INTRODUCTION

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1.1 Early History of Petroleum

Today, scientists say that the oldest of oils are more than 500 million years old. The most widely accepted theory about the origin of the crude oils is that it was formed by the decay of marine organisms and even vegetation. These were deposited on the sea bed. Owing to gigantic earth movements, massive sedimentary rocks were deposited over them so as to completely entomb the marine organisms which became later converted into crude oil (1).

Known and used for thousands of years, though, petroleum made sensational history with the discovery of Drakewell in 1859, which paved the way for its large scale production (2). Petroleum rose from mere 2000 barrels in 1857 to 500,000 in 1860 and over 2,000,000 in 1861 in the U.S.A. (3).

Transportation of crude oil was one of the most pressing problem of those early days. The only means of transportation by team and wagons had its own drawbacks and the teamsters made the problem more difficult. The high cost of transportation necessitated the development of more economical means and plans for pipeline began to take shape. A 1000 feet pipeline was completed in 1862, and in 1865 a five miles in length was built up.

In early days, kerosene was obtained from coal. Kier (4) at the instance of Professor J.C. Booth, tried repeated distillation for purifying the crude oil and became the first petroleum refiner even before the discovery of Drake well. For the early refiners, there was only simple apparatus for refining and kerosene was the only product of interest. Even the kerosene obtained was not of uniform nature. When a man lighted a lamp he never knew what it would do, smoke or explode (5). A little later, by about 1865, some lubricants too were looked upon as products of interest. Rockfeller successfully managed, to get the people concerned associated into a group and evolved the Standard Oil Company in 1870. A decade later, with the help of saybolt, the company evolved a system of standardization of products specifications and test methods. This can be taken as a landmark in the progress of oil industry.

Roughly speaking, 1900 marks the end of the "Kerosene age " of the petroleum industry. Over

900,000,000 barrels of crude oil had been produced. New production areas continued to be found (3). In addition to kerosene, refiners produced fuel oil, lubricants, greases, waxes, candles and asphalt.

Growing recognition of the importance of the viscosity came into the picture about 1925, when the industry became highly concenned over the cold-starting problems. By 1930, viscosity index was an established yardstick of the lubricant industry. Solvent treating of lubricants was initiated in 1929 with phenol as the solvent. A chlorex unit was installed in 1932, a plant for furfural operation in 1933 and the first Duo-Sol (Cresylic acid-propane) process in 1934. The first synthetic, which was the polymerization product of the cracked waxes, appeared in 1930. Application of high pressure hydrogenation to lubricating oil stocks began in 1932 with resultant improvement in quality.

The use of chemical additives has played an important role in improving the quality of lubricants. Oleic acid as an additive obtained from vegetable and animal oils has been used for imparting oiliness to lubricating oils. Pour-point depressors were introduced in 1930. Use of viscosity index improvers began about 1933. The first of these was polyisobutylene. The new silicone antifoam agents appeared about 1941.

1.2 Oil Industry in India

Compared to the position in advanced countries, the petroleum industry in India is quite significant. This is illustration by the fact that while the total world resources of crude oil are about 400 million barrels, India's proved resources in Assam and Gujarat amount only to about 700 million barrels. World crude oil production in 1966 was over 1500 million tonnes of which India's share was less than 6 million tonnes (1). With the development of industries in the Third Five Year Plan and with the proposed investments in the Fourth Plan, the consumption of petroleum products is expected to reach 22 million tonnes by the end of the Fourth Plan. It is thus obvious that the development of the oil industry in India is seriously deficient and that it will continue to be so unless large quantities of oil are located in Indian territory.

Exploration

The history of exploration of crude oil in India begins with a successful drilling for oil in Digboi in 1899 though records existence of oil date as far back as 1825 as noted in the diaries of explorers who dared penetrating the thick jungles of Assam (6). A new company known as Assam Oil Company Ltd. came into existence soon thereafter. At the same time, oil exploration was carried out by the Assam Oil Company in Naharkatia and Moran in upper Assam which proved successful and oil was struck at a depth of about 4500 meters.

In 1955, after the independent of India, the Oil and Natural Gas Commission (ONGC) was formed by the Governement of India to promote oil exploration activities throughout India. The efforts of the Oil & Natural Gas Commission, ably guided by technical experts from the USSR and Rumania have been remarkably successful wells drilled in the State of Gujarat. For the last 20 years oil from the Ankleshwar fields is being processed by the refineries at Bombay. Almost simultaneously in 1959 a joint venture by Government of India and Burmah Oil Company resulted into the formation of Oil India (P) Ltd. a pumping of regular supplies of crude oil to Gauhati Refinery was started.

The discovery of Bombay High Oil Field is yet another success story of the ONGC. Many more offshore fields are under scientific exploration. Bombay offshore oil field is the largest in terms of total annual production of oil in India. More activity in this direction seens to be well planned (7,8). With the development of oilfields in Gujarat it became necessary to construct another refinery near Baroda in Gujarat and was commissioned in 1965.

Marketing :

At the time of independence and upto 1960, the marketing of oil products was entirely in the hands of private companies and the bulk of oil was distributed by three major oil companies viz., Burmah-shell, Stanvac and Caltex. It was only in 1961 that the Indian Oil Corporation, completely owned by the Government of India. In order to achieve the distribution of products in an efficient manner, a number of major products pipelines have been planned and some of them have already been implemented. This was achieved by the pipeline division of the Indian Oil Corporation which has completed a major products pipelines from the Gauhati refinery to the Siliguri installation, over a distance of 400 km. Another pipeline from the Koyali refinery to Ahmedabad has already been completed. Crude oil pipelines, natural gas transmission lines and products pipelines are going to play a very significant role in the development of the oil industry in India.

Petrochemicals :

In the field of petrochemicals, India made a beginning when Fertilizers and Chemicals of Travancore used a process for partial oxidation of naphtha to produce synthesis gas required for the manufacture of fertilizers. The Trombay fertilizers plant is based on refinery gas as well as naphtha from the refinery at Trombay, Gujarat Fertilizers which went into production in 1967, is using natural gas and naphtha from the refinery at Gujarat. In the Fourth Five Year Plan a large petrochemical complex has been planned in Gujarat. No doubt, petrochemicals are going to play a major role in the development of India's chemical industry, particularly in the case of chemicals required for defence and agriculture.

1.3 Crude Petroleum and its Nature

Crude petroleum is defined (9) as a naturally occuring mixture consisting predominantly of hydrocarbons and/or sulfur, nitrogen and/or oxygen derivatives of hydrocarbons, which is removed from the earth in liquid state or is capable of being so removed. The composition of crude petroleum varies from field to field and from well to well of the same field. Crude petroleum is commonly accompanied by varying quantities of extraneous substances such as water, inorganic matter and gas. The chemical compositions of crude oils are surprisingly uniform even though their physical characteristics very widely. It contains a very large number of compounds whose nature and distribution vary widely with the source of the crude oil (10, 11, 12). It mainly consists of carbon and hydrogen with small quantities of sulfur, nitrogen and oxygen and traces of metals (Table 1) (13).

Table 1

Elementary composition of crude oil

Element	% by weight
Carbon	84-87
Hydrogen	11-14
Sulfur	0-2
Nitrogen	0.2
Oxygen	0.5
Metals	0.02

For practical purposes, all petroleum hydrocarbons found in gasoline belong to paraffins, olefins, naphthanes (cyclo-paraffins) and aromatics. Olefins do not occure in crude oil but are formed as a result of certain refinery processes. Gasoline and kerosene fractions contain 4 to 11 and 12 to 16 carbons atoms respectively in the molecule. Considering only the paraffin hydrocarbons, gasoline may be composed of 306 and kerosene of 17721 isomers (14). Natural gasoline contains primarily paraffinic hydrocarbons with possible admixtures of 10 to 20% of naphthenes and not more than 1 to 2% of aromatics (15). Some typical paraffinic compounds in crude oil as, methane, ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, neopentane, Naphthenes in crude oil are found as, cyclopentane, methyl-cyclopentane, dimethylcyclopentane, cyclohexane, methylcyclohexane, 1,2-dimethylcyclohexane, decalin (decahydronaphthalene). Aromatic hydrocarbons in crude oil as, benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, cumene and naphthalene.

Waxes are predominantly n-paraffin hydrocarbons but also contain iso-paraffin, branched paraffins and a few hydrocarbons having a cyclic structure. Branched paraffins are found in appreciable quantities in [illegible] soft waxes and cyclic hydrocarbons in the high molecular weight waxes. The waxy hydrocarbons of progressively lower melting points separate from oil on chilling to various temperatures levels. Some crude oils may be solid even at room temperatures. The wax content of the crude oil thus depends on the temperature to which the oil is chilled. Similar considerations apply to asphaltic materials except that their melting points are arbitarily defined by the loss in fluidity beyond some value chosen at random and varying with the test. The oil may thus be regarded as a mixture of waxy and asphaltic substances which happens to behave as a liquid with in a certain range of temperature. The melting points of pure hydrocarbons are not related to the pour test of the oil because of the melting point depression effects due to the presence of other components. The wax may be regarded as a colourless, more or less translucent mass, without taste, slightly greasy to touch and having a crystalline or semicrystalline structure.

