29 and 2θ = 22.142°, d = 4.0114 Å, I/I_o = 9 Fig. 3 (b). This interaction leads to a depression in pour point. APP_{500}= 6°C . The x-ray diffraction of the CP2 (dodecyl ester of 1-tetradecene maleic anhydride copolymer) shows similar crystalline feature as the CP1 due to the C_{12} side chain of dodecyl ester. Interaction with the crude oil, Fig. 3 (c), leads to a decrease of the crystalline peak at 2θ = 20.953°, d= 4.2363Å and I/I^o = 100, with a halo in the range

2θ = 18-21°. This interaction leads to ΔPP_{500} = 9°C. The x-ray diffraction of CP3 (NAFOL 1822B ester of 1-octene maleic anhydride copolymer) interaction with the crude oil. Fig. 3 (d), shows a peak at 2θ = 21.292 °d=4.1694Å and I/I^o=100, with a broad halo in the range 18-25°. This interaction leads to significant ΔPP_{500} = 18°C. The CP4 (NAFOL 1822B esters of 1-tetradecene-maleic anhydride copolymer) with the crude oil is depicted in Fig. 3 (e) that shows a broad plateau halo at 15-23°, with a peak at 2θ = 21.123°, d = 4.2026 Å and I/I_o=100 due to the interaction between C_{21} side chain of the additive and wax in the crude oil. The additive achieves an optimum ΔPP_{500} = 24°C.

Conclusions

- Some of the prepared esters of C_8 or C_{14} α-olefin maleic anhydride copolymers with average molecular weights in the range of 26300 to 38200 are found to be effective as pour point depressants for the investigated waxy crude oil.
- The NAFOL 1822B ester of 1-tetradecene maleic anhydride copolymer proved to be an adequate ΔPP_{500} = 24 °C.
- The alkyl chains of the prepared copolymers are an essential factor for an intensive the interaction of the additives with the crude oil.

References

1-Wang, S.L.,A.Flamberg and T.Kikabhai,(1999): Select the optimum pour point depressant. Hydrocarbon Processing February. pp.59.

2-Andre, L.C.M. and F.L. Elizabete,(2001): The influence of vinyl acetate content of the poly (ethylene co-vinyl acetate) (EVA) additive on the viscosity and the pour point of Brazilian crude oil. Petroleum Science and Technology Vol.19 (1&2) pp.197-204.

3-Al-sabagh, A.M., T.T.Khidr,A.M.Atta (2002):Effect of abietic acid derivative surfactants on calorific value and flow of crude oil and some distillates.Petroleum Science and Technology. Vol. 20 (7&8) pp.693-711.

4-Zhang,J.C. Wu,W.Li,Y.Wang and H.Cao (2004) : DFT and MM Calculation: the performance mechanism of pour point depressants study. Fuel. Vol.83.pp.315-326.

5-Sedersen,K.S. (2003) : Influence of wax inhibitors on wax appearance temperature. pour point, and viscosity of waxy crude oils. Energy & Fuels, vol. 17 (2), pp..321-328.

6-Mohamed,M.M.,H.H.Abou El Naga and M.F. Meneir (2001) : Synthesis of multifunction additives for fuel 3rd International Conference of Fuel Germany. pp.375

7-El-Gamal, I.M. N. El-Eman and A.A. El-Sayed (1991) :Flow improvers in GPY-3 waxy crude oil. Indian Journal of Technology,29December, pp.584-588.

8-El-Gamal, I.M, El-Batanoney and F.M. Ghuiba (1993) :Synthesis and evaluation of some acrylate polymers as pour point depressants for waxy crude oils. Al-Azhar Engineering International Conference December 18-21, pp.93.

9-Andre, L.C.M.and F. L. Elizabete (2002):Influence of ethylene-co-vinyl acetate copolymers on the flow properties of wax synthetic systems.Journal of applied polymer science Vol.85 (6), pp.1337-1348.

10-El-Gamal, I.M., and A.M. Al-Sabbagh (1996) : Polymeric additives for improving the flow properties of waxy distillate fuels and crudes. Fuel, Vol.75 (6) pp.743-750.

11-El-Gamal, I. M, O.M.O. Habib and A.A. Amer (1992) : Copolymer as pour point depressant, for distillate fuel. Bulletin of Faculty of Science Mansoure University. Vol. 19,(1) pp.1-18

12-Katritz, A.R. and B.Yany (1997) : Snthesis of dendramines, dendramides and their new application in the oil industry. Journal Chin.Chem. Soc. Vol.44 (6) pp.575-580.

13-Smid,J.X.Chen and C.L.Xia (1997): Star -shaped alkyl carbamates as Pour Point Depressants.Tribology Transactions, Vol.40,(2) pp..279-282.

