CHAPTER-III

APPLICATIONS OF SYNTHESIZED POLYMERS ADDITIVES ON CRUDE OILS

3.1.1 Area selected for the study of this work

Composite oil from three oil fields from South Gujarat has been selected for the study.

Field Selected are[5]:

1. Gandhar
2. Kosamba
3. Nada

Field History:

Gandhar:

Gandhar field is located in Western India, within the established oil province commonly referred to as the Cambay Basin. It is 50 Km from Ankleshwer project. One big CTF plant is made at one part of the field having latest facilities for storing the crude from the field. The field has multiple producing sandstone layers, designated as GS-1 through GS-12. These sandstone layers are separated by distinct shale markers promoting the different layers of reservoirs of separate identities. These producing zones belong to Middle Eocene age and are locally referred to as Hazad Member. The Hazad member overlies the thick cambay shale section, which is the source of hydrocarbons in this province.

The Gandhar sand display two intermixed feature: a major dip-fed deltaic system, modified by a minor strike fed marine influence. The sand are generally shaly and silty, and carry the print of various progradational, aggradational and retrogradational phases.

On individual well examination, the lithostatic column always consists of sand-shale alterations, it is tempting the individual to correlate the individual sand bodies between the well in continuous units, giving the false impression that the sand bodies are present all throughout the field. This over-simplification leads to misunderstanding the dynamic flow behaviour of the field, thus rendering proper planning for optimum recovery. The Initial production from the Gandhar field was started in October'1986 at rate of $87m^3$ per day. In march 1997 the field production was 492TPD with a water cut of 11%.

Kosamba:

This oilfield is situated Narmada-Tapti block of Cambay Basin. This field was discovered in 1962 is situated 15Km. South West of Ankleshwer. Production from the field was started in January '1968 but well were not put on sustained production because of operational difficulties like downhole paraffin deposition inadequate facilities, for storage and transportation of crude oil. The field has five hydrocarbon bearing reservoirs designated as Sand S-I,Siltstone-III,Siltstone-VI,Siltstone-VII, Siltstone-VIII. Siltstone-III is the main hydrocarbon producing reservoir. The pressure production history of the field indicates active water drive. The initial reservoir pressure of Siltstone-III was 71.0 kg cm^2 at 680m(MSL) and the current and the current reservoir pressure in stabilized about 58 kg cm^2 at 680m(MSL).The initial in place oil reserves of the field is 1.52MMt .The ultimate oil reserves of the field are 0.47 MMt are proved and 0.11 MMt are probable. Cumulative production from the different wells currently leaves vast scope to enhance, productivity of the field. All the wells in Kosamba oilfield are operating on SRP and water cut showing increasing trend(63%). The production rate at Kosamba GGS is around 108-120 M^3/D.The Oil from Kosamba GGS is transported to Ankleshwar CTF through 4" line of 14 km. Kosamba GGS has two 4" line of 14 km. Old line is used to receive oil from CTF Ankleshwer, while the new one is used for pumping the crude from Kosamba GGS to CTF Ankleshwer. At present the Kosamba composite crude oil is being transported through pipeline by blended with 40% Ankleshwer oil. But in winter season this process fails as blended oil has pour point of 30°C. Composition of crude oil and the infrastructure available for transporting the crude oil is fixed. Hence, the chemical intervention technique remains the only viable solution among other available options.

Nada:

Oil field is located in 14 km North West of Gandhar oil field in Bhroach-Jambusar block of Cambay Basin. Two hydrocarbon bearing sands are encountered in Nada fields viz Nada main Pay and Upper pay, of which the former is the main reservoir. Correlation of these two reservoir sand is quite problematic due to rapid vertico-lateral facies variation.

Nada main pay has in place oil reserves of 4.0MMt and initial reservoir pressure of the pay was super hydrostatic. Recently the reservoir pressure has declined to 203

$kgcm^2$ which is below the saturation pressure of 235 $kgcm^2$ has resulted in gradual increase in total GOR.