The petroleum industry distinguishes four types of waxes :

(1) Parrafin wax

It is obtained by chilling and pressing the light viscosity distillates and sweating the wax in order to separate the oil which it may contain.

(2) Slope wax

It is present in the high viscosity distillates and is unpressable.

(3) Petroleum or microcrystalline wax : (C_{resin})

It is associated with the residual stocks.

(4) Rod wax

It separates from the crude oil in the well around the sucker rod. Rod wax might be characterized as paraffin wax of very high melting point.

Crude paraffin wax which is easily sweated contains needles. The type of crystals formed by the wax depends on the condition under which the crystals are obtained, such as visoosity of the crystallization medium and the rate of cooling. However, the type of crystals formed by very narrow fractions of wax cannot be altered, except for size by changing these conditions (16).

The observations of crystal forms of waxes suggest that paraffin wax is composed not only of normal paraffin hydrocarbon but of several hydrocarbons series. The crystalline form may be impressed by one of the hydrocarbon series on the other series depending on the relative proportions of the individual series present and conditions of crystallization (17).

The pour point of the oil is affected not only by the presence of wax but also by the presence of asphalt. If the high pour point is caused by the asphalt it is usually referred to as viscosity pour. Heavy residual oils may show no change in pour point even after drastic dewaxing, but the pour test of such dewaxed oils is reduced by the removal of asphalt. Asphalt may not only raise but also lower the pour point of the oil if both asphalt and wax are present depending upon the amount of asphalt. This is due to the pour point depressant characteristics of asphalt, caused by the changes in the structure of wax crystals precipitated in the presence of asphalt. For this reason removal of the asphalt from a waxy oil may raise and not lower the pour test. The increase in viscosity after dewaxing is particularly noticeable with oils containing large quantities of asphalt.

Very little is known about the exact nature of asphaltic substances. They may be hydrocarbons of complex ring structures or heterocyclic compounds with oxygen, sulfur and nitrogen in some of the rings (18). Their separation can be effected by their preferential solubility in solvents (19) and conditions of extraction (20,21). Asphaltics are present in the crude oil as a colloidal system. Solubility in solvents increases with the increase in the hydrogen to carbon ratio of the hydrocarbon constituents and on this basis asphaltics are divided into the following classes :

Carboids : Substances insoluble in all organic solvents.

Carbenes : Substances insoluble in benzene but soluble in carbon disulfide.

Asphaltenes : Substances insoluble in petroleum ether but soluble in benzene.

Resins : Substances soluble in petroleum ether but retained from the petroleum ether solutions on percolating them through clay.

The apparent solubility of asphaltenes in kerosene and other solvents of a similar nature is due to occluded resins acting as a protective colloid. Asphaltenes can be free from the resins only with difficulty.

Carboids are seldom found in crude petroleum, but may be present in the products of thermal decomposition and cracking. Asphaltenes can be dehydrated to carbenes and carbenes to carboids. All of these substances contain, appreciable quantities of hydrogen and the so called ' coke ' formed in engines is far from pure carbon. Besides the above mentioned substances, asphaltic substances include asphaltous acids and their unhydrides.

Resins are converted to asphaltenes by dehydration and vice versa (22). Resins are comparatively lower in molecular weight than asphaltenes. A variety of sulfur compounds are present in petroleum and they are mercaptans, aliphatic and cyclic sulfides, disulfides and thiophenes (23,24). Nitrogen compounds in petroleum are derivatives of pyridine, quinoline and iso-quinoline (25). The neutral compounds are derivatives of pyrrole, indole and carbazole. The oxygenated compounds present in the crude oil may contain fatty naphthenic acids (26). Phenols and heterocyclic oxygen compounds. The phenolics are phenols, cresols, xylenols, naphthols, quinols and others.

Metal constituents too are present in traces in crude oils. These metals are normally present as soaps of naphthenic acid (27), phosphides and sulfides of arsenic or in the asphaltic fraction mostly with asphaltous acids.

The united, states Bureau of Mines (28) has developed a system which classfies the crude according to two key fractions obtained in distillation No. 1 from 250° to 275°C at atmospheric pressure and No. 2 from 275 to 300°C of 40 mm Hg pressure.

Table 2

Type	Key fraction, °API No. 1	No. 2
Paraffin	$\geqslant 40$	$\geqslant 30$
Paraffin Intermediate	$\geqslant 40$	20 - 30
Intermediate Paraffin	33 - 40	$\geqslant 30$
Intermidate	33 - 40	20 - 30
Intermediate naphthene	33 - 40	$\leqslant 20$
Naphthene Intermediate	$\leqslant 33$	20 - 30
Naphthene	$\leqslant 33$	$\leqslant 20$

1.4 Pour point of crude petroleum

Cloud point is defined as the temperature at which wax or other solid substance begins to separate from the oil. From crude oils, since they are opaque, the cloud point is normally not determined. Pour point of a crude oil is an important criterion which significantly contributes to their handling including transportation. The pour point is the temperature at which the oil is just capable of flowing under specified conditions of testing (29).

Pour points is usually associated with the wax content of the oil and viscosity with the asphaltene content. Depending on the nature of the oil the pour point is either waxy pour or viscosity pour. At equal boiling points viscosity of the paraffin base crude oils is lower than that of the asphaltic crude oil. The naphthenic crude oils have generally low pour point. For paraffinic crude oils pour point depends on the paraffin-paraffin wax ratio. The advantage of a waxy crude oil is partly compensated by the disadvantage of high wax content, which results into a high pour point and under certain conditions of low temperature could create operational difficulties. Characteristics of some waxy crude oils are summarized in Table 3.

Table 3

Crude oil	API Gravity	Pour Point in °C	Wax content % by wt.
Bombay High	38	30	12.5
Moran (Assam)	34.9	30	13.5
Nahorkatia (Assam)	31.3	30	10.1
Nigeria	38	12	9
Minas (Sumatra)	36	35	32
Bahia (Brazil)	40	35	28
C.65 Libya	36	24	18

1.5 Fluid behaviour

The consistency behaviour of fluids is classified in accordance with the relationship found to exist under conditions of laminar motion between an applied unit shearing stress and the resultant velocity gradient (or rate of shear) normal to the shear plane. Fig. 1 and 2 describe the relationship of rate of shear to unit shear stress and shear rate to viscosity.

Newtonian Fluid

It is defined as that for which, for all shear stresses below those giving rise to tusbulence, the relationship between unit shear stress and rate of shear is linear. r

Non-newtonian Fluid

Whose viscosity is dependent on rate of shear and may be dependent on time of shear.

Bingham plastic

Which exhibit a yield stress below which elastic deformation takes place rather than flow and above which the shear stress, in excess of the yield value, is directly praportional to the shear rate.

