RESULTS

AND

DISCUSSION

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4.1 Preliminary Results and Discussion

The crude oils collected for the study are from the well known oil fields of India which have been under operation for a much long time by now. Yet little or no published work incorporating their basic rheological characteristics is available. In order that the object of this investigation is well attempted to be realised, the selected crude oils have been subjected to a primary examination for their contents ; the investigation reveals that paraffin wax, asphaltene and resin materials are present as components. They are by and large waxy which justifies their high pour points though paraffin wax is not the sole component responsible for such characteristic. Based on the content of asphaltene and resin, which contributes considerably to the viscous nature of the oils, the samples may be classified into three main categories.

I. Low asphaltene and resin content :

a. Bombay High Oil (BH)

II. Medium asphaltene and resin content :

a. Naharkatia oil (Nq)
b. Moran oil (Mo)

III. High asphaltene and resin content :

a. North Kadi oil (NK)

b. Amta oil (Am)

The pour points as determined under this investigation for all the above oils are given in Table 38.

Rheograms of these five crude oils are given in Figs. 14 to 18. The plots are of shear stress vs. shear rate. Very useful information is derived from these rheograms regarding the basic characteristics of the crude oils. Firstly, the basic nature of the crude oils is that of Newtonian or near Newtonian fluids about 6°C above their observed pour points. The Newtonian behaviour is indicated by a linear nature of the rheogram passing through the origin. The Newtonian behaviour is gradually transformed into non-Newtonian one as the temperature is lowered. As for example, the Bombay High Oil (Fig. 14) yields two rheograms at 33° and 36° ; both are straight lines and when extended to the left pass ideally through the origin. At 30°C, however, the Newtonian characteristic is changed to non-Newtonian, there being a slight curvature indicated between 200 and 300 shear rate per sec. From this region the rheogram can be extrapolated to the left in keeping