The production Facilities at Kosamba & Nada oilfields are susceptible to wax precipitation and deposition problem due to waxy nature of crude oil. In adequate reservoir fill up during water flood is one of the factors that might promotes wax deposition. Such problems, seriously affects economic production from the reservoir due to high cost of remedial measures and increasing operating cost. This implies that it is utterly important to find out cost effective methods to sustain production. Chemical solution to the wax problem has emerged as an effective tool because of its flexibility, selectivity and ease of intervention. The present work explores the feasibility of this approach for Kosamba, Nada and Gandhar oil fields in South Gujarat. All the characteristics of crude oil of the selected fields are studied to reach on valuable conclusion.

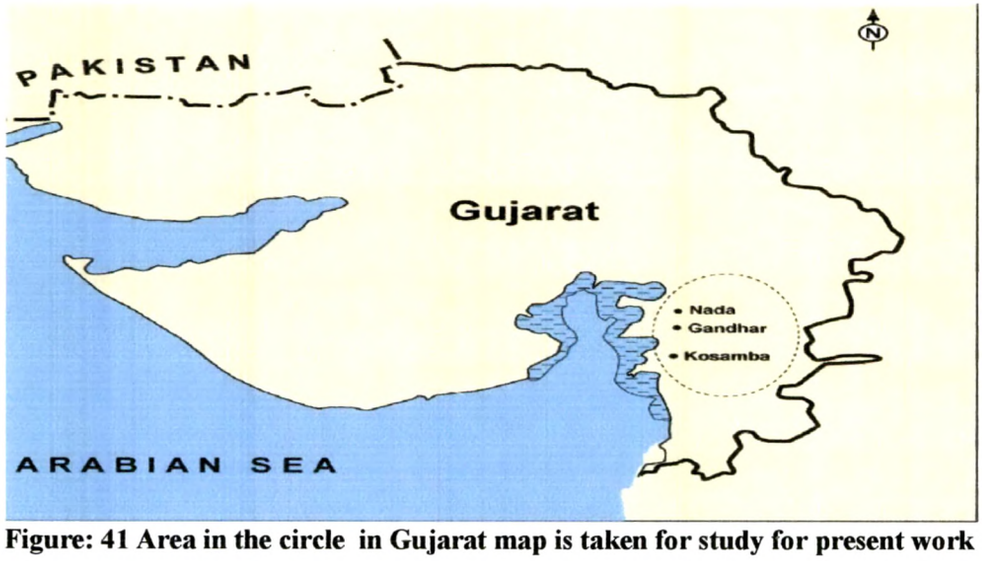


Figure: 41 Area in the circle in Gujarat map is taken for study for present work

3.1.3 Reaction Scheme for the synthesis of chemical additives:

Pour point depressants are used to improve the flow behavior of waxy crude oils at low temperature by modifying wax crystallization process. Wide varieties of materials are now available as pour point depressants with varying degrees of success, which include polyacrylates, styrenated polyesters, polymethacrylates, ethylene-vinyl acetate copolymers[146,147], alkylated polystyrenes, and maleic anhydride copolymers. The

present work is concerned with preparation of fatty acid esters-maleic anhydride copolymers. These copolymers are tested for their physical and chemical properties of these polymers. The polymers are used as pour point depressants because their structures are somewhere near to waxes present in the crude oil. Polymer stop aggregation of wax crystals in crudes controlling pour point. It can be understood in this way that these polymers exhibits properties of the pour point depression below the ambient temperatures. The geo-scientists are constantly in search for PPDs that can achieve optimum low temperature flow performance at low concentrations. Present work comprises experimental processes, which are developed with accurate methods with specific conditions of synthesis.

Kosamba, Nada and Gandhar oil fields are selected specifically as these fields exibit prominent wax problems for storing and transporting the crude. The present work has been emphasized on flow improvers for the selected fields. Main problem in these fields is wax deposition that too very high in winter season. Wax dispersed easily from the crude oil significantly as the temperature goes below the pour point that is ambient temperature. Chemical solution is searched in the present research[164].