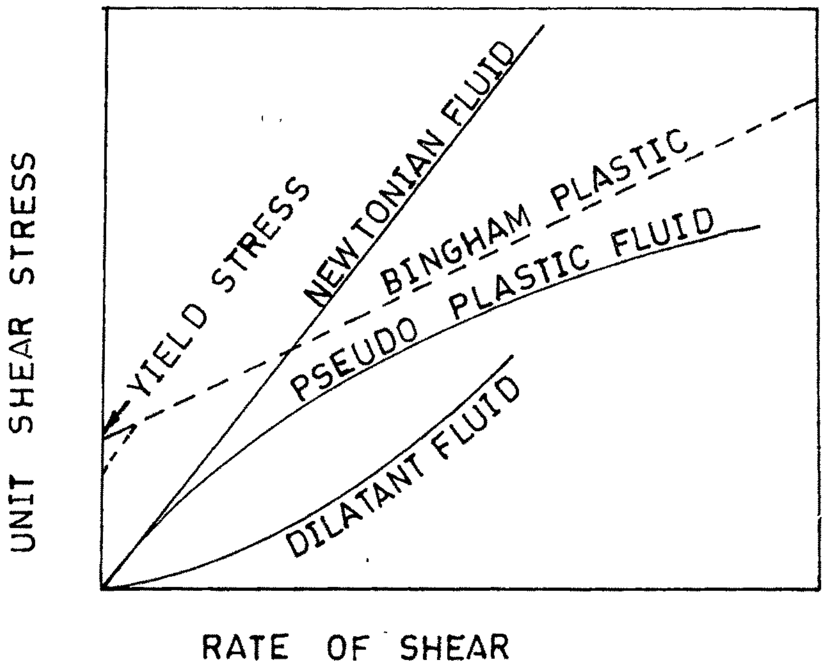

UNIT SHEAR STRESS
YIELD STRESS
NEWTONIAN FLUID
BINGHAM PLASTIC
PSEUDO PLASTIC FLUID
DILATANT FLUID
RATE OF SHEAR

FIG.1

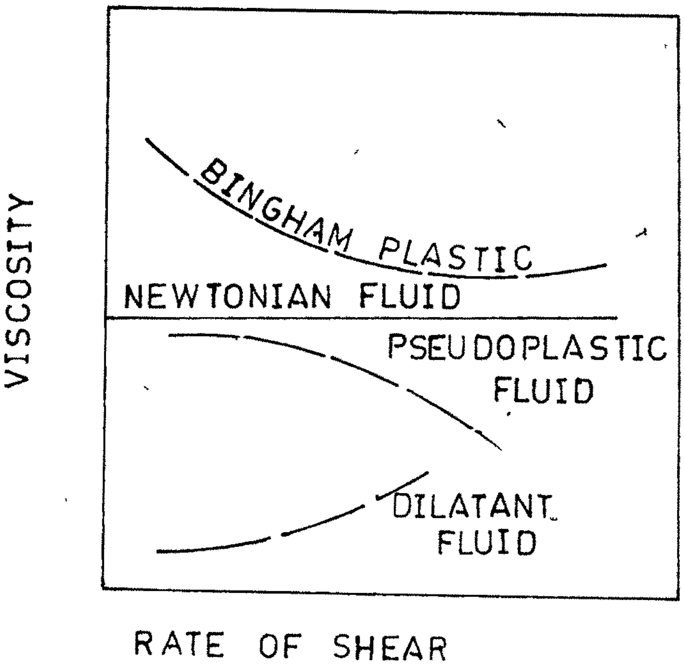

VISCOSITY
BINGHAM PLASTIC
NEWTONIAN FLUID
PSEUDOPLASTIC FLUID
DILATANT FLUID
RATE OF SHEAR

FIG.2

Pseudoplastic Fluid

In this case the relationship between unit shear stress and rate of shear is generally complex and on arithmatic coordinates is represented by a curve, the slope of which decreases with increasing rate of shear ultimately reaching a constant value.

Dilatant fluid

The slope increases with increasing rate of shear.

Thioxotropic Fluid

Viscosity will normally decrease upon increased shearing, but this depends upon duration of shearing and viscosity of fluid and rate of motion before shearing.

1.6 Rheological behaviour of crude oil

Based on careful study of the rheological behaviour of a number of crude oils many generalizations are made. All crude oils are Newtonian fluids about 10°C above the pour point. Non-newtonian behaviour starts at and below such temperature is further decreased. Pseudoplasticity and thioxotropy, both normally associated are most commonly encountered. Non-newtonian behaviour is due to development of a network structure in the liquid phase and to some extent to crystallization of waxy compounds at lower temperatures. Thixotropic behaviour break~~e~~s down readily with time under sustained shear and crude oil behaves as a normal pseudoplastic. Pseudoplasticity approaches Bingham plastic behaviour upon initiation of shear stress particularly in crude oils which have been cooled from a higher temperature. Mild dilatency is observed occasionally.

Apparent Viscosity

Strictly speaking, only Newtonian fluids possess the property of viscosity and that the consistency of the various non-Newtonians is properly defined only by their unit shear stress-shear rate of the shear curves. Not withstanding this, the term " apparent viscosity " is frequently applied to non-Newtonians. The concept of apparent viscosity has been adopted to describe the viscous properties of non-Newtonians. Apparent viscosity is the ratio of shear stress to shear rate at a specified shear rate (or shear stress) as shown in Fig. 3.

For Newtonian fluid (A)

$$\eta = \text{viscosity} = \frac{T_1}{S_1} = \frac{T_2}{S_2} = \text{constant}$$

For non-Newtonian fluid (B) (pseudo plastic)

$$\eta_a = \text{Apparent viscosity} = \frac{T_3}{S_3} \text{ at shear rate } S_3$$

$$\eta_a = \frac{T_4}{S_4} \text{ at shear rate } S_4.$$

The apparent viscosity of a Newtonian fluid is the same as its viscosity ; the apparent viscosities of Bingham plastic and pseudoplastics decrease with increasing rate of shear (to limiting values). The apparent viscosity gives no information of the rheological nature of the fluid or the way in which consistency may change with rate of shear.

Effect of temperature

Temperature has a marked effect upon the consistency of crude oils whether it is Newtonian or not. Upon cooling wax crystals start separating initially, which get interlocked to give a net work and the ultimate result will be a gel structure. The gradual change from Newtonian to non-Newtonian behaviour upsets the direct proportionality of shear stress to shear rate and hence the proportionality constant. The proportionality constant is the viscosity upon heating a non-Newtonian crude oil system the apparent viscosity at a particular shear rate starts decreasing and a stage comes when the ratio of shear stress to shear rate is constant. This stage is the transition from non-Newtonian to Newtonian behaviour and is illustrate in Fig. 4.

1.7 Flow Improvers

The general term " petroleum " refers to crude oils. The category known as middle distillate fuels such as aviation turbojet fuels, fuel oils and diesel fuels are petroleum refinery products. The middle distillates are highly specific in nature.

The low temperature behaviour of all these materials is important either from handling or performance point of view or both. The pour point is an indication of the low temperature behaviour of crude oils where as freezing point and cloud point are for middle distillates. The pour point is the lowest temperature at which the oil will still flow ; the

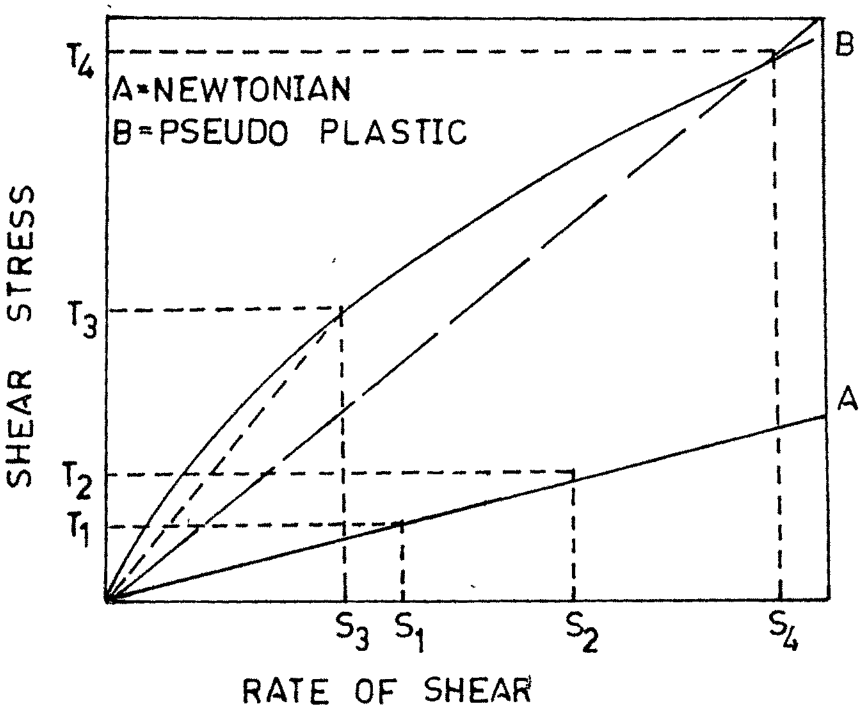


FIG. 3

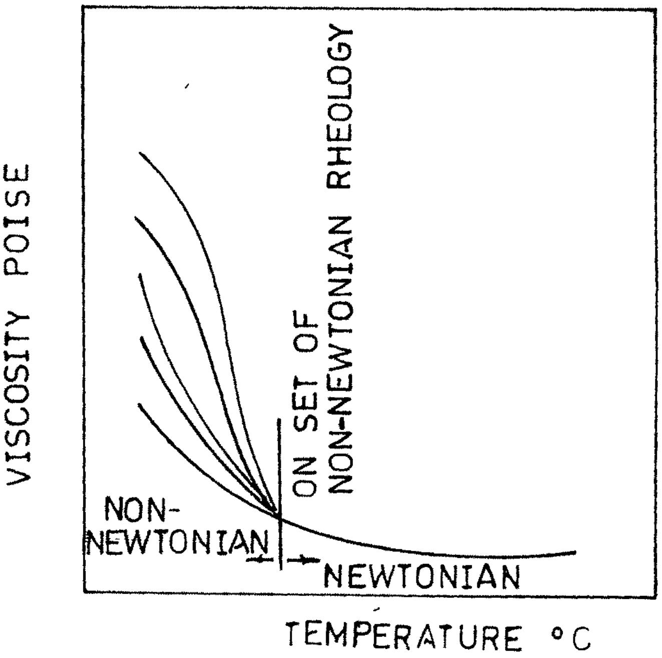


FIG 4 VISCOSITY Vs. TEMPERATURE AT VARIOUS SHEAR RATES

cloud point defines the temperature at which the separation of wax is first observed and the freezing point is the temperature at which sufficient amount of wax separates from the oil to cause its gelation. When the temperature goes below the pour point the oil is then no longer freely flowing as a result its transportation becomes difficult through pipe lines. The wax crystals that come out of the solution tend to plug the pipelines, values, etc. This is a well recognised problem and various additives have been suggested to alleviate it. These products are known as pour point depressants. The function of such an additive is to change the nature of the crystals that precipitate from the fuel oil, thereby reducing the tendency of wax crystals to interlock and set into a gel. They are believed to function not only to arrest the wax crystal growth but also to destroy the cohesive forces between the crystals.