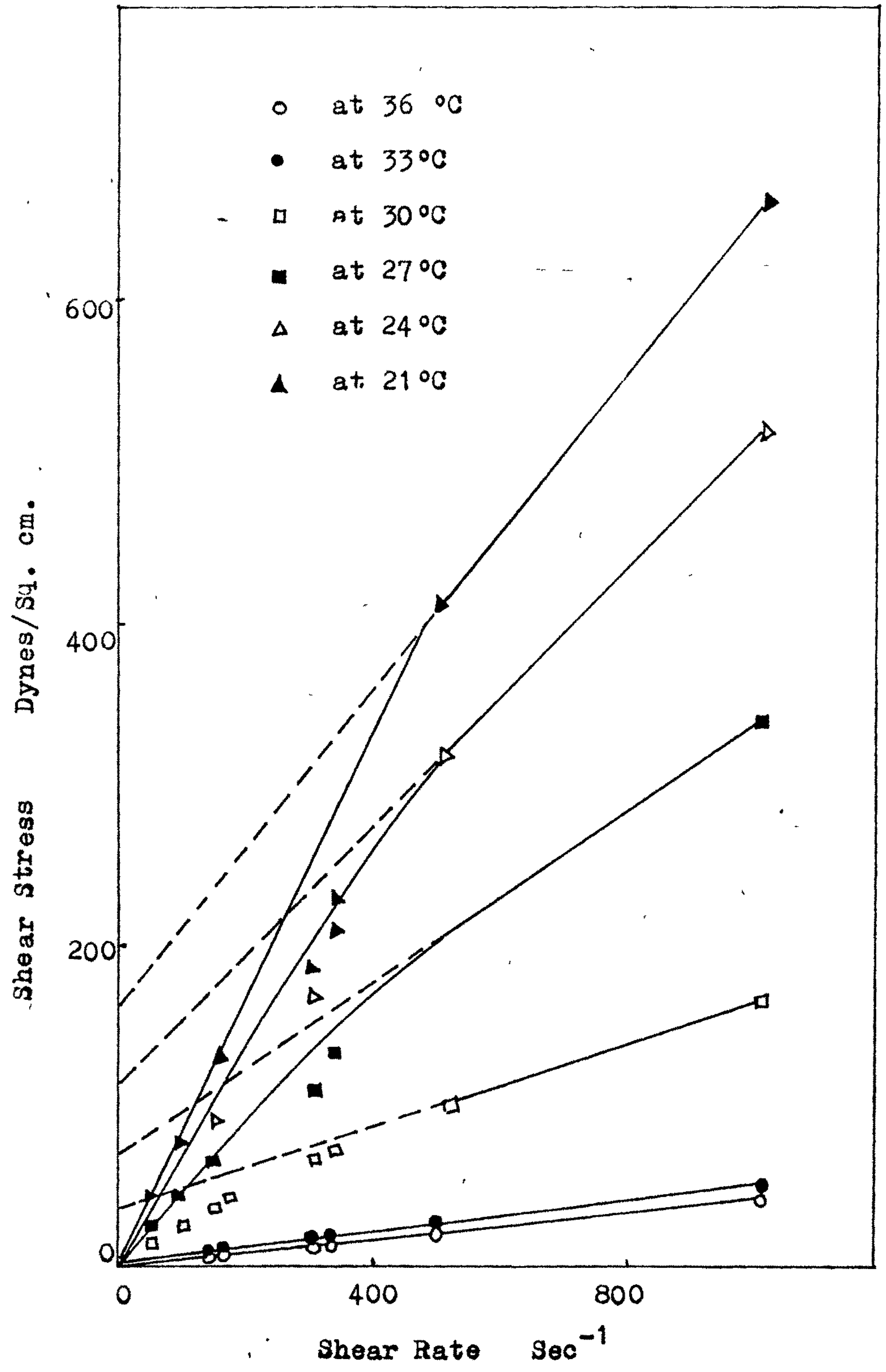


Fig. 14 : Rheogram of BH Oil

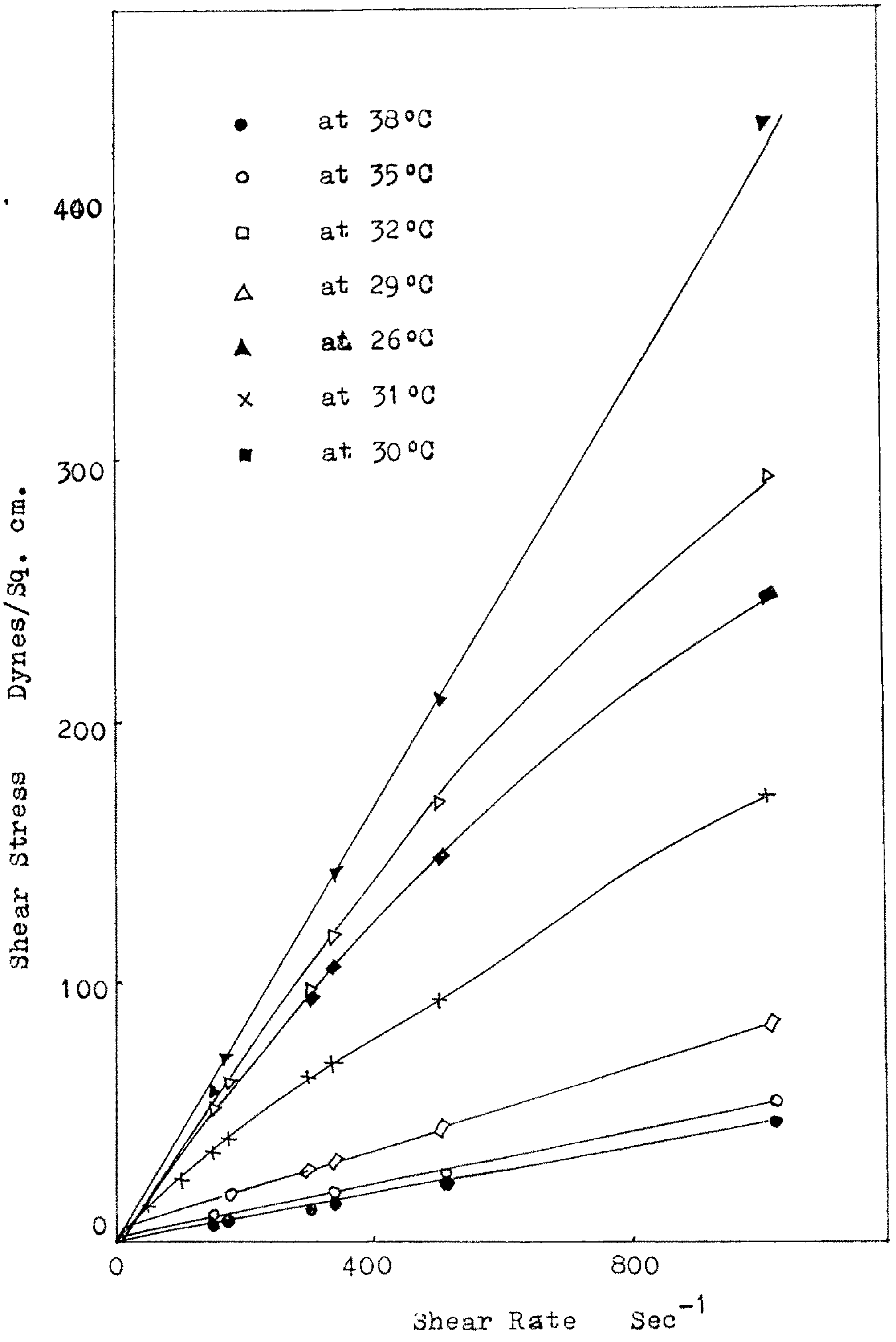


Fig. 15 : Rheogram of Na Oil

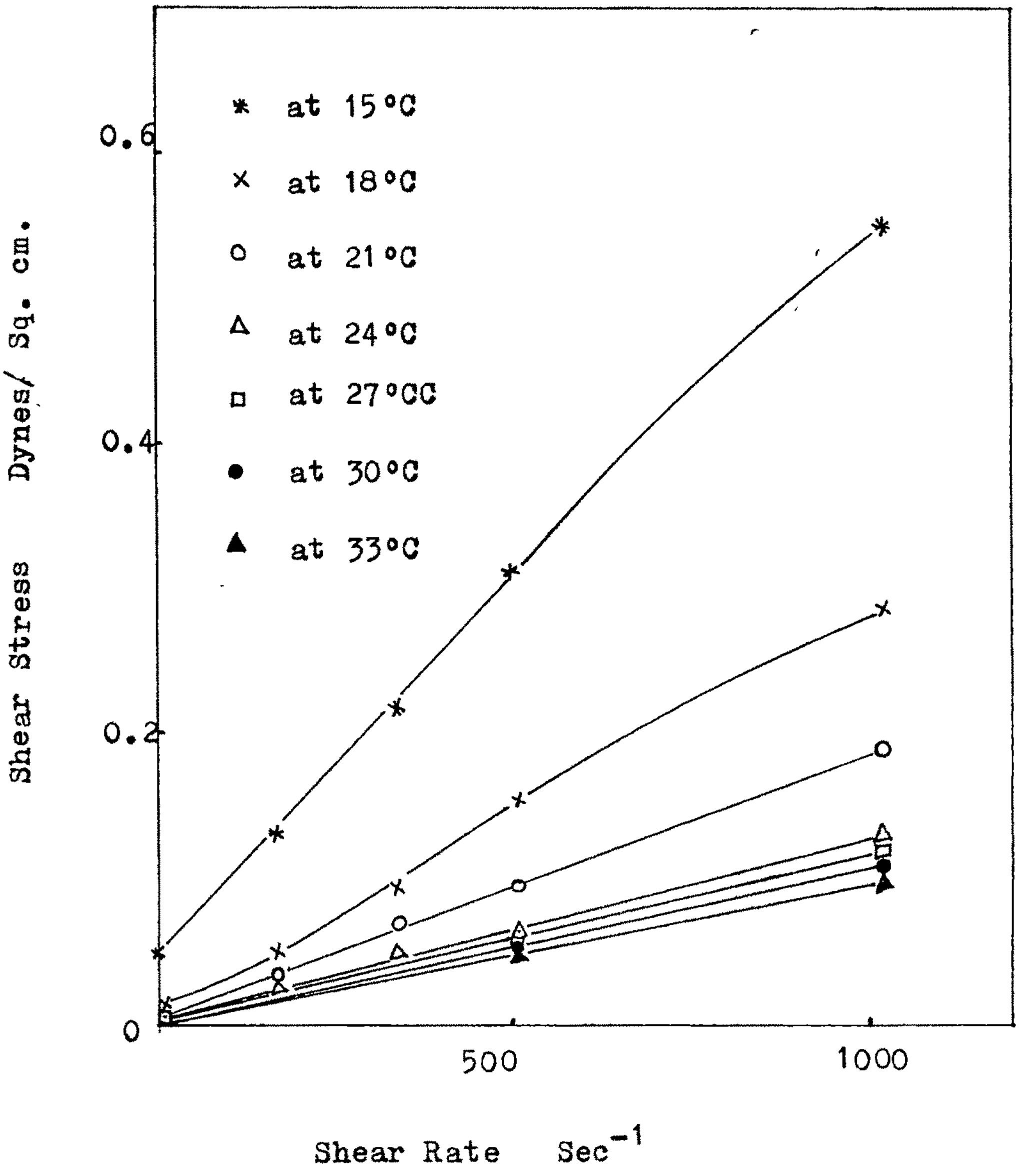


Fig. 16 : Rheogram of Moran Crude Oil

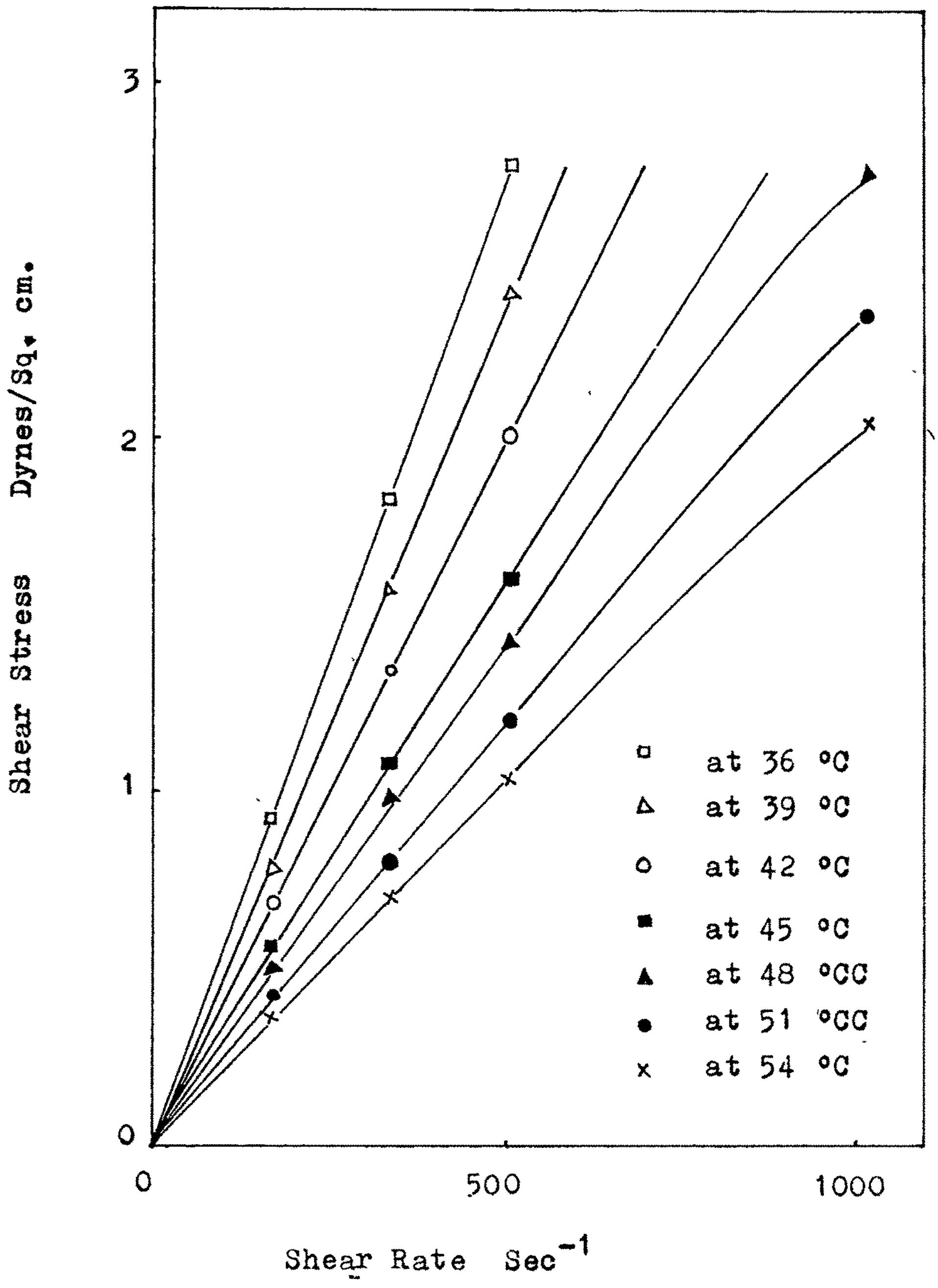


Fig. 17 : Rheogram of North Kadi Crude Oil