In this research work four series of the pour point depressants which are polymers chemically speaking are prepared. Listed below :

A. Diester of Poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate

B. Diester of Poly(n-alkyl oleate-co-maleic anhydride)dialkylate

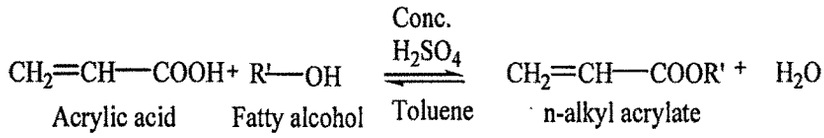
C. Diester of Poly(n-alkyl methacrylate-co-maleic anhydride)dibenzylate

D. Diester of Poly(benzyl undecylenate-co-maleic anhydride)dialkylate

Practical procedure for the synthesis of all these polymers and copolymers and their diesters has already been explained in chapter-II. Chemical reaction for the above procedures have been explained as under. Synthesis work is carried out with taking care of all physical conditions and standard methods.

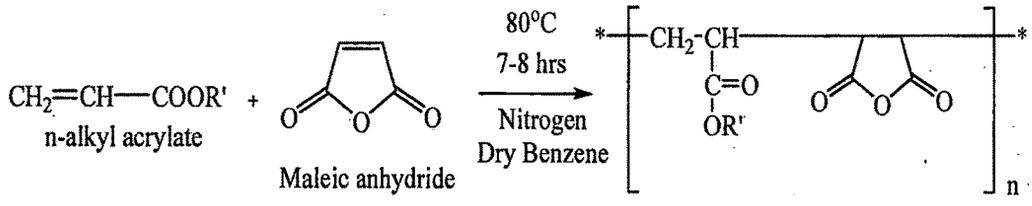
A. Synthesis of poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate

(i) Synthesis of n-alkyl acrylate:



Where R'=Aliphatic fatty alcohol 8, 10, 12, 14, 16, 18 carbon chain

(ii) Synhesis of poly(n-alkyl acrylate-co-maleic anhydride)



(iii) Synthesis of diester of poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate

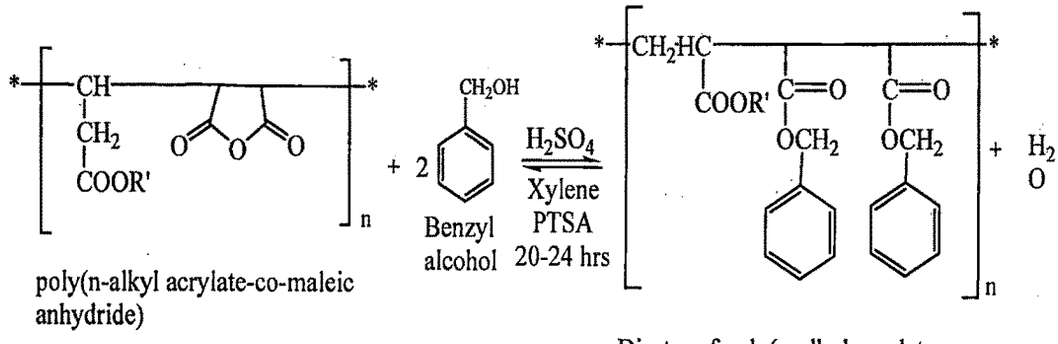
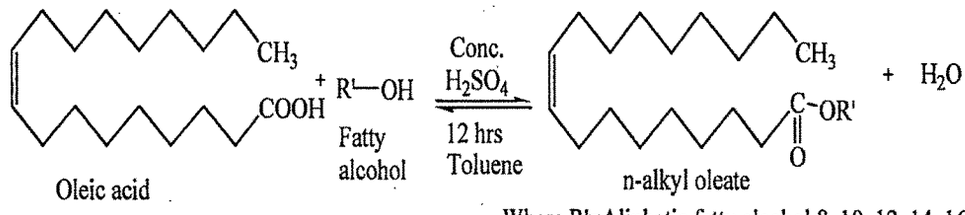


Figure:42 Synthesis of diester of poly(n-alkyl acrylate-co-maleic nhydride)dibenzylate