Pour point depressants that function by changing the crystal size and shape are thus referred to as flow improvers. Flow improvers are specifically used in residual fuel oils. The environment of working of a flow improver is different from pour point depressant or wax crystal modifiers in middle distillates. Wax crystal modifiers are commonly used as a dewaxing aids during filtration to increase the filtration rates.

1.8 Pour Point Depression

The cloud point of a hydrocarbon oil system is the starting point of paraffin wax separation. The pour point is a few degrees below the cloud point. Pour point is affected by the following factors :

(i) The amount of wax which separates from the solution when the temperature is lowered. This is determined by the solubility and the initial concentration of wax in the oil.

(ii) The crystal habit of wax i.e. its mode of crystallization in extensively interlocking structures.

(iii) The shear stability of the different wax structures.

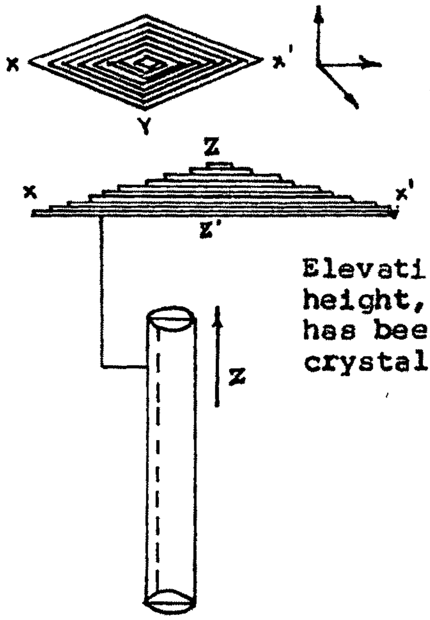
All of these contribute to the enhancement of pour point.

The waxes most common in crude oils are

n-paraffins, isoparaffins and cyclic structures of varying chain lengths. The distillate fuel oils generally contain C_{16} to C_{28} n-paraffins. Pour point depressants do not appreciably change the temperature of wax crystal separation as well as the amount of wax separated and its composition (30). Microscopic examination shows reduction in wax crystal size in the presence of a depressant. With the incorporation of an ideal pour point depressant, whatever be the reason, the ability of the wax crystals to grow and interlock is greatly reduced. The combination of these two effects lowers the pour point of oil. The mixed crystals, besides being different in appearance from the single n-paraffin crystals, are much more responsive to pour point depressants. Further it was experienced by Holder and Winkler (31) that the response to the pour point depressant was much more a function of structure of the precipitating wax crystals, than that of the n-paraffin chain length.

The basic structure of n-paraffin crystals is illustrated in Fig. 5 (32). As can be seen from the top portion of the figure, the crystals have the appearance of very thin diamond shaped plates. The lower part of the figure shows that the plates consists of layer upon layer on n-paraffin molecules. In each layer the n-paraffin molecules are stacked side by side with their long axis parallel to the z-axis (i.e. the vertical axis) of the crystal.

Experiments of pour point depression of middle distillates show that at certain lower level of additive dosage, the wax crystal produced have the characteristic shape of dentrites. The theoretical treatment of two dimensional dentrite growth as reported by Saratovkin (33) is summarized in figure 6. The basis of the theory is that as any crystal face grows, "poisons" present in the solution will accumulate around the faces, as a result, the crystal will tend to grow as rapidly as possible, when the impurity concentration is at a minimum. Fig. 6(a) shows how as the crystal nucleus ABCD increases in size to EFGH, poison must be accumulate along the faces EF, FG, GH and HE as they have through the solution. However there is clearly much loss poison accumulation at the corners E, F, G and H, since less solution is displaced by a growing corner than by a growing edge (in the three dimensional phase). Accordingly growth will



Plan view spiral growth not shown

Elevation views relative height, i.e. ZZ' of the Crystal has been exaggerated: real crystals are very thin

FIG.5 : STRUCTURE OF n-PARAFFIN CRYSTALS

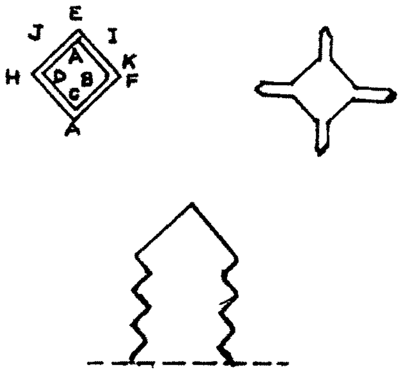


FIG.6 : MECHANISM OF THE FORMATION OF DENDRITCIC CRYSTALS

occur relatively faster at the corners. Thus a later stage in crystal growth will be like Fig. 6(b), which shows needle like projections developing from the corners of the crystal nucleus. Each of these needles will not be smooth, but will be made up of projections which are free crystallographic faces Fig. 6(c). These projections will be the sources of further growth.

The hypotheses advanced to explain depressant activity are many and are based on adsorption cocrystallization, nucleation, etc. After cooling an oil containing polymethacrylic acid alkyl esters the long side chains of the alkyl group probably behave as wax and enter into the wax crystal. The length of the alkyl side chain governs the adsorption of the polymer on the wax in much the same waxy as molecular weight of the paraffin governs the solubility in an oil. A detailed mechanism explaining the action of pour point depressants on paraffin wax as suggested by Holder and Winkler (31) confirms this.

Zhuze (34) believes that as adsorption of an additive takes place, wax crystal growth is inhibited and the additive by steric hindrance prevents crystal aggregation. Gavlin et al., (35) say that adsorption of pour point depressants causes a decrease in the growth rate of that crystal face and the accommodation of crystals for intercrystalline growth is reduced by adsorbed additive. Koch (36) believes that adsorption of depressant prevents normal growth.

The proposed mechanism of crystal modification of Holder and Winkler is illustrated in Fig. 7 stage I shows as isolated wax crystal unmodified by an additive. Stage II shows a wax crystal which is formed in the presence of a low additive concentration. The growth of the four faces is restricted. Accordingly the crystal grows relatively quicker at the corners than at the sides and also thickens. Stage III shows a typical dentrite. At higher additive concentration side ways growth becomes so much more difficult for the wax crystals that even dentrite cannot be formed. Instead, as indicated by stages IV and V the wax crystals become so thick by virtue of the increased growth along the Z axis, that block like or pyramidal crystals result. In conclusion it should be emphasized that pour depression occurs because concurrent with the progressive changes in crystal shape which have been described, the ability of the wax crystals to interlock is progressively diminished.