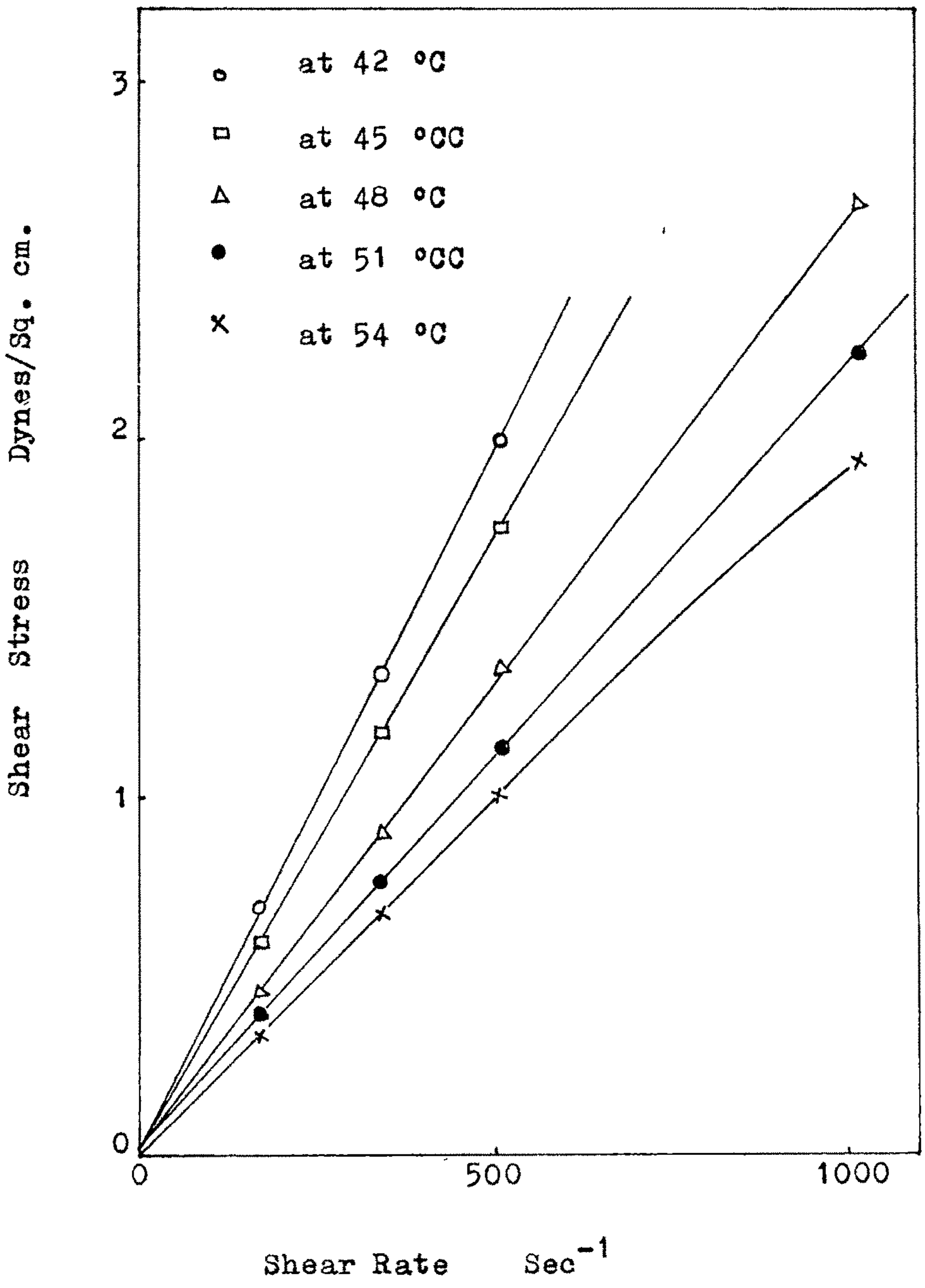


Fig. 18 : Rheogram of Amta Crude Oil

with the linearity of the rheogram ; the extrapolated line does not pass through the origin. Instead it gives an intercept of definite value which is clearly indicative of the fluid acquiring a Bingham plastic characteristic. This can be taken as a shift from Newtonian characteristic to Bingham plastic nature with fall of about 3°C. As the temperature is further decreased, Bingham plasticity too gets fully stabilised. Almost the same Bingham plastic characteristic is shown at 27°C ; however, a strange nature of the rheogram is observed at 24°C. The curvature is attained (at about) between 500 and 1000 shear rate ; the rheogram between 100 and 500 shear rate is almost ideally linear. This results into a very wide intercept and almost establishes firmly the non-Newtonian characteristic of the fluid.

