CHAPTER-V

SUMMARY AND CONCLUSIONS

Most commonly used fossil fuels are petroleum, coal, and natural gas. Worldwide deposits of fossil fuels are limited. Demand is increasing day by day. To sustain the supply of petroleum various method are employed by the companies. As usual the production of petroleum also associated with various problems. When it is transported from field to the refinery it get deposited because of the presence of waxes in various proportions. Below the ambient temperature, the wax molecule comes out from the solution and forms the gels and the gel transformed into solid as temperature decreases further. Typical paraffin managements include the use of chemical wax inhibitors and the implementation of mechanical pigging operations. The chemical comprises the use of pour point depressants or flow improvers, wax dispersants.

As explained earlier crude oil is the biggest amenity of the world. Exploration, production and transportation are itself very costliest and risky processes. Three fields from the South Gujarat were selected which are having crude oils of very high waxy in nature. These fields are facing main problems in transporting and storing the crude oil during winter season. Because of this problem there is a loss of huge money every year. Mechanical scrapping i.e pigging, solvent solutions are in use to overcome this problem. But these solutions are not cost effective. So chemical solution has been tried in this work. Fields selected are Kosamba, Nada and Gandhar, predominant oil and gas producing fields in South Gujarat, India. Physico-chemical characterization of the crudes of the selected fields was carried out in the laboratory. Four series from different studies are prepared in laboratory and tested on the crude oils from above mentioned fields. Extensive studies are carried out to reach at right conclusion. Main tests carried out are pour point, rheology and cold finger before and after treating with the prepared polymers. Results are outlined. Pour point of Kosamba field oil has been decreased from 36 to 15°C, Gandhar from 33 to 15°C and Nada from 33 to 21°C. If implemented in the field in the prescribed conditions can help in reducing the problem to a great extent.The present work is emphasized mainly on the problems encountered during production and transportation of crude oil , So it is necessary to know the uses, exploration, physico-chemical characteristics and problems encountered in oil industry.

Petroleum is a very complex mixture consisting of paraffin, naphthene (cycloparaffin) and aromatic hydrocarbons as well as nitrogen, oxygen, sulfur containing compounds and traces of a variety of metal-containing compounds and inorganic compounds. Waxes are complex mixtures of high molecular weight alkanes of three structural types as straight chain, branched chain and cyclic. The wax present in petroleum crudes primarily consists of paraffin hydrocarbons (C_{18}-C_{36}) known as paraffin wax and naphtenic hydrocarbons (C_{30}-C_{60}). Asphaltenes also precipitated in addition to paraffin adding to the transportation problem. The present work has been elaborated on chemical solution for the crude oil transportation problem. Three fields from South Gujarat were selected where the wax deposition problem is predominant. Almost 27 polymers were prepared in the laboratory after lots of study of crude oil properties and type of chemical additives so that better results can be obtained.

Synthesis of these chemical additive is explained in chapter-2. Four series were selected namely

n ABA = Diester of Poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate

n OA n = Diester of Poly(n-alkyl oleate-co-maleic anhydride)dialkylate

n MBA = Diester of Poly(n-alkyl methacrylate-co-maleic anhydride)dibenzylate

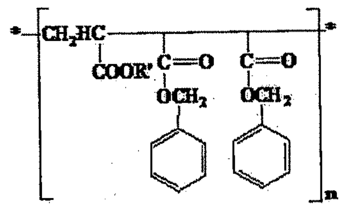
BAUn n = Diester of Poly(benzyl undecylenate-co-maleic anhydride)dialkylate

Structural properties of polymeric flow improving additives like polyalkyl acrylates, polyalkyl methacrylates and their copolymers with maleic anhydride as flow improvers were studied. Also the synthesis of polymer additives by esterification, copolymerization by free radical polymerization and diesterification process is followed as the main steps of the synthesis part. Reaction scheme for the synthesis is given in chepter-3. In free radical polymerization, the advantage of free radical polymerization, various types of initiators used for polymerization and alternating copolymers of maleic anhydride were studied. The effect of temperature, solvent and gel on the molecular weight of the polymer, were also seen in detail. In esterification reaction, excess mole of acids (acrylic, methacrylic, oleic and undecylenic) was reacted with alcohol (benzyl alcohol and aliphatic fatty alcohols of varying carbon chains of C_8 to C_{22}) to produce ester using concentrated H_2SO_4 as a catalyst and toluene as a solvent. The water was azeotropically distilled off by Dean and Stark method. The synthesized ester was analyzed by IR spectroscopy. Then ester was reacted with one mole of double recrystallized maleic anhydride in presence of benzoyl peroxide and dry benzene as a solvent in presence of inert atmosphere of nitrogen to keep the reactant molecules blanketed to give the alternating copolymer. The copolymer was purified by repeated solvent non-solvent method. The solvent non-solvent method was used in the experiments comprised benzene as a solvent and methanol as a non-solvent. Further, the copolymer was reacted with two moles of benzyl alcohol and different fatty alcohols using H_2SO_4 and PTSA in traces as catalyst and xylene as a solvent to produce the diester with long and aromatic pendant chains.