14-Adewusi,V.A.(1998): An improved inhibition of paraffin deposition from waxy crudes. Petroleum Science and Technology Vol.16 (9&10) pp.953-970.

15-Srivastava, S.P., T. Butz,C.B.Tiwari,H.J. Oschman and I.Rahimian (2002):Gel formation in vacuum gas oil. II. Composition versusthermal behaviour and additive response. Petroleum Science and Technology Vol.20 (3&4) pp.291-304.

16-Lewates,K.,R.D.Tack; D.H.M.Being and J.W.Mellin (1991):Wax crytallization in diesel fuel:Habit modification and growth of n-alkane crystals, J.Adv. Ing. Cryst. pp.166-176.

17-Vazquez,L.O.A.and Ibarra; J.R.V. (2001):Polyisobutenyl succinimides as detergents and dispersants in fuel infrared spectroscopy application. Fuel, Vol.80,pp. 960-968.

18-Zhang, J.;C.Wu; .W.Li; Y. Wang and Z.Han (2003):Study on performance mechanism of pour point depressants with differential scanning calorimeter and x-ray diffraction methods. Fuel, Vol.82, pp.1419-1426.

19-Diawar, S.V.K.; S.P. Srivastava; G. C. Joshiand S. D. Phatak (1994): Crystallization characteristics of waxes from undoped / doped crude oil.Erdol and Kohle Erddas Petrochemie. Journal Vol.47 (4) pp.150.

20-Battarjee,S. M.,W.M.Abd El-Azim and K.M.H. ElEsawy (1997):Some chemical studies on gas oil obtained from Egyption crudes. Egypt. J. Petrol (6) pp.39-52.

Table 1. Properties of NAFOL 1822B alcohol.

Properties	NAFOL 1822B
Composition, wt%:	
C_{16}- OH	0.2
C_{18}-OH	15.0
C_{20}-OH	14.8
C_{22}-OH	69.8
C_{24}-OH	0.2
Average carbon number(calculated)	C_{av} = 21.3
Density g/cm^3 at 70 °C	0.802
Solidification point, °C	63-65
Ester No mg KOH/g	0.16
Acid No mg KOH/g	0.01
Water, wt%	0.04
Flash point, °C	204
Iodine No. mg I/100mg	0.23

Table 2. Physico chemical properties of the tested Umbarka waxy crude oil

Test	Method	Result
Sp .Gr.wt 60/60 °F.	IP 160/92	0.8119
API Gravity at 60°F	Calculated	32.8
Pour Point, °C	ASTM D-97	21
Kinematic viscosity, cSt - at (40°C) - at (100°C)	IP 71/95	4.2 1.9
Flash. point °C	ASTM D-93	77.7
Wax content(wt%)	ASTM D-3344	18.9
Sulfur content (wt %).	IP 242/83 ·	1.76

Table 3. Characterization and evaluation of the synthesized additives as pour point depressants for the waxy crude oil

Copolymer	Composition	Av. m. wt.	PDI	Additives Concentration, ppm					
				0	100	250	500	1000	2000
				Pour Point, ^{o}C					
CP 1	Dodecyl ester of 1-octene maleic anhydride copolymer	26300	1.56	21	15	15	15	18	21
CP2	Dodecyl ester of 1-tetradecene maleic anhydride copolymer	30400	2.05	21	15	12	12	12	18
CP3	NAFOL 1822B ester of 1-octene maleic anhydride copolymer	33600	2.45	21	6	6	3	9	9
CP4	NAFOL 1822B ester of 1-tetradecene maleic anhydride copolymer	38200	2.66	21	0	-3	-3	3	9

Av. m. wt. = Average molecular weight; PD I = Polydispersity Index.