Plots of plastic viscosity and yield value Vs. temperature for all these oils are quite linear and show a decreasing slope as the temperature is increased, upto their respective pour points (Figs. 19 and 20). Beyond the pour point no significant change in yield value or plastic viscosity is observed on increasing temperature. Thereafter, with further increase of temperature the curves seem to be running almost parallel to the temperature axis, while there is an insignificant slope

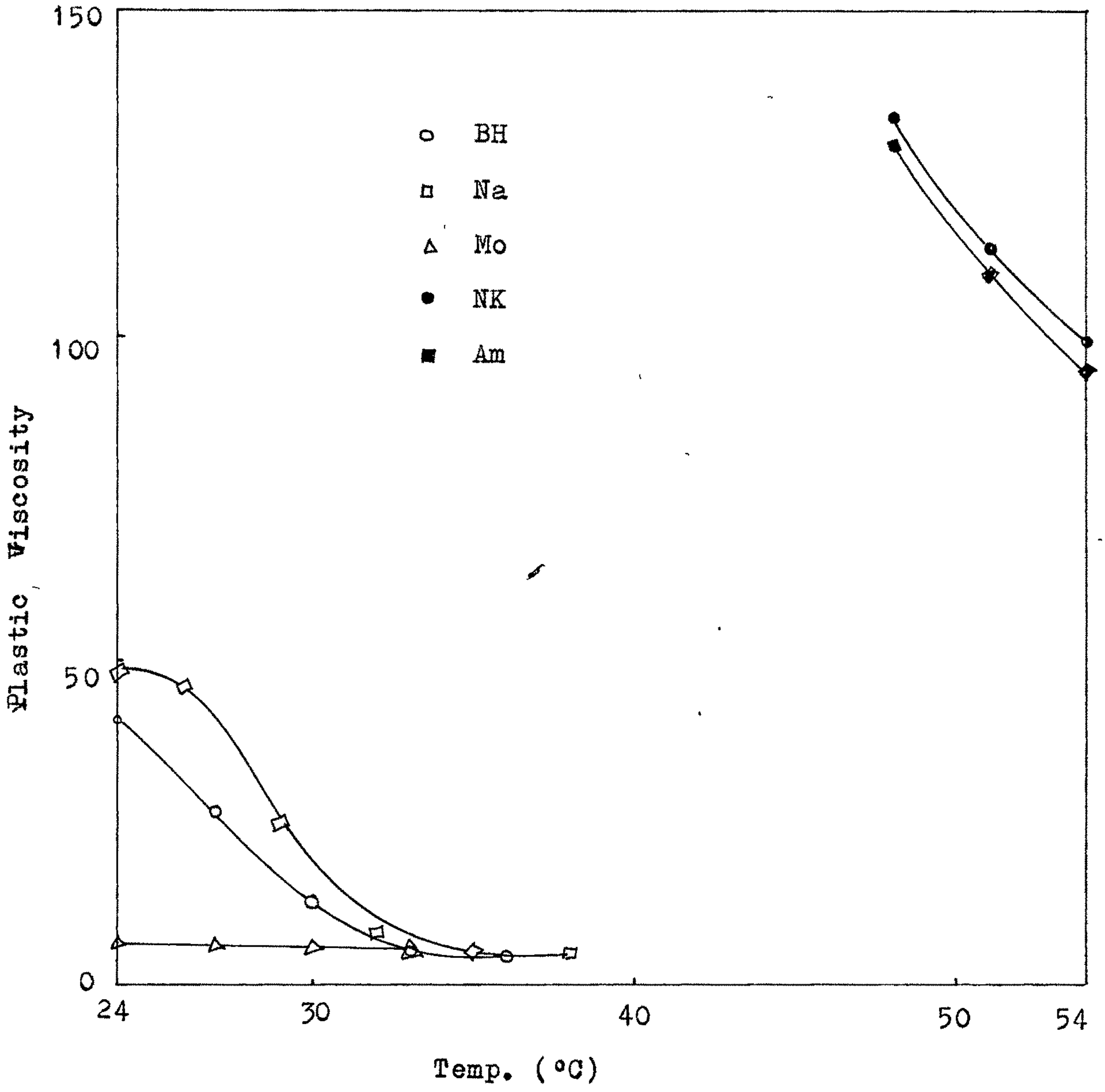


Fig. 19 : Temp. (°C) vs. Plastic Viscosity of different Crude Oils

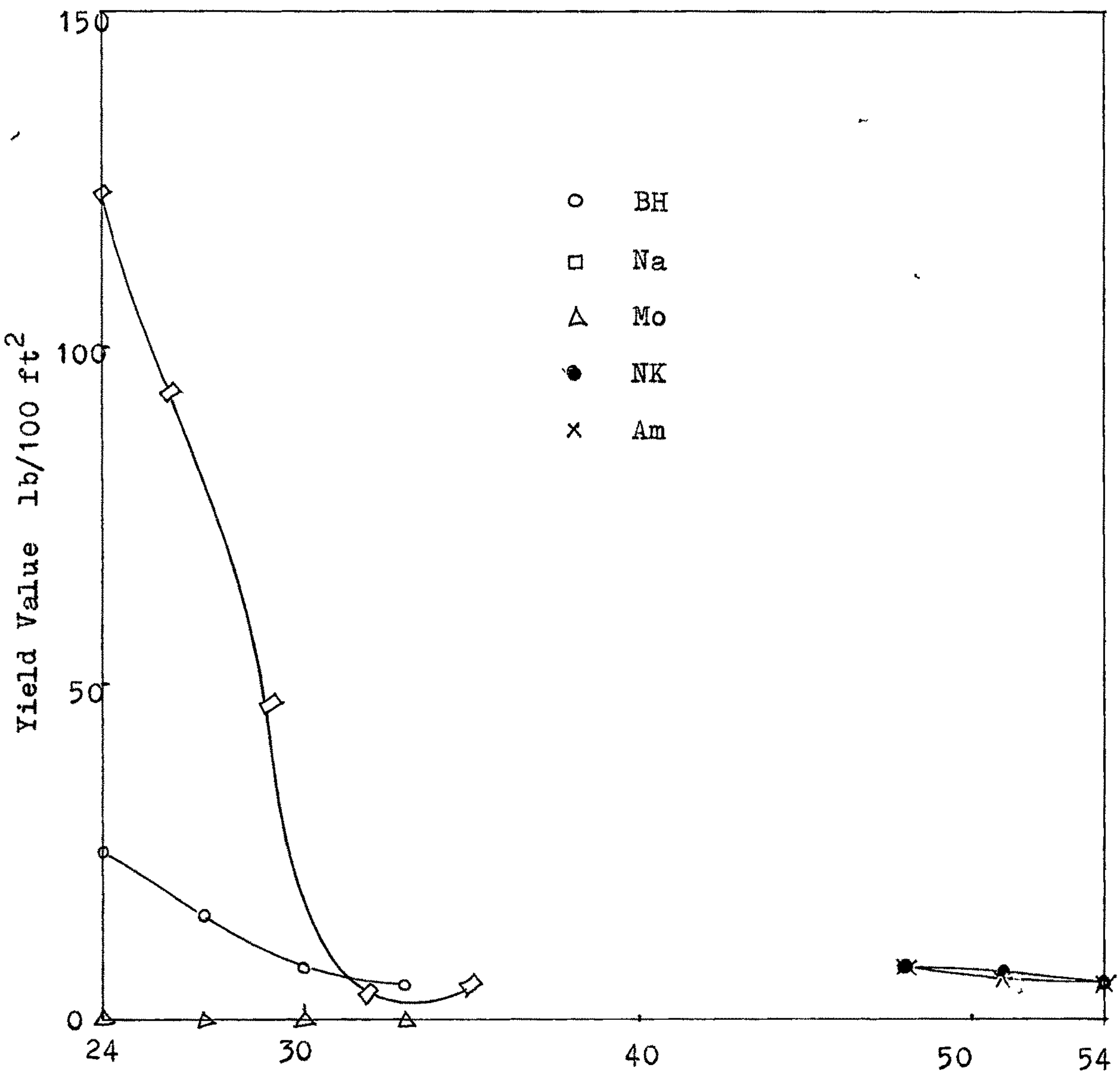


Fig. 20 : Temp. (°C) vs. Yield Value of different Crude Oils

which in fact is indicated on account of the curve, beyond a certain temperature, intersecting temperature axis. The temperature at which the intersection occurs can be taken as the temperature at (and above) which the oil will assume the characteristics of a Newtonian fluid since at the temperature the yield value will turn out to be zero.

While the plots follow a regular pattern in the case of crude oils with low and medium content of asphaltene and resin, their nature is quite typical in the case of the crude oils with high content of asphaltene and resin. The plastic viscosity curves show a decreasing slope with the rise of temperature and an indication of intersecting the temperature axis at relatively very high temperatures and absence of a sector when they would run almost parallel to the temperature axis beyond their pour point. But no abrupt breaks are observed. Since the oils under consideration are purely Bingham and not pseudo plastics this behaviour may be attributed to very high asphaltene and resin content. However, in the case of the plottings of the yield value versus temperatures the curves after a considerable fall with increasing temperature, show abrupt break. After the break, the curves run parallel to the temperature axis.

It appears that the increasing thermal agitation has a stepwise effect in breaking down the blocking factors while the resistance to the effect due to thermal agitation is sufficiently strong, which behaviours suggest that the effect is quantized. If breaks were more repeated, a temperature though very high relatively could be visualized at and beyond which the fluid would acquire Newtonian character. The high temperature technology for transformation to Newtonian characteristic is indeed unsuitable from any view point and therefore it need not be pursued any further.