All the process explained above is presented in chemical reactions. The synthesized co-polymeric additives were tested on the selected Gandhar, Kosamba and Nada field's crude oil for their performance. Experimental and results of these studies are explained in Chepter-IV(I,II and III). For this purpose the pour point studies and rheological behavior studies were done in detail on all the three field oils and with various concentrations of all the additives prepared. The pour point was determined by conventional pour point tester and rheology was studied by AR 500 Rheometer. Higher dosages were selected for both studies as the selected crude oils are waxy in nature. Detailed methods for determination of pour point and rheology are explained in the chapter-III. Further studies were extended to the cold finger tests also to reach at a better conclusion for the performance check of the additives. Standard methods were chosen for all the tests.

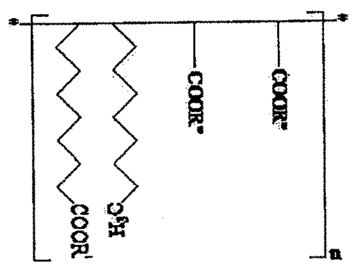
For the pour point studies, the additive dosages of 500, 1000,1500, 2000, 2500 and 3000 ppm were selected. Detailed studies were carried out by selecting almost six doses so that results can be seen from low to high doses. Rheological studies are also done on all the doses that too on the pour point of that oil at that particular dose. It could be possible because of the AR 500 Rheometer which is highly sensitive to temperature and 1-2 ml of sample is required for the detailed study. Four different classes additives synthesized under this investigation, which differ from one to another in their basic polymeric unit and length of pendant alkyl chains. The structural formulas of the synthesized four classes are shown as follows,

Class I



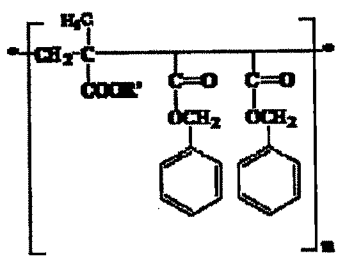
Diesters of poly(n-alkyl acrylate-co-maleic anhydride)dibenzylate

Class II



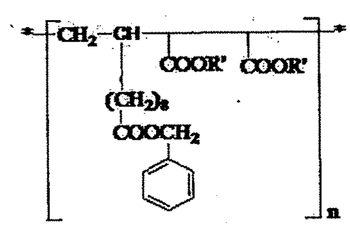
Diesters of poly(n-alkyl oleate-co-maleic anhydride)dialkylate

Class III



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

Class IV



Diesters of poly(benzyl undecylenate-co-maleic anhydride)dialkylate

In pour point studies, among the twenty seven synthesized additives, most of them has given good results. The Gandhar crude oil the best results are given by 16 OA16 and BAUn 22 as both have reduced the pour point of Gandhar oil from 33 to 18°C. 12 OA 12 and 18 ABA has given the pour point to 24°C. 18 MBA has reduced the pour point to 21°C. These are the excellent results. In case of Nada 16 ABA and 16 MBA has given pour point 21°C showing the 16 pendent chain length has been found very effective for Nada crude oil. But Undecylenate additives has worked reversely in case of Nada crude. In case of Kosamba crude oil 16 OA16, 16 ABA and 16 MBA has reduced the pour point from 36°C to 21°C. 18 ABA has worked excellently as given pour point of Kosamba oil 15°C. In case of Kosamba oil also all the diesters of undecylenate has given reverse effect by enhancing the pour point from 36°C to 39 and 42°C. So rest of the additives prepared has worked effectively for the crude oils selected from South Gujarat.

