Chapter - 4
SUMMARY AND CONCLUSION
Summary and Conclusion

The complex nature of crude oil creates many problems during its transportation through long distance pipelines. Crude oil containing high amount of wax exhibits high pour point and non-Newtonian viscosity behaviour below the cloud point. At lower temperature crystallization of waxes creates problem in restartability of crude oil after shutdown of the pipeline. The waxes generally crystallize as an interlocking network of fine sheets, thereby entrapping the remaining oil in cage like structure and cause the blockage of pipeline.

To overcome such problems crude oils have been widely treated with chemical additives (flow improvers/pour point depressants) to improve their flow properties at low temperature. A flow improver application is often the most economic and effective solution for the crude oil flow problem. These additives results in the formation of smaller wax crystals with more regular shape by one or more of several postulated mechanism, viz. nucleation, adsorption, co-crystallization and improved wax solubility.

Consequently, recent works have been directed to the introduction of new additives which can effectively disperse the wax of crude oil. This type of additive is referred to as wax dispersant flow improver. It is often applied to modify the size and shape of wax crystals. The reviews, on flow improvers for waxy crude oils of last fifty years reveals that a linear polymer or copolymer with pendant alkyl side chains of specific length and nature is one of the general characteristic of flow improvers for waxy crude oils. The structure and composition of wax dispersants is similar to conventional flow improvers in some features but different in others. They often possess highly polar functional groups. This polarity may reach a surfactant character which is considered as the basic prerequisite for the dispersant potential. Polar nitrogen containing polymers can function as wax dispersant and flow improver simultaneously in one component additive. The one component multipurpose additive has the advantage of complete compatibility between the two restrictive functions in one chemical structure while may lack
this characteristic when comprising more than one component. When an additive comprising two components is used, one component serves as the conventional polymeric flow improver while the other component including mainly a hydrocarbon oil soluble chain and polar dispersant group functions as a wax dispersant. The component of lower solubility acts as a nucleator while the other acts as a wax growth arrester.

Keeping in view the experimental execution of the planned work, the significance of the results obtained the correlation that is sought to be built up as a bridge between the existing theories and their eventual extension in the light of the specific findings of this investigation, etc., the gist of this dissertation including its salient features can be presented as follows:

Forty new polymeric compounds have been synthesized in a planned sequence of variation in their basic polymer units. The synthesis is accomplished in an appropriate manner, setting proper conditions and establishing the standards for proper yields. All the newly synthesized compounds are terpolymers. Syntheses of monomers, copolymerization and incorporation of polar nitrogen group in the prepared terpolymer have been the main steps of the synthesis part. Two prime objectives of the investigation are:

1) To explore the use of the newly synthesized polymeric compounds as additives for pour depression activity for a host of crude oils collected from different oil fields of North and South Gujarat (India) and to assess further their impact on the rheological properties and

2) To find the correlation of the extent of pour depression and yield value characteristics with the molecular structure of the basic polymer unit.

The crude oils differ in their characteristics without any specific relevance to geographic locations. The characteristics of the crude oil change from geographic
location to location and even from well to well of the same location. For the present invention, five crude oils from the different oil fields of Gujarat have been selected. They are as follows:

1) Langhnaj (North Gujarat)
2) Jolwa (South Gujarat)
3) Gandhar (South Gujarat)
4) Lanwa (North Gujarat)
5) Balol (North Gujarat)

All the selected crude oils are waxy in nature as they contain high wax content with low content of asphaltene. Pour point and rheological behaviour of these crude oils have been determined during this investigation. All these aspects are included in the preliminary study and discussion. All of them are non-Newtonian near their pour point.

The additives synthesized during this investigation, fall under five different classes, which differ from one another in their basic polymeric unit and length of pendant alkyl chains. The structural formulas of the synthesized five classes are shown as follows:

Class I

Poly (hexyl ricinoleate-co-hexadecyl maleimide-co-alkyl ricinoleate)

Where R = C₆, C₈, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, and C₂₂
Chapter - 4

Summary and Conclusion

Class II

Poly (hexyl oleate-co-hexadecyl maleimide-co-alkyl oleate)

Where R= C6, C8, C10, C12, C14, C16, C18, and C22

Class III

Poly (hexyl methacrylate-co-hexadecyl maleimide-co-alkyl methacrylate)

Where R= C6, C8, C10, C12, C14, C16, C18, and C22

Class IV

Poly (hexyl cinnamate-co-hexadecyl maleimide-co-alkyl cinnamate)

Where R= C6, C8, C10, C12, C14, C16, C18, and C22
Chapter - 4

Summary and Conclusion

Class V

Poly (hexyl undecylenate-co-hexadecyl maleimide-co-alkyl undecylenate)

Where R= C₆, C₈, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, and C₂₂

Chapter - 2 of the thesis deals with the synthesis of polymer additives by esterification, terpolymerisation by free radical polymerization and incorporation of polar nitrogen group in the prepared terpolymer are the main steps of the synthesis route of the pour point depressant additives. The structure elucidations of additives were done by Fourier Transform Infra Red spectroscopy and molecular weights of terpolymers were determined by Gel Permeation Chromatography.