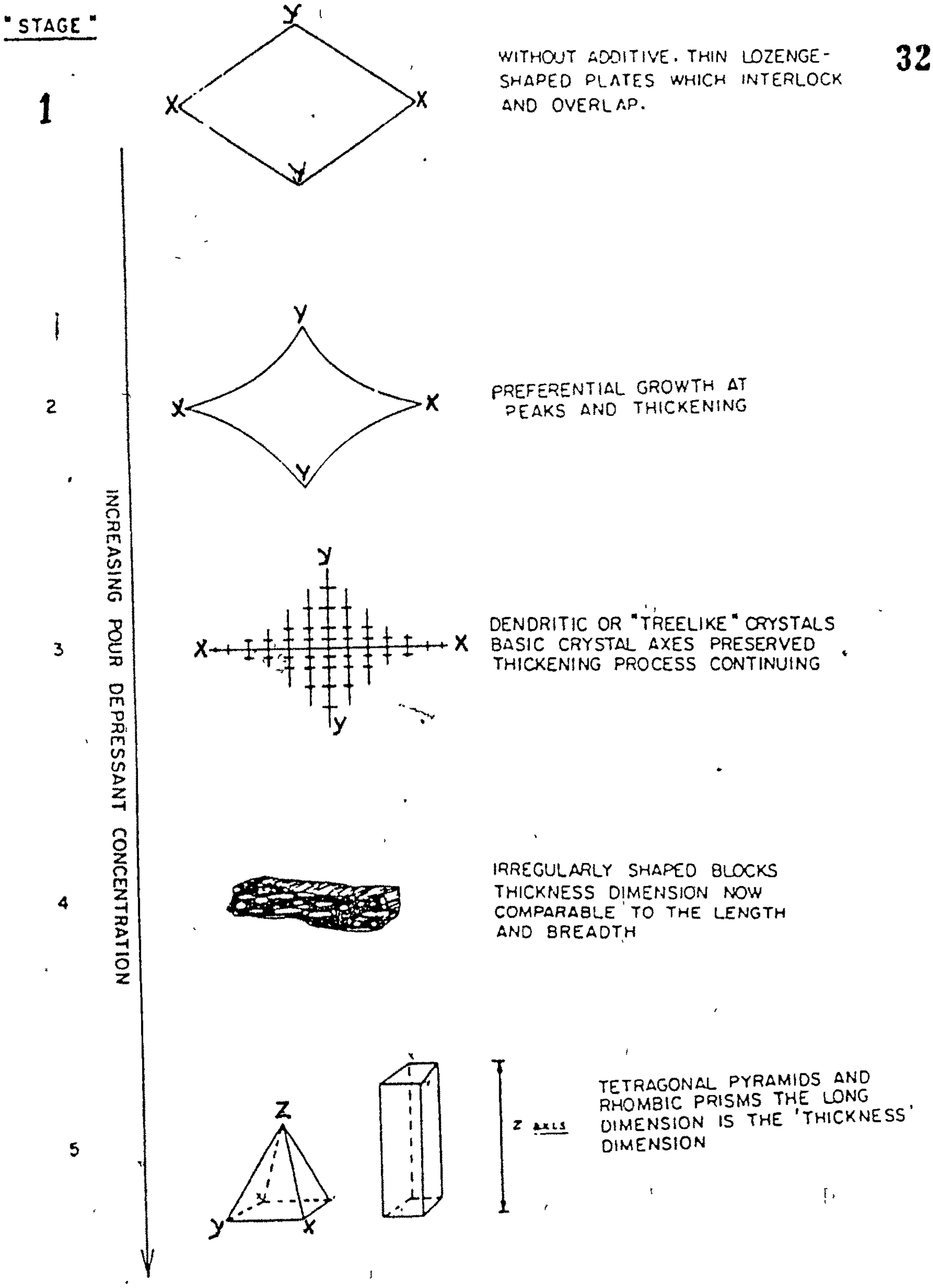


Fig. 7. STAGES IN WAX- CRYSTAL MODIFICATION

In the case of acrylates and methacrylates pour point depressants cocrystallization is believed to be involved. Both polymer backbone stiffness and side chain crystallinity are involved in the cocrystallization phenomenon and hence the activity. The spacing between polymer side chains has a mild effect upon the depressant activity. In a recent work it is reported (37) that chain length and physico-chemical structure similar to those of n-paraffins hardly slow down the crystallization of n-paraffins in a hydrocarbon medium and do not create any significant disturbance in the crystal faces. On the other hand additives having either very long chains with several non paraffinic groups or sufficiently great steric bulk with alkyl radicals grafted to a non-paraffinic group delay crystallization and modify the faces of n-paraffin crystals.

The strong supporting evidence for cocrystallization mechanism comes from the synergestic effect of added wax on the pour point depression and from the pour point depression behaviour of polyoctadecene. It is a known thing that mixed crystals can be induced much more readily by adding a small amount of a higher n-paraffin. n-Paraffins of about C_{20} are able to assist the polymethacrylates in further lowering the pour point by many degrees. The maximum effect occurs in cases where the added wax crystallizes at about the same point as the wax responsible for the original high pour point (38). One can speculate that the added highly crystalline n-wax cocrystallizes with the iso and naphthenic waxes responsible for original pour point ; thus they are rendered more crystalline and hence more ameable to cocrystallization with the polymeric additive. Polyoctadecene (av. DP = 8) is found to be capable of depressing the pour points of blends of straight chain waxes in white oil. Since there are no polar or aromatic structure in this molecule, the activity would appear to come about by virtue of cocrystallization.

Paraffin Inhibitors

The nature and occurrance of paraffin deposits have been extensively studied (39). Paraffin deposition occurs in down hole equipment, surface lines, separators and storage tanks. In many cases the problem is seasonal.

Paraffin deposits form by two mechanisms :

(1) a growth process directly on the pipe surface and

(2) accumulation of wax crystals in the oil which in turn attach to each other and to the metal. Paraffin inhibition can be obtained either by affecting the wettability of the metal surfaces through film forming action (40) or by the use of materials which modify and disperse wax crystals (41 to 46). It is reported that the inhibition by crystals modification is the most promising and potentially the most economical means for paraffin control. Paraffin inhibitors are a class of compounds closely related to pour point depressants both in chemical composition as well as the mechanism of their functioning.

Paraffin inhibitors prevent the growth of wax crystals. Some prevent nucleation by breaking up the molecular clusters. Others low down the crystallization by coating the molecules of wax as they come out of solution thereby keeping them in the liquid state. A third type of inhibitors interferes with crystal growth by incorporation into the growing wax crystal. Much extensive work has been done by the French Petroleum Institute on the use of polymeric additives (47 to 49).

The oil soluble polyethylene (50) is an important class of wax inhibitor.

Cold Flow Improvers

The term cold flow improvers refer to any additive which modifies the pour point, cloud point and cold filter plugging point simultaneously. Additives of this class are generally used in fuel oils and lubricating oils. Keroflux M (51) is a typical commercial product manufactured by BASF (West Germany).

Drag Reducing Agents

Drag reduction in crude oil pipe line is accomplished by changing the structure of turbulance and friction of the film at the wall. The additives used for this purpose are known as drag reducing agents. These additives as flow improvers are used in small dosages and they increase the through put of a pipeline without additional pumping capacity. These types of products are the latest addition to the family of transportation aids. Products such as poly isobutylene (52 to 54), poly acrylamide (55), polystyrene (52) and other propritory materials (56) are reported in the literature.

1.9 Stability of Flow Improvers

During cooling of a heated crude oil, the effect of shear on the crystal structure produced by heat treatment is an established fact (57). The paraffins may be considered as a " low molecular weight " polyethylene chain. The effect of shear on the breakdown of the so called low molecular weight polymer is not known, but the effect is surely known for higher molecular weight polymers. A typical example is lubricating oils wherein higher molecular weight polymers are used as viscosity index improvers. One of the important desired properties of an additive is to be a stable under shearing stress in lubricants. This applies to flow improvers as well as drag reducing agents treated crude oils. The additive treated crude oils experience shearing stress during the pumping and is of two types :

(i) the limiting shearing stress known as the static yield value of the oil ; the pressure available at the centrifugal pumps applies shearing stress to the gel sufficient to start flow and,

(ii) the shearing stress to break down the gel structure to give lower viscosities.

The additives under the shearing action during pumping should not undergo degradation or break up into fragments which result into loss of their activity. The other desirable property of these additives is their chemical stability towards various constituents of a de-emulsified crude oil. For example, many of the flow improvers deteriorate gradually in the presence of small amounts of moisture, naphthenic acid, etc. and loose their activity. An effective flow improver should retain its efficiency for comparatively longer periods.

1.10 Pour Point Reversion

Some oils containing pour point depressants show an increase in pour test in winter storage. The greatest increase is observed with daily temperature fluctuations somewhere between ± 10^{o}F to ± 20^{o}F about the pour point. The pour point may rise by 40^{o}F and even more. This phenomenon is known as pour point reversion. Pour point reversion occurs in storage but not in service (58, 59). Pour point reversion is usually explained by the difference in rates of dissolution of wax. Several factors are responsible for pour point reversion. Small quantities of higher melting wax is believed to cause pour point reversion to a greater extent than large quantities of low melting wax. Extra large doses of pour point depressant and the nature of the depressant also cause the pour point of revert. The presence of additive other than the pour point depressant also sometimes cause pour point reversion.

Significance of Alkyl side chain length in pour point depressants

The length of the alkyl side chain determines the temperature at which the oriented side chains will crystallize and condense on the surface of a wax particle in the oil. The longer alkyl polymers are effective in depressing the pour point of the high pour oils while shorter alkyl polymers are effective in the lower temperature pour oils. The specificity of the side chain length depends some what on the nature of the backbone of the polymer. Ethylene vinyl acetate copolymers are a typical example of this. If the alkyl chains are too short, they are adsorbed on the wax below the pour point of the oil and are ineffective in lowering the pour point. If the alkyl chains are too long, the polymer crystallizes from the oil solution at a temperature above the pour point of the oil and cannot be adsorbed as a monolayer.