B. Synthesis of poly(n-alkyl oleate-co-maleic anhydride)dialkylate

(i) Synthesis of n-alkyl oleate

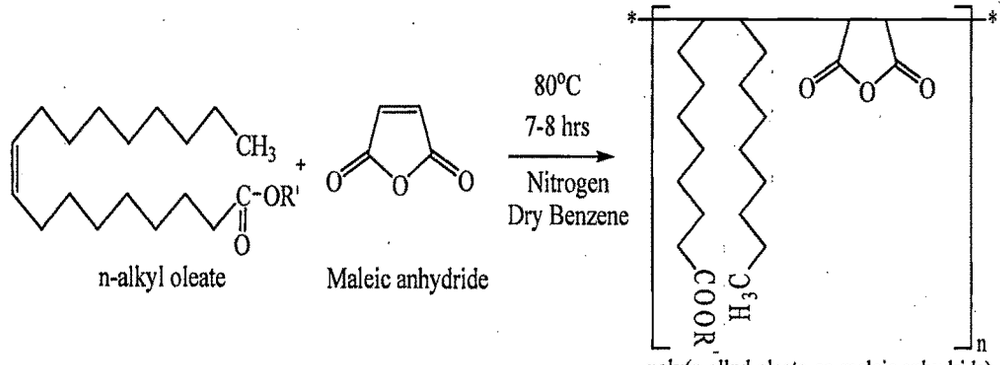


Oleic acid

n-alkyl oleate

Where R'=Aliphatic fatty alcohol 8, 10, 12, 14, 16, 18, 22 Carbon chain

(ii) Synhesis of poly(n-alkyl oleate-co-maleic anhydride)

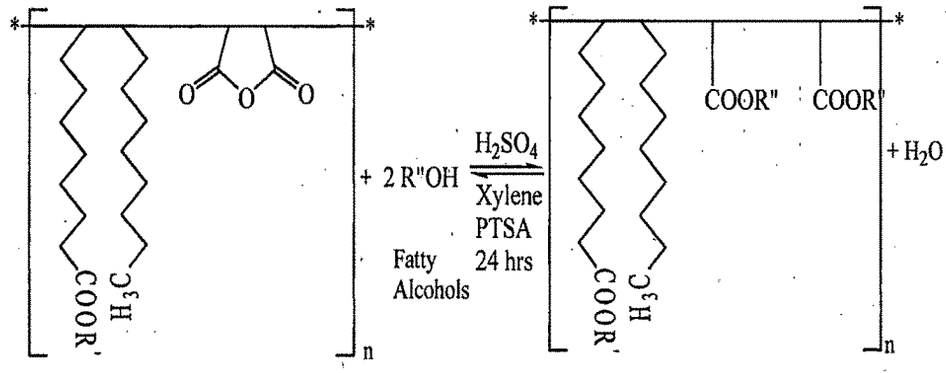


n-alkyl oleate

Maleic anhydride

poly(n-alkyl oleate-co-maleic anhydride)

(iii) Synthesis of diester of poly(n-alkyl oleate-co-maleic anhydride)dialkylate



poly(n-alkyl oleate-co-maleic anhydride)

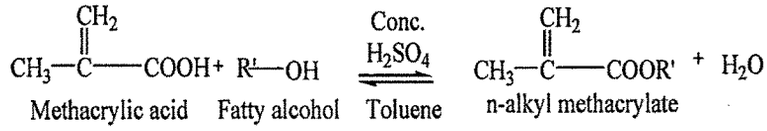
Diester of poly(n-alkyl oleate-co-maleic anhydride)dialkylate

Where R"=Aliphatic fatty alcohol 10, 12, 14, 16, 18, 22 Carbon chain

Figure 43 Synthesis of diester of poly(n-alkyl oleate-co-maleic anhydride)dialkylate

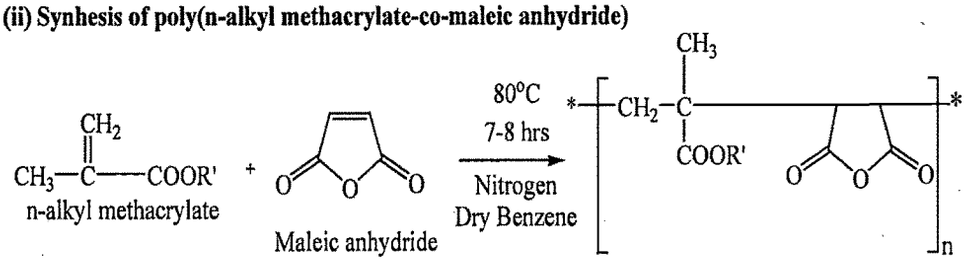
C. Synthesis of poly(n-alkyl methacrylate-co-maleic anhydride) dibenzylate