The efficiency of the additive depends on the total wax content in the crude, length of pendant chain, type of pendant chain (aliphatic, aromatic, branched) and type of wax present in the crude. The pour point depressant follows mechanism that additive molecule when configured with paraffin molecule, it interacts with the n-paraffin molecules at the growing ends of the paraffin crystals and alteration in the crystal size and morphology of the paraffin. The pour point depressant molecule prevents additional paraffin molecules from adding to the crystal, thereby limiting the dimensions of existing crystal. Thus, the pour point depressant or flow improver keeps the wax in solution form. The performance can be enhanced by using the appropriate carbon chain in pendant side. The additive with sufficient pendant chain shows efficiency in decreasing the pour point. If the synthesized additive closely matches with the wax present in the crude and properly co-crystallizes with wax and thus prevents wax crystal growth through steric hindrance, the pour point of the oil will be reduced. It is closely observed that as the work is mainly carried out on the waxy crudes selected from the South Gujarat, the main role of additives prepared is observed for inhibiting the wax crystallization only. Ashpaltenes and resins also plays important role for the pour point of any crude oil. When wax quantity is very less and oil is ashpaltic in nature, the pour point is somewhat lower side. In many cases even below zero degree. It is further observed from the experimental work that if wax and resins are present in high quantity the pour point raises to even above 50°C

Rheology of treated and untreated Gandhar, Kosamba and Nada crude oils was determined by AR 500 Rheometer at different selected shear rates and temperatures. 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. Procedure is explained in chapter-III.

In rheological studies, almost all the four series have shown excellent flow improving property for Gandhar, Kosamba and Nada crude. It has been observed clearly from the results that increasing concentrations of additive has improved flow behavior and reduced viscosity and yield stress proportionately. All the crude selected are waxy in nature and gives sharp pour points. Increasing concentrations has hardly any effect in pour point of crudes. So once the additive added in 500ppm concentration the pour point has no effect on increasing to 3000 ppm also. But case is not true in rheological studies. It has been observed from the results that all the doses are important for seeing the proper effect of every additive. It is noticed that most of the additive have reduced viscosity and yield stress with 3000ppm much more than 500ppm doses. In cases where the pour points have been reduced the higher dose has nearly made the crude oil to be Newtonian. All the series prepared have given good results in all the three field crude oil selected for the study

Higher viscosity observed due to strong cohesive forces, established among the resins and asphaltenes through the hydrogen bonds and mutual overlapping of aromatic condensed rings among the resins and asphaltenes. The additive molecule can form hydrogen bonds with resin and asphaltene molecules and there are fewer tendencies for mutual overlapping of aromatic condensed rings among the resin and asphaltene molecules. Thus, the viscosity of the crude oil decreases.

The maleic anhydride based flow improver or pour point depressant with appropriate aliphatic pendant alkyl chains with polymer backbone matches with the wax structure present in the crude and gives better solubility properties. The ester based co-polymer shows excellent pour point depressing property with viscosity reduction with optimum concentration of the additive.

The cold finger test run for the confirmation of the results obtained from pour point studies and rheological studies. Two additives from each series were tested with each of the crude studied. Results shows that deposition of wax is inhibited to a great extent with the flow improvers which has decreased pour point of the crude oil.

In microscopic studies, wax crystal appears as plate and needle shaped. Crystallization of waxes depends upon the chemical composition of the crude oil and crystallization condition. 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.

Pour point depressant shows its activity by inhibiting the growth of wax crystal in X-Y crystallographic plane and produces smaller crystals of higher volumes. The change in crystal size, shape and ability of the wax crystals to interlock and intergrowths is greatly decreased due to pour point depressant. Larger wax particles result in more aggregation. Hence, rapid aggregation is formed at a lower cooling rate. This effect of the crystal size also plays an important role in the action of pour point depressant. The flow improver prevents the aggregation of wax crystals through co-crystallization results in formation of smaller wax crystals and depression in pour point of the crude oil is obtained. The studies were extended to Cold finger test to confirm the results from pour point and rheological studies and further to see the result's viability in the crude oil field, because the area of application is the crude oil field where the actual problem exists. In many cases it is seen that in laboratory the work done by any additive is very good but not in the field conditions. So the field conditions were created in the laboratory and results were recorded for optimized dose on all the three oils selected. It is clearly seen from the tables 38, 48 and 58 that results are very much matching with other studies.

Studies were further extended to Aging effects, but results are not recorded as it was observed that there is not any change in rheology and pour points of the crudes. This may be because of That the crude studied are waxy in nature and there is very less quantity of asphaltene and resins. These studies are rather helpful in studying the restartability problems of pipeline shutdowns. It is very much seen that area of application is very big and very less work is done in this field specially considering the oil field conditions in India. There is lot of scope for research work in this area which can be very helpful in oil industry and can save a huge amount of money wasted every year in handling pipeline transportation of crude oil and its pipeline maintenance.