Chapter - 3 of the thesis involves the evaluation of efficiency of prepared polymer in terms of pour point depression and study their effect on viscosity parameter of Langhnaj, Jolwa, Gandhar, Balol and Lanwa crude oils from oil fields of Gujarat (India). Detailed method for determination of pour point and viscosity of the crude oil at different temperatures and concentrations of additives were evaluated by using Fann viscometer.

All the forty new polymeric compounds have been tested for their pour depression activity. As the experimental determination of the pour depression activity proceeded, the growing realization of a probable correlation with the molecular geometry of the copolymers suggested the basic changes in the polymeric pendant
chains and structures. Not all the experimentally tested additives gave encouraging observations; besides recording of all such observations evidently was presenting an enormously expansive prospect in terms of the written number of pages. Therefore the results of some additives have been recorded and discussed in detailed. Some of these additives have yielded excellent results in terms of pour depression while many others may be acclaimed as quite good. Some of these additives were chosen for finding out their impact on the rheological behaviour of the crude oils. Among all the synthesized flow improvers, some are evaluated as pour point depressants and some are showing good viscosity with yield stress reduction property. The synthesized five classes of polymeric flow improver show variable results regarding pour point depression and low temperature performance with the selected crude oils. Most of the additives are able to give satisfactory results.

From the previous chapters, it can be concluded that additives from any of the five series behaves differently with crude oils of different oil field. Not a single additive is equally effective on all the crude. Additives having C14 to C22 pendant alkyl chain from all the series except cinnamic acid series favourably interact with Langhnaj crude oil. Additives which containing C12 to C16 carbon chain are best for Jolwa crude oil but cinnamic acid series is not effective on Jolwa crude oil. Gandhar crude oil may have paraffin wax of C14 to C22, so the additives containing C14 to C22 carbon chain as pendant alkyl chain are efficient for Gandhar crude oil. Additives from all the five series which contain C17 to C18 carbon chain are very favourably interact with Balol crude oil. But on Lanwa crude oil only methacrylic acid series and undecylenic acid series additives which contain C8 to C12 carbon chain are showing good performance and rest of the series are average for Lanwa crude oil. These additives which are effective for crude oils are matched with the carbon number of wax present in crude oils and they are successfully adsorbed and co-crystallized on the wax surface and inhibited the wax crystal growth and extended the pour point of crude oil.
From the results it is also proved that all the additives do not reduce the pour point but they reduce the viscosity and vice versa. The reduction in viscosity is mainly due to sufficient pendant alkyl chain present in the additives, which matches with the wax crystal present in the crude oil. The probable mechanism for viscosity reduction is that the additive molecule reduces the strength of cohesive forces in the crude oil by reducing formation of hydrogen bonds between resin and asphaltene molecules. The additive molecules inhibit the mutual overlapping of condensed aromatic rings of asphaltene and resin. The additive molecule put the resin and asphaltene molecules stretched in the space by making stronger bonds with resin and asphaltene and resin and asphaltene do not come in contact with each other. Thus viscosity of crude oil does not increase and the oil remains in the flowing state. In some cases the viscosity of the crude oil increases. This is because at such conditions, the polymeric molecules cannot adsorb on the wax surface and if they adsorbed it cannot change the crystal shape and size but instead of that the pendant chains of polymers interlock into one another like a zipper. So, the polymeric molecule cannot slide over one another and these results in increase in viscosity.

The efficiency of flow improvers depends on the total wax content in the crude oil, length of pendant chain, type of pendant chain (aliphatic, aromatic, branched) and type of wax present in the crude. It has been shown that performance of additives can be optimized through proper polymer design. The more similar the polymer structure (back bone and pendant chain) to the wax components, the better is its performance. Performance of an additive is determined by its ability to keep the wax components in solution its ability to attach the wax components and create a barrier for networking or coalescence of the wax particles.

Cold flow improvers contain an oil-soluble long chain alkyl group and a polar structure moiety in the molecular structure. The long chain alkyl group can insert into the wax crystal in the crude oil, and the polar moiety exists on the surface of...
the wax crystal, thereby inhibiting the crystal lattice formation and reducing the wax crystal size. The synthesized nitrogen based one component polymeric structures exhibit dual function both as wax dispersants and flow improvers simultaneously. They possess the advantage of inevitable compatibility of both functions in one compound. The dispersing effect is primarily dependant on the polar effect of nitrogen/oxygen containing functional groups incorporated in the terpolymer moiety. On the other hand, flowability relies mainly on the well matching of alkyl chain pendant group of terpolymer with the average carbon number of paraffin content present in crude oil. The higher the paraffin contents in the crude oil the lower the response to flow improvement.