(i) Synthesis of n-alkyl methacrylate



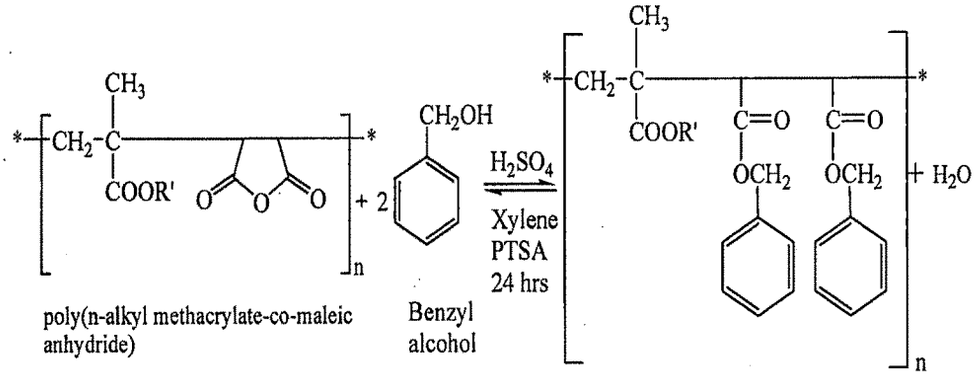
Where R''=Aliphatic fatty alcohol 08, 10, 12, 14, 16, 18 Carbon chain

(ii) Synhesis of poly(n-alkyl methacrylate-co-maleic anhydride)



poly(n-alkyl methacrylate-co-maleic anhydride)

(iii) Synthesis of diester of poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate

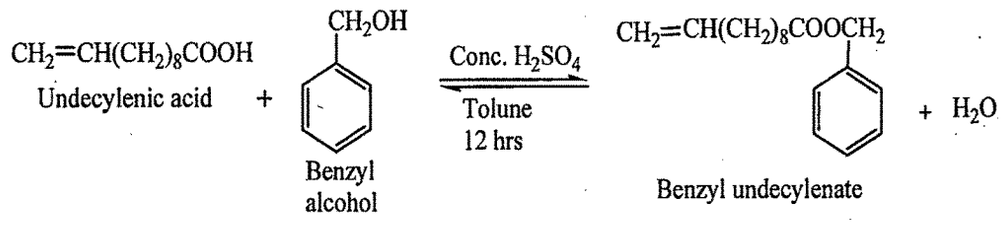


Diester of poly(n-alkyl methacrylate-co-maleic anhydride) dibenzylate

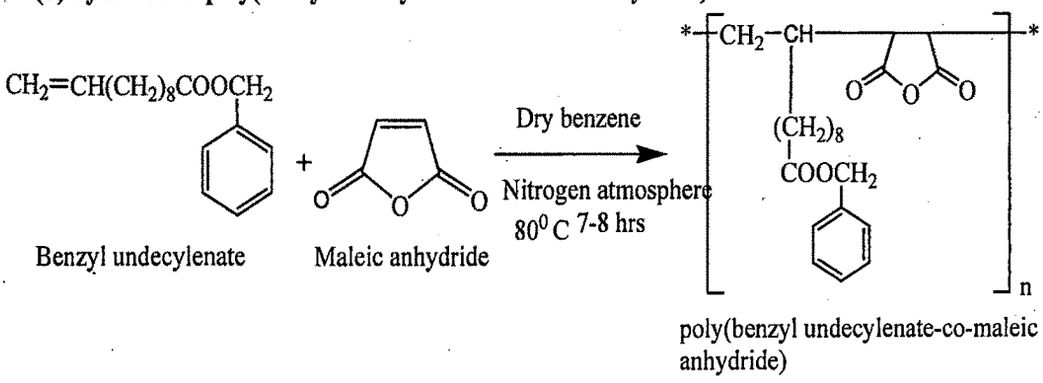
Figure 44 Synthesis of diester of poly(n-alkyl methacrylate-co-maleic anhydride) dibenzylate