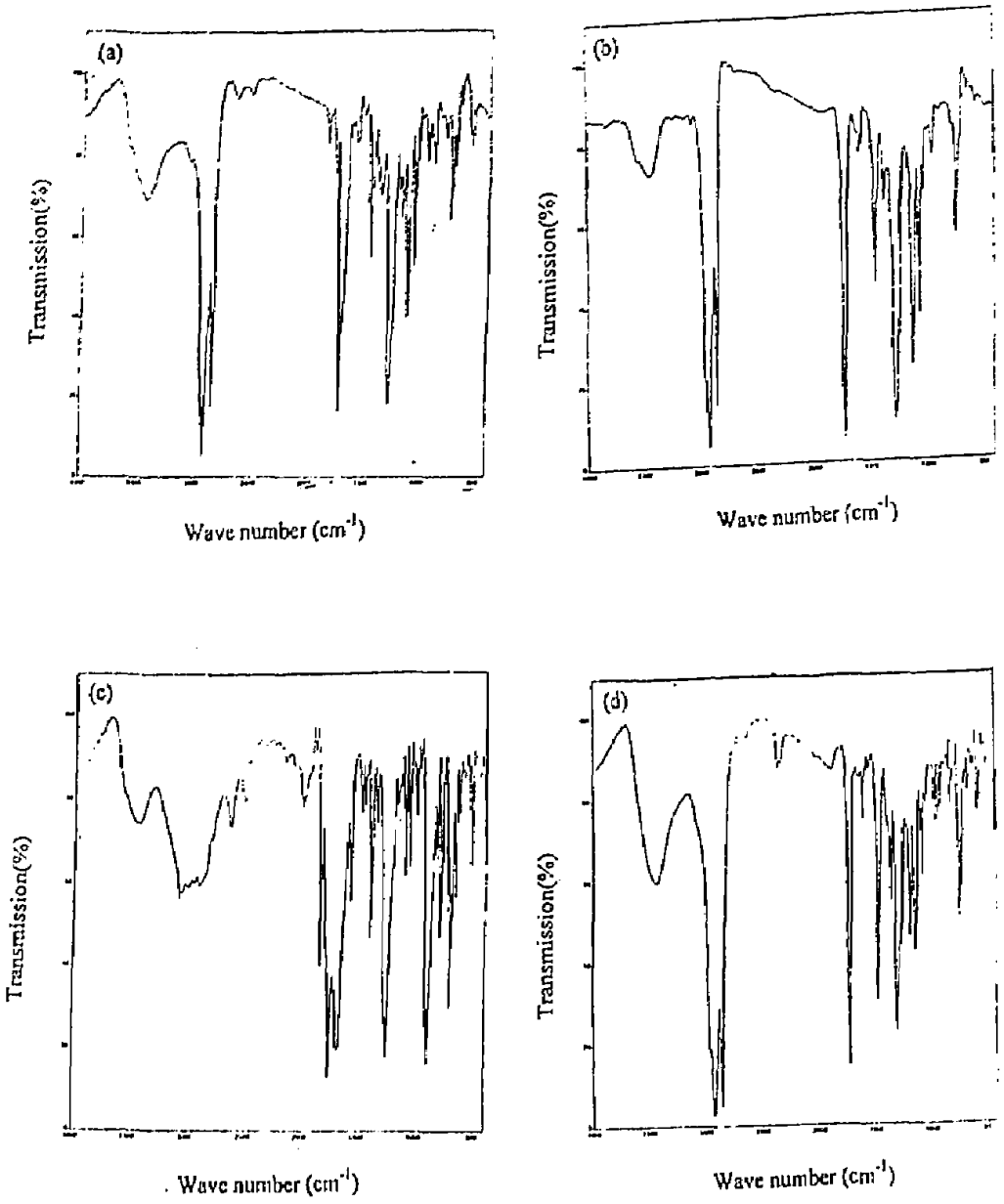


Fig. 1: Infrared spectra of the
(a) Dodeyel ester of 1-octene-maleic anhydride copolymer (CP1).
(b) Dodeyel ester of 1-tetradecene-maleic anhydride copolymer (CP2).
(c) NAFOL 1822B ester of 1-octene-maleic anhydride copolymer (CP3)
(d) NAFOL 1822B ester of 1-tetradecene-maleic anhydride copolymer (CP4)