In the case of ethylene vinyl acetate copolymers used as pour point depressants, the side chain crystallinity does not come into picture since there is no alkyl side chain for cocrystallization. The crystallinity data on the paraffin wax and ethylene vinyl acetate copolymer cocrystallization as revealed through the study of Edwards (60) indicate that parts of the copolymermolecule, which form part of an amorphous phase in the pure product, crystallize together with wax molecules in blends. The long chain portions of the copolymermolecules then crystallize along the wax molecules to form what is essentially a two dimensional solid solution. End to end crystallization can occure on the wax section of the two dimensional solids solution. The X-ray results indicate that this is quite limited compared to that occuring in unmodified waxes.

1.11 Viscosity Index Improvers

Viscosity of mineral oil, including lubricating oil is a measure of its flow characteristics and normally varies with temperature, but not with shear rate. Viscosity index is an empirical number indicating the effect of change of temperature on viscosity of an oil. A high viscosity index will indicate a low rate of the change of viscosity with temperature.

Paraffinic oils are found to have the lowest rate of change of viscosity and hence possess high viscosity index. Naphthenic and aromatic oils have quite low viscosity index. Fig. 8 illustrates the behaviour of the various fractions, L and H being those which possess the absolute minimum and maximum limits of viscosity temperature sensitivity with values of 0 and 100 on a 100 point viscosity index scale (61).

The following formula has been employed for determining the viscosity index numbers :

$$VI = \frac{L - U}{L - H} \times 100 = \frac{L - U}{D} \times 100$$

where : L = viscosity at $100^{\circ}F$ at the o viscosity index fraction of the oil 'L' having the same viscosity at $210^{\circ}F$ as the oil under test.

H = viscosity at $100^{\circ}F$ of the 100 viscosity index fraction of the oil 'H' having the same viscosity at $210^{\circ}F$ as the oil under test.

U = Viscosity at $100^{\circ}F$ of the oil under test.

D = L - H

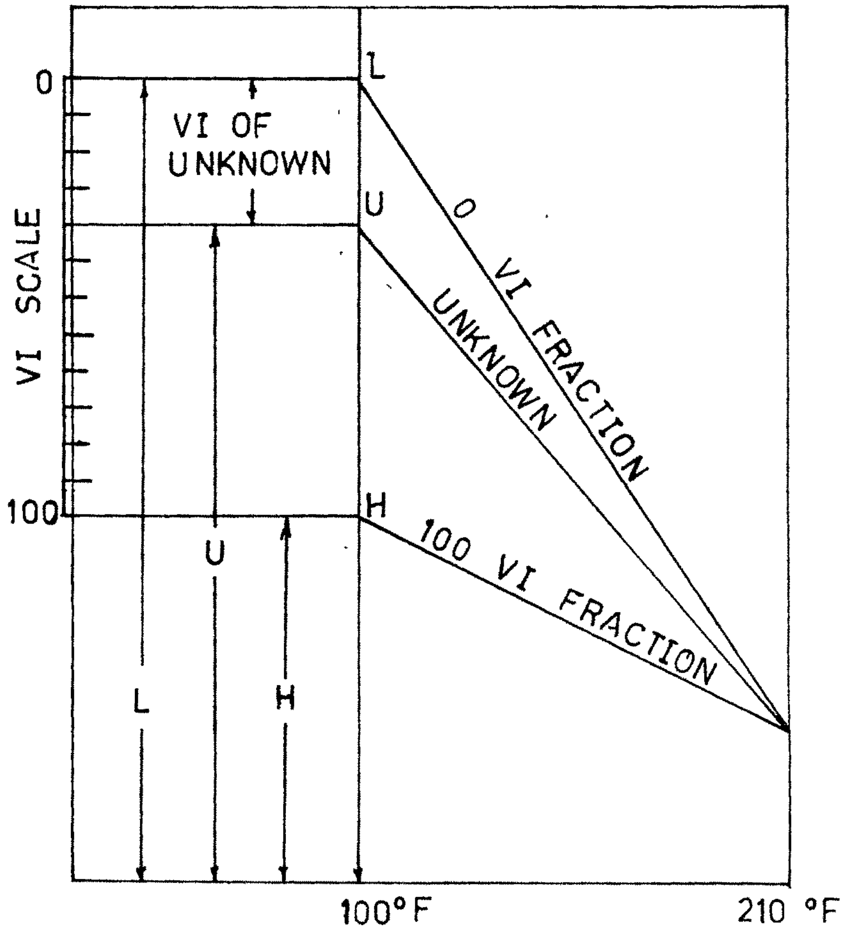


FIG 8 A SCHEMATIC ILLUSTRATION OF THE VISCOSITY INDEX SYSTEM

Modern VI improvers are generally compounds of long chain molecules having high molecular weights, some as high as 1000,000. The chief amongst them are butene polymers (59, 61 to 75), polymethacrylates (76 to 90) and nitrogen containing polymers (91 to 103). Generally the effectivity of a VI improver is evaluated by comparing the viscosity contribution of the polymer at $210^{\circ}F$ and $100^{\circ}F$. The following formula is used :

$$V_{sp} = \frac{V - V_o}{V_o}$$

where ; V_{sp} = specific viscosity

V = viscosity of the blend

V_o = viscosity of the base oil

and

$$\text{the specific viscosity ratio} = \frac{V_{sp}(\text{at } 210^{\circ}F)}{V_{sp}(\text{at } 100^{\circ}F)}$$

In the specific viscosity ratio is greater than 1, the polymer is a VI improver and the higher the ratio the better it is.

Viscosity improvers restrain the movement of the oil molecules hence their function is to increase the viscosity. Molecules of viscosity improvers have function better at higher temperature than at lower temperatures. The best VI improvers are linear polymers which have the characteristics of getting curled or enlarged at the maximum temperature encountered.

1.12 Transportation of Crude oil

The transportation systems of crude oils are (i) tanker transportation and (ii) pipe line transportation. With highly waxy crude oils becoming the order of the day in the ever increasing quest for more and more crude oils, the petroleum industry stands obliged to finding out more economically feasible chemical systems of treating them for easy transportation and other handling aspects. Pipe line transportation system on a long distance scale began in 1887 (104), since then, the system is more and more used in abroad and India.

There are definite advantages of the pipe line system of transportation. It may be taken as the best protected system against environmental conditions. While the capital investment at the first instance may seen to be unprofitable, the long duration of its service and continuous and unhindered flow can make it a profitable system in the long run.

However, the nature of crude oils can cause a number of problems in the transportation system, be it tanker or pipe line. Highly waxy crude oils cause difficulty in flow the very important and the foremost requirement of pipeline transportation. There are various methods for pipelining the high pour point oils :

(1) Preheating the crude oil to a higher temperature and a to allow it to reach the destination before cooling down. Intermediate heating or passage through heated pipelines may or may not be involved.

(2) Pumping the crude oil at a temperature below the pour point.

(3) Cutting i.e., adding a hydrocarbon diluent as less waxy crude or light distillate or condensate.

(4) Injecting water to form a layer between the pipe wall and the crude.

(5) Emulsification or suspension of crude oil in water using surfactants.

(6) Processing the crude before pumping to change the wax crystal structure and reduce the pour point and viscosity-thermal conditioning.

(7) Injection of paraffin inhibitors.

(8) Combination of these methods.

Various factors such as crude characteristics, heat transfer, restart after shutdown, etc. are to be considered before designing a pipeline system.

1.13 Shear stress yield value and Plastic viscosity

The relationship between shear rate and shear stress is determined to describe the laminar flow. Also the manner in which shear rate varies with respect to shear stress should be determined to classify the non-Newtonian types. While Newtonian fluids have a linear relationship between shear stress and shear rate, the non-Newtonian, Bingham plastics require a finite pressure to initiate the flow. This initial pressure is the yield stress of the fluid. Although a plot of viscosity versus shear rate is non linear (Fig. 2), Bingham plastics are usually considered to have a constant " plastic viscosity " together with a yield stress. This relationship is represented mathematically as, shear stress

$$(\lambda) = \text{yield stress } (\lambda y)$$
$$+ \; (\text{shear rate } \mu_p)$$

where, μ_p is the plastic viscosity. Plastic viscosity is obtained by determining the slope of the shear stress vs. shear rate curve. The yield stress (λy) is the value of the shear stress at zero shear rate.

The handling of waxy crude oils in pipe lines developed a gel structure when oil has cooled. Then the breakdown which can be accounted for the chance in yield value decreases as shearing stress increases.