D. Synthesis of poly(benzyl undecylenate-co-maleic anhydride) dialkylate

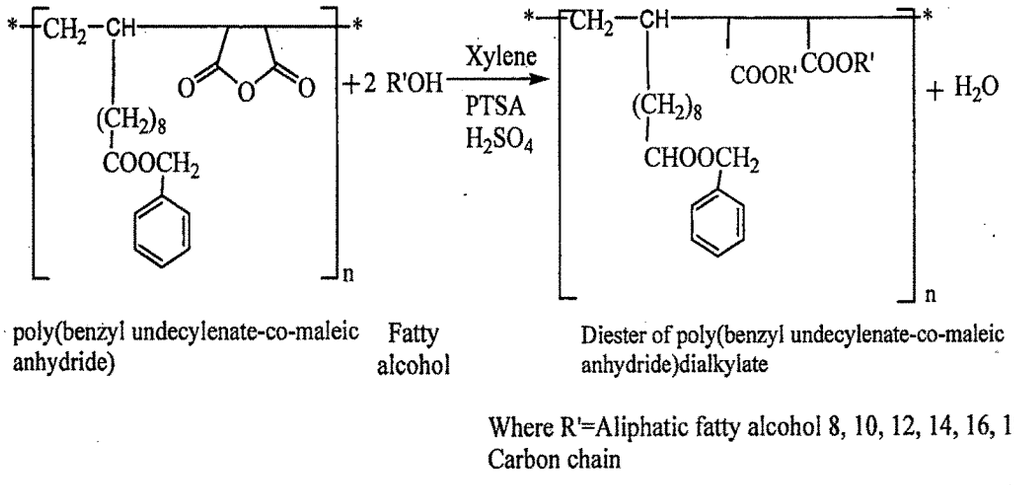
(i) Synthesis of benzyl undecylenate



(ii) Synthesis of poly(benzyl undecylenate-co-maleic anhydride)



(iii) Synthesis of diester of poly(benzyl undecylenate-co-maleic anhydride) dialkylate



Where R'=Aliphatic fatty alcohol 8, 10, 12, 14, 16, 18 Carbon chain

Figure 45 Synthesis of diester of poly(alkyl undecylenate-co-maleic anhydride)dialkylate

3.1.4 Performance Testing of PPDs:

Experimental: As explained earliar the conventional pour point apparatus and Advanced Rheometer AR 500 was used for the determination of viscosity and yield values respectively.

a) Pour point determination[122,123]

The pour point determination was done by the standard method ASTM D-97/IP -15. During pumping and transportation of crude oil, it is subjected to thermal treatment and also it experiences the shear. It is very important to remove the shear history of the crude oil sample for establishing a repeatable starting point. To ensure this, the oil was heated to above the non-Newtonian temperature limit i.e above cloud point. If shear history is not removed than crystallization of waxes may start earlier than the expect temperature which may not be very correct measurement. Normally the pour point obtained is higher one. Above wax crystallization temperature, good mixing is done for quicker dissolution of wax crystals and dissolution of asphaltene micelles. It is also taken care that crude should not be heated to very high temperature other lighter fraction may evaporate and again the studied may not be correct. So the cloud point of each oil is determined and is used carefully in pour point studies separately.

For determination of pour point of neat crude oil, 50 ml of neat oil sample was measured and transferred into a 250 ml reagent bottle. At this stage, the crude oil shows totally non-Newtonian behaviour. The measured crude oil sample was subjected to 55±1°C for 30 minutes. At this temperature, the wax crystals are soluble in the oil and sample is assumed to show Newtonian behavior. The neat crude oil sample was transferred to pour point tube. The pour point tube was kept in pour point apparatus surrounded by ice bath. After each 3°C interval, the pour point tube was taken out from the apparatus and tilted to see the flow of oil. The pour point of the neat crude oil was noted when the oil was just pourable.

After that, the desired concentration of the additive was doped to the neat crude oil and the contents were shaken vigorously for five minutes to make uniform mixing of the additive. Again the sample was subjected to 55±1°C for 30 minutes and transferred to pour point tube and cooled to 33°C, kept in pour point apparatus surrounded by ice bath. After each regular 3°C interval, the pour point tube was taken out from the apparatus to see the flow ability of oil. The pour point of the additive treated crude oil was noted when the oil was just pourable.

b) Rheological properties[89]

To remove the crude oil sample memory, the crude oil sample was subjected to 55±1°C for 30 minutes. Then the PPD's were doped at 55±1°C. The experimental temperature was approached under controlled conditions of shear rate and cooling rate because of the sensitivity of the measured flow properties to the shear and thermal history. Doses were selected by taking care of effectiveness. Doses selected were (500,1000,1500, 2000, 2500,3000 ppm) because the selected crude oil is highly waxy in nature.