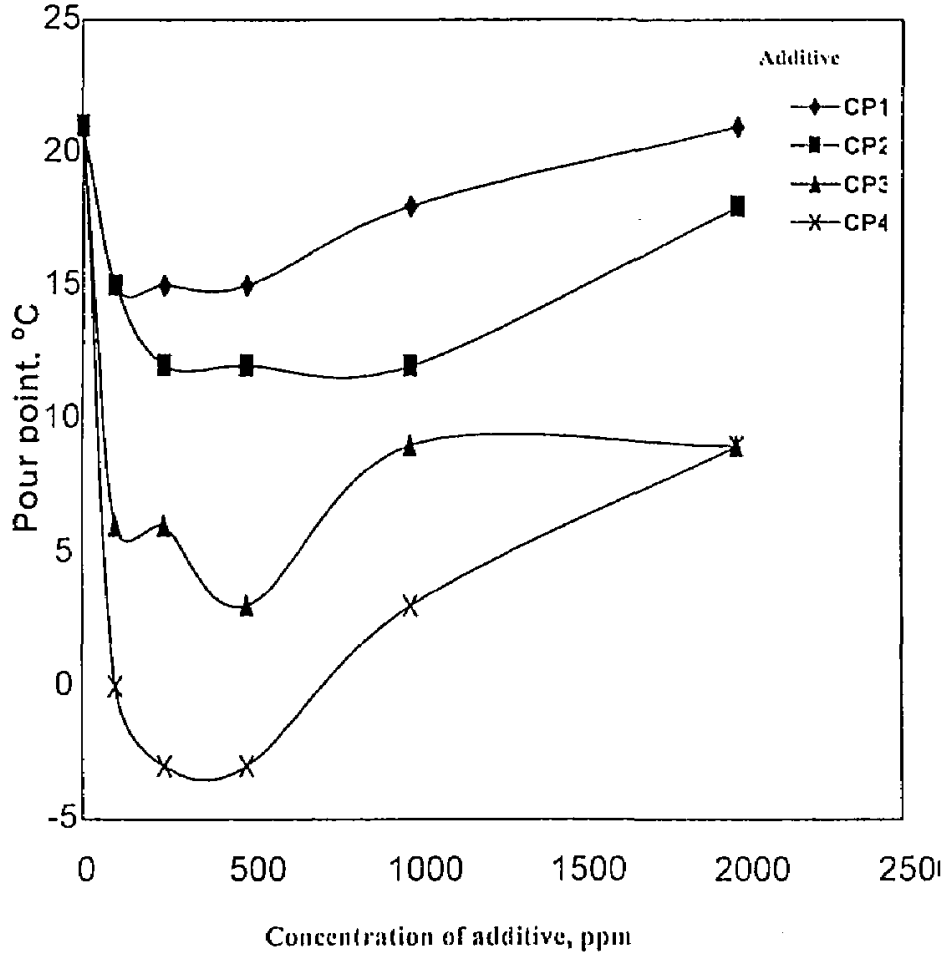


Fig. 2. Effect of concentrations of the additives on the pour point of the studied crude oil.

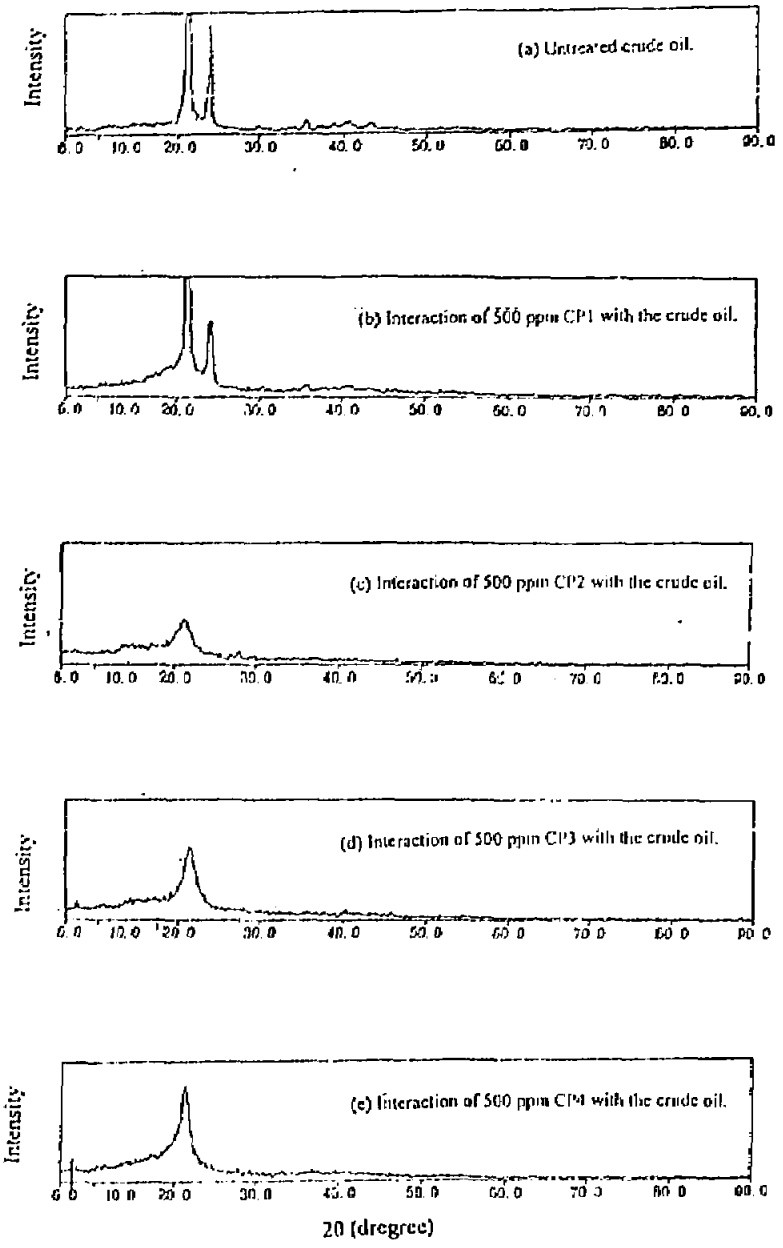


Fig 3: X-ray diffraction patterns of the prepared additives (CP1-CP4) with the studied crude oil