The plastic viscosity and the yield value of the additive treated crude oils are the two parameters generally considered in the evaluation of flow improvers. Some features which have been found common in many instances where additive is effective are as follows :

(1) transportation of the waxy crude from a non-Newtonian to a near Newtonian fluid as an economical dosage of the additive ;

(2) rapid increase in flow rate after yielding, indicating rapid breakdown in viscosity and,

(3) change in restart behaviour after a shut down.

1.14 Indian consumption of flow improvers

The comsumption of flow improvers and paraffin inhibitors put together amount to about 3550 MT/year. The major consumer is the Bombay offshore project which alone uses flow improvers of the order of 3500 MT/year. The second consumer is M/s Oil India Ltd., Dulianjan. On an average 10 MT of paraffin inhibitor and 40 - 50 MT of flow improver are used currently. A substantial increase in the consumption of flow improvers is indicated in the Bombay offshore project, perhaps of the order of 5500 - 6500 MT over the next 3 - 5 years.

1.15 Analysis and evaluation of flow improvers

A majority of flow improvers in use are polymeric substances. Many of there are available as mixtures of two or three different types of compounds with or without an added solvent. Products marketed are generally either patented or are given trade names

(Table 4) and their composition other than nature, sometimes chemical nature too, is a closely guarded secret because of the business interest involved in these (Table 5).

All commercial pour point depressants are preliminary evaluated for the depressant activity as per the ASTM D97-IP 15 method. The rheological studies start with laboratory evaluation. Usually coaxial rotational type viscometers are used. After a laboratory screening the evaluation is done on a model pipe line duplicating the actual operating conditions. Extensive literature on this is available in various publications (105 to 107).

Table 4

Commercial products, brand name & manufacturer

Sr. No.	Brand Name	Manufacturer
1	Acryloid	Rohm & Hass, U.S.A.
2	Baroid	Baroid, U.K.
3	EC Series	Enjay Chemicals, U.S.A.
4	Ergacryl	Rohm & Hass, U.S.A.
5	Keroflux series	BASF, West Germany
6	Paraflow	Esso, U.K.
7	Plexol	Rohm & Hass, U.S.A.
8	Polyflow	Standard Oil Co.,U.S.A.
9	Santo pour	Mosanto Chem. Co.,U.S.A.
10	Servo C W series	Servo, Holland
11	Shell Swim series	Shell International
12	Viscoplex	Rohm & Hass, U.S.A.

Table 5

Commercial Flow improvers, pour point depressants, cold flow improvers, etc.

Sr. No.	Brand Name	Chemical Type
1.	Acryloid series	Poly alkyl methacrylate
2.	Depressant D & H series	Alkylated polystyrene
3.	E C series	Ester type
4.	Elvax series	Ethylene-vinyl acetate
5.	Ergacryl series	Poly methacrylate
6.	* OFA 410	N-Aliphatic-hydrocarbyl succinamic acid
7.	Paradin series	Ethylene-vinyl acetate
8.	Paraflow	Chlorinated paraffin wax naphthalene condensate
9.	Paramin	Ester type
10.	Plexol series	Poly methacrylates
11.	Reonyl 1500	Alkyl naphthalene type
12.	Santopour	Di-ter-paraffin phenolphthalene
13.	Shell swim series	Poly methacrylate, styrene based etc.
14.	Tolad series	Substantially ethylene containing polymer with varying amounts of chlorine
15.	Viscoplex	Polymethacrylate

* Informations given are collected from available literature.

1.16 Natural Pour Point Depressants

The asphaltic substances present in the crude oils are found to have pour point depressing activity. These natural pour point depressants are isolated from spent percolation clays by extracting with solvents. The best pour point depressant qualities are usually exhibited by the highest molecular weight asphaltic fractions. These natural pour point depressants have a number of drawbacks, viz., carbon forming tendency foul odour, low oxidation stability and undesirable colour which makes them unsuitable for use in finished products. The efficiency of these natural products is low compared to synthetic pour point depressants which are free from all objectionable properties. Even then many of the patented products are synergestic mixtures containing natural products in combinations with synthetic pour point depressants (108, 109). Microcrystalline wax also contributes towards synergestic activity with synthetic pour point depressants (110 to 112).

1.17 Synthetic Pour Point Depressants

These products are generally either purely synthetic or derivatives of natural polymeric materials.

which are of high molecular weight and oil soluble and which depress the pour point to the desired degree economically. Many of them are multifunctional ; they act as viscosity index improvers, oxidation inhibitors, detergents, etc. Polymers are being used as additives for many phases of crude oil production, transportation and processing. The products reported in the literature over the last four decades are listed in twelve classes.

1. Ethylene-Vinyl Ester Copolymers

In majority cases the molecular weight of ethylene-vinyl acetate or vinyl ester copolymers range from a few hundreds to few thousands and vinyl ester contribution ranges from 20 to 50% of the copolymer composition. The synergestic combination with a paraffinic hydrocarbon results in improved properties (113 to 121). The following copolymers are reported as either pour point depressants or flow improvers or both :

(i) Ethylene-vinyl acetate copolymers (122-142,251).

(ii) Ethylene-vinyl fatty ester copolymers ; with both saturated and unsatureted fatty acids (143-152).

(iii) Ethylene-vinyl fatty ester-alpha olefin terpolymers (153).

(iv) Ethylene-vinyl acetate terpolymer with vinyl fatty ester or fumaric or maleic ester or methacrylate or acrylate ester (154-167).

(v) Poly vinyl acetate grafted with ethylene (168, 169).

(vi) Ethylene-vinyl pyrrolidine copolymer (164).

(vii) Ethylene-vinyl acetate + metallic soaps (170).

(viii) Ethylene-vinyl acetate - alkylmercaptan terpolymer (171).

(ix) Ethylene-vinyl acetate + alkyl naphthalene or olefin - SO_2 polymer or styrene - maleic acid or acrylic or methacrylic acid derivatives (172 - 182).

(x) Chlorinated (ethylene-vinyl acetate copolymer) (183).

(xi) Ethylene-vinyl acetate - vinyl chloride terpolymer (184 - 186).

(xii) Ethylene - vinyl acetate - carbon monoxide terpolymer (187).

2. Ethylene - alpha olefin(s) copolymers

The alpha olefins used range from C_3 to C_{22} olefin ; rarely alpha olefins beyond C_{22} upto C_{30} are used as comonomers (188). Both copolymers as well as mixed polymers are extensively used as pour point depressants (188 - 197). Viscosity index improvers (64 - 66, 103, 198, 199) and paraffin wax inhibitors (200). Majority products are of the molecular weight range of 1,000 to 70,000 although 650 to 1,000,000 are also reported (201, 198).

3. Higher fatty ester or amide or imide of ethylene alpha olefin or any vinyl monomer-maleic anhydride copolymer or alkenyl succinic anhydride

Pendant chains with amide linkage, imide linkage or ester linkage used as flow improvers pour point depressants and viscosity index improvers too. The reported products may be subdivided into the following types :

(i) Lower alpha olefin - maleic anhydride copolymer as basic units in the form of ester, amide or both (63, 100, 102, 203-208).

(ii) Cyclo alkene-N-alkyl maleimide copolymers (209, 210).

(iii) Higher alpha olefin-maleic anhydride copolymers as basic units in the form of alkyl esters, amides or imide derivatives (211 - 217).

(iv) Alkyl vinyl ether - maleic anhydride copolymers as basic units in the form of alkyl esters, amides or imides (218, 219).

(v) Ethylene, propylene or alpha olefin - maleic anhydride terpolymer (217, 220, 221).

(vi) Copolymer of higher dialkyl itaconate - maleic anhydride as basic unit in the final form of ester, amide or imide (222).

(vii) Higher fatty ester of styrene - maleic anhydride copolymer (223 - 225).

(viii) Unsaturated polymer copolymerized with maleic anhydride and further esterified with long chain alcohols (226, 227).

4. Vinyl monomers copolymerized with acrylate or methacrylate esters :

The following sub-divisions may be made :

(i) Ethylene as comonomer (82, 83, 228-235, 202).

(ii) Styrene as comonomer (78, 81, 236-239).

(iii) Alpha olefin as comonomer (240-242).

(iv) Vinyl pyridine as comonomer (92, 94, 97, 243, 244).

(v) N-Vinyl pyrrolidine as comonomer (79, 95, 96, 245).

(vi) Allylic ester as comonomer (246).

(vii) Fumarate ester as comonomer (247).

(viii) Vinyl acetate as comonomer (80, 248-250).

5. Poly(alkyl vinyl or alkyl allyl esters)

Copolymers and homopolymer of long chain alkyl vinyl and alkyl allyl esters with molecular weight in the range of 500 - 20,000 are in the use as pour point depressants (143, 251-254).

Viscosity index improvers (255) and cold flow improvers (256). In a study to compare these with acrylates and methacrylates it was found that this corresponds to acrylate polymers rather than methacrylate polymer.