Rheology of treated and untreated crude oil was determined by AR 500 Rheometer at different selected shear rates and temperatures. The Rheometer consists of a smooth stainless steel truncated cone plate geometry (4 cm in diameter, cone angle 2°, truncation of 55 μm) was used. The respective oil samples were placed on the plate and geometry was attached. Temperature was controlled with a peltier element inside the plate without any error.

The rheological studies were performed for both neat and additive treated crude oil. In first case, the viscosity of neat crude oil was determined at different temperatures by continuous temperature ramp. Then the crude oil were treated with the selected PPD and pour point were determined with method described above and rheological studies were carried out on the pour point temperatures. These studies are specially carried out exactly to know the effect of the PPD with a particular dose in viscosity and change in flow behavior. All these experiments were done to study the effect of thermal conditions on the rheological properties of the crude oil with and without PPD treatment.

Initially the sample was heated to 55±1°C, mixed uniformly and kept at room temperature for two hours. It was then heated to the specific heat treatment temperature for thirty minutes. The sample was then cooled to the test temperature of 33 °C (pour point) at a rate of approximately 0.1°C/min and determined its viscosity and yield stress. The experiment was repeated at different temperatures and different concentration of various additives.

c) Cold Finger Test[126]

800 ml of crude oil sample was taken in one litre glass bottle. Maintain the temperature of the crude oil at nearly pour point i.e inlet temperature of crude oil. Dope it with PPD with selected dose i.e 2000ppm optimized dose with respect to the crude oil. Mix it thoroughly by giving 50 shakes each by inverting the bottle up and down carefully allowing the vapors to escape away from body by gently loosening the stopper. Place the same in water bath maintained at temperature (pour point). When crude oil attains the temperature required , it is circulated at a constant flow rate of ml/minute for three a cooper coil ID-5mm, Length 5.5 ft
maintained at 20±1°C in a second water bath. After completion of the test, coil is flushed with HSD oil till the clear HSD oil comes out from out from the other end of the coil. The coil is inverted to drain the HSD oil and is dried overnight. The paraffin deposit formed in the coil is weighed after flushing it with chilled acetone to remove lose oil if any.

Run a blank without any additive maintaining similar test conditions.

Calculate percent wax inhibition as under:

% wax inhibition – efficiency = (B-C) / (B-A) X 100

Where A= wt of empty coil

B = wt of copper coil + wax deposited with untreated crude oil.

C = wt of copper coil + wax deposited with treated crude oil.

d) Microscopic studies for waxes

A preliminary studies were carried out on wax crystal size and shape for Gandhar crude oil. Extensive work has been done on the microscopic studies of waxes. Generally, wax crystal appears as plate and needle shaped. Crystallization of waxes depends upon the chemical composition of the crude oil and crystallization conditions. Crude oil possessing higher melting point waxes crystallizes in plates and low melting waxes crystallizes in needle shaped crystals. Plate shape crystal contains normal alkanes and needle shape crystals contain both aliphatic and cyclic hydrocarbons. Plate crystals can transform into needle shape crystals. Also, the shape of plate and needle increases with decreasing the temperature. At room temperatures, crystal appears as a bright field. The PPD lowers the pour point by preventing the

needle star formation.On treatment of additive, the larger wax crystals are transformed into smaller wax crystals[100-104]. The microscope system used for determination of wax crystal size and shape was Leitz, Laborlux 12 Pol D with Cannon 12 X zoom Digic 5 Mega pixels connected to a computer with the software Zoom browser EX and software connected is Leica Qwil. Microscopic studies had been carried out at room temperature to find size and shape of the wax crystals with and without additive treatment. The neat and additive treated crude oil samples were directly applied on the glass slide covered by cover slip and identified the change in wax crystal size and shape at magnification 25 X.