6. Poly methacrylate or acrylate esters or substituted acryl amides or their copolymers

There is a distinct difference in activity between acrylates and methacrylates. The major aspects which are important in this respect are (a) polymer backbone stiffness (b) side chain crystallinity and (c) the brittle point of the polymer (257).

The following types of products identified

(i) Homopolymer of substituted acryl amide (258, 259).

(ii) Esters of alkanol substituted morpholino or oxozolidino or aziridino with acrylic acid homopolymer or copolymer with alkyl methacrylate (84, 98, 99, 260).

(iii) Ethoxylated copolymers of hydroxyl alkyl methacrylate and acrylic acid (261).

(iv) Polymers of styrene and alkyl methacrylate (84).

(v) Polymethacrylate or acrylate alone (85-91, 262-276) or with additives such as alkyl naphthalene, wax, asphaltene, etc. (277-280).

(vi) Poly alkyl methacrylate + alkyl maleate (85, 281).

Many polymer formulations of today incorporate relatively small amounts of some polar comonomer units (282, 283).

7. Higher alkyl fumarate - vinyl acetate copolymer

The short chain vinyl esters used as comonomer in preparing copolymers are vinyl esters of low molecular weight acids containing from about 2 to 6 carbon atoms per molecule other than acetic ester alone. The higher alkyl chain of the fumarates is generally from fatty alcohols of 12 to 22 carbon atoms (284-298). Many of the products of this class are multifunctional additives too, eg. viscosity index improvers (284, 289-292, 299). Modification of the system by incorporating a third component to boost the properties also are seen in the patent literature (300-304).

8. Phosphorus Derivatives

Phosphorus containing compounds of both known and unknown structures are used as viscosity index improvers and as pour point depressants in lubricating oils. The following types of compounds are reported.

(a) Known structure :

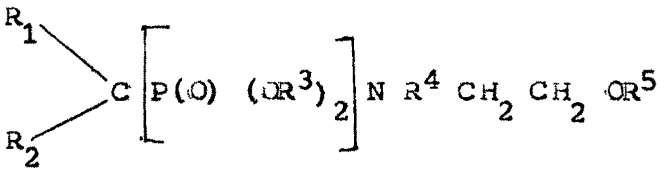
(i) Poly hydroxy oxyalkyl-polyalkene thio phosphanates (305, 306) of the general structure

$$RP\ (X)\ (OH)\ OCHR^1 - CHR^2O\ CHR^3\ CH(OH)CHR^4O)_n\ H$$

and

$$RP\ (X)\ (OH)\ O\ (CHR^1CHR^2O)_n\ H.$$

(ii) Amino methane phosphonate copolymers (307) of the general structure



$$\begin{matrix} R_1 \\ R_2 \end{matrix} \!\!> C \left[P(O)\ (OR^3)_2 \right] N\ R^4\ CH_2\ CH_2\ OR^5$$

(iii) Metal salts of higher alkyl phosphates or thio phosphates of the type (308-315)

$(RO)_2\ P(S)SM$; R = alkyl or alkyl phenyl

$(R\ CONH\ CH_2CH_2O)_2\ P(S)\ SM$; R = alkyl or alkenyl. $(RO)(R'O)\ P(O)\ OH$ or OM ;

R & R' = alkyl or alkenyl M = Ba, Al, Zn, Na, La, Nd, Ce, Pr, Sm, etc.

(b) Compounds of complex structure :

Products made out of the following are reported

(i) Naphthalene, wax and phosphorus sulfide (316).

(ii) Olefins and sulfuric or phosphoric acid (317).

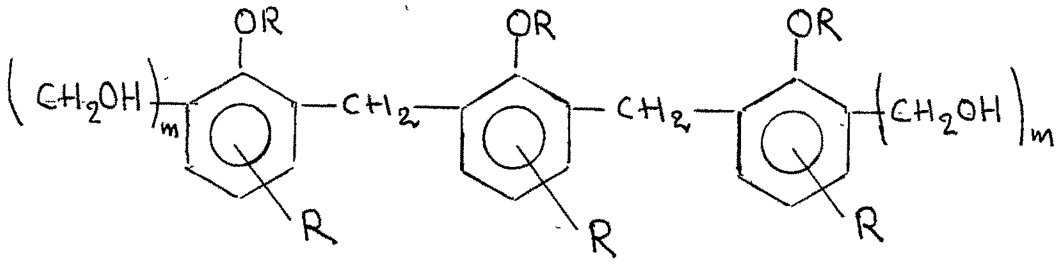
(iii) Phenol, chlorinated wax and ortho phosphito benzoyl chloride (318).

(iv) Phenol, chlorinated wax, salicylic acid and phosphorus trichloride (319).

(v) Wax substituted diphenyl dithio phosphate (320).

9. Phenol Formaldehyde Polymers

Heavy metal salts (321-323) or fatty acid partial esters (324) of phenol or cresol or higher alkyl phenol formaldehyde condensation products are used as viscosity index improvers (321) as well as pour point depressants (322-324). The general structure assigned to these products is



m = 0 or 1, R = H higher acyl chain or metal

R_1 = alkyl chain of $-CH_3$ to $-C_{21}H_{43}$

10. Esters of carbohydrates, poly saccharides and polyhydric alcohols

The products of this class are generally pour point depressants for waxy crude oils. Higher fatty acid esters of amylose (325-328), dextria (326), sorbitan (329,330) alpha methyl glucosides (331) and penta erythritol poly esters with poly carboxylic acids (329) are reported in the literature. The use of amylose itself for the removal of waxy compounds also is mentioned (332, 333).

11. (a) Monomeric or polymeric higher alkyl or acyl substituted hydrocarbons or phenols

The alkyl chains are usually derived from paraffin wax (chlorinated paraffin wax) or higher alpha olefin and the acyl group from higher fatty range. The monomer unit of the polymers of this class are usually derived from an allyl radical.

(i) Wax-alkyl benzene, toluene, naphthalene or acenaphthalene with or without hydrogenation (334-351).

(ii) Alkyl and acyl poly styrene (352 - 361).

(iii) Alkyl benzenes, indenes etc. (362).

(iv) Alkyl allyl phenol homopolymer (363).

(v) Alkyl benzyl chloride homopolymers and copolymers (364).

(vi) Alkyl phenols (365-368).

(b) Pure hydrocarbon type :

The products classified under this title are mainly viscosity index improvers and to a certain extent many of them are pour point depressants :

The following general types are identified

(i) Alpha olefin polymers (369-377).

(ii) Mono olefin or diene-styrene copolymer as such or hydrogenerated (67, 69, 71, 72, 378-386).

(iii) Poly styrenes (387, 388).

(iv) Hydrogenated poly butadiene - isoprene block polymers (70, 389-391).

(v) Poly butadienes (392-393).

(vi) Thermally cracked ethylene - propylene copolymers or wax (394-398).

12. Miscellaneous type of products

A lot of different types of products which do not fit into the above eleven classes of products are grouped together in this class.

(i) Silicon derivatives

Tetra alkyl silanes belong to one of the earliest types of products reported. Many of the products in commercial use today are poly alkyl silanes. A majority of them are efficient viscosity index improvers for lubricating oils rather than pour point depressants (399-402).

(ii) Esters of aryl substituted fatty acids

The esters are generally of fatty alcohols polyhydric alcohol and the aryl fatty acid is invariably phenyl stearic acid (403, 404).

(iii) Poly alkylene oxide (405-408).

(iv) Poly ketones based on carbon monoxide (187, 409, 410).

(v) Fatty esters of epoxy resins (411).

(vi) Copolymers of ethylene and vinyl alkyl ketone (412, 413).

(vii) Aromatic, aralkyl carboxylic acid or fatty acid salts of higher dialkyl amines (414-417).

(viii) N-Dialkyl recinolamides (418-420).

(ix) Poly alkylene glycol methyl esters and poly esters (421-424).

(x) N-Acyl amide ethyl esters of poly carboxylic acids (425). Esters of the type of compounds

$$R^1 \ CO \ NR^2 \ CH_2 \ CH_2OH$$

where

$R^1 = C_{11} - C_{29}$ alkyl or alkenyl

$R^2 = H, C_1 - C_{11}$ alkyl

(xi) Higher fatty esters or higher alkyl substituted carboxylic esters of poly glycol (426-430).

(xii) Poly sulfones (431).

(xiii) Poly vinyl alkyl ethers (432).

(xiv) Derivatives of oil soluble Mannich bases (433).

(xv) Imino-di-imides (138, 434).

(xvi) Hydrazine derivatives (435).

(xvii) Alkyl cyanamides (436).

(xviii) Substituted urea and urethane type (139).

(xix) Phenol + stratal water (437).

(xx) Olefin sulfonates (438).