With such high pour points and rheological characteristics of these Indian crude oils, as revealed by this study, the problems that the oil and petroleum industries have to face could be varied and typical. The rheological properties of all these five oils have to be modified if pumping and transporatation difficulties are to be minimised. As already mentioned earlier, the Nahorkatia crude oil is thermally conditioned and transported. The Bombay High oil field is potentially the biggest in the country presently. The transportation system of Bombay High oil is much different from that of Nahorkatia, it being a pipe line system. The pipe line is partly under sea (a few hundred kilometer) and the rest is underground upto Trombay refinery ; the pipe line from Urban terminal to Mathura Refinery is the longest. Most of the north Gujarat oils are relatively heavy besides being waxy and the problems encountered are quite severe. All these cases will require a pretreatment either through pour point depressants and or flow improvers. The characteristics as discussed above will undergo a change if the crudes were treated with the proper type of additives.

4.2 General Consideration

Keeping in view the object of this investigation, and the treatment the Indian Crude Oils may be required to be subjected to, polymeric compounds to the tune of 118 belonging to different classes, have been newly synthesized under this investigation. The five classes to which these 118 polymeric substances belong are as follows :

(1) Esters of poly(n-alkyl undecylenate-Co-maleic anhydride)

(2) Esters of poly(n-alkyl cinnamate-Co-maleic anhydride)

(3) Esters of poly(n-alpha monoolefin-Co-maleic anhydride)

(4) Polymers of dibehenyl maleates

(5) Polymers of dioctadecyl maleates

A considerable volume of literature continues to appear on the modification of oils, fats and carbohydrates by esterification to yield products with tailomade properties. Obviously thus, while similar compounds might have been synthesized earlier and the routes of their synthesis might have many common features with those adopted in this investigation the accurate methods with specific conditions of synthesis have been experimentally developed during this investigation without relying much on the available literature. Therefore certain steps of synthesis may find relevance for a brief discussion. The experimental processes are developed to the need of the fulfilment of objective in mind, but since the main aspect of the object was to study their application to various oils from the additive point of view. The yields of the products synthesized under this investigation are better than those reported for similar reactions in the earlier work.

The structure of the products of the all the five classes may be depicted as follows on the basis of the primary consideration of the starting materials and the steps of the reactions :

1. (i) $CH_2{=}CH(CH_2)_8COOH \quad + \quad R{-}OH \xrightarrow{\text{Catalyst}}$

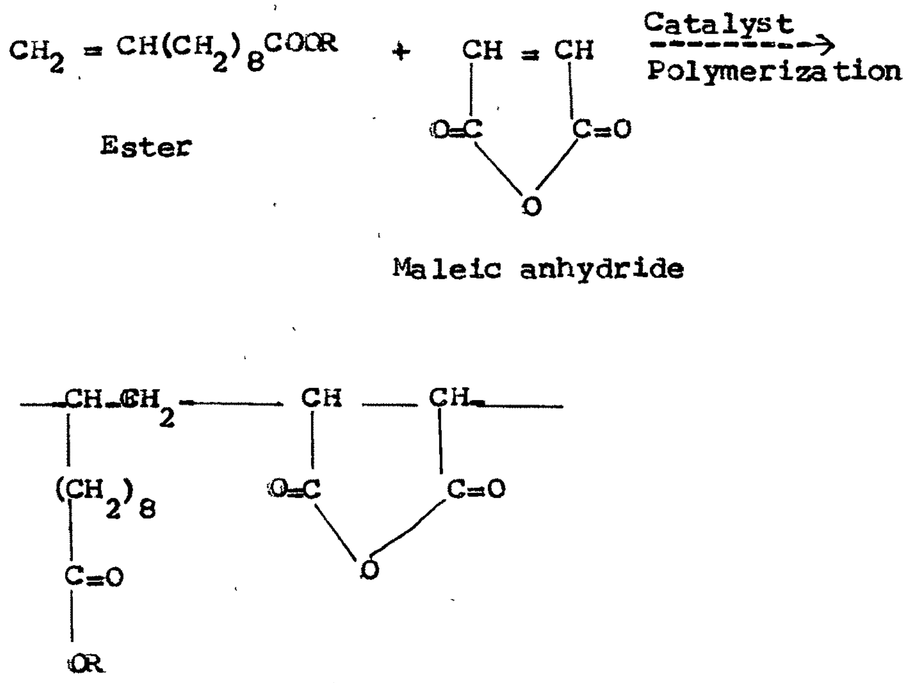
Undecylenic acid

$$CH_2{=}CH(CH_2)_8COOR$$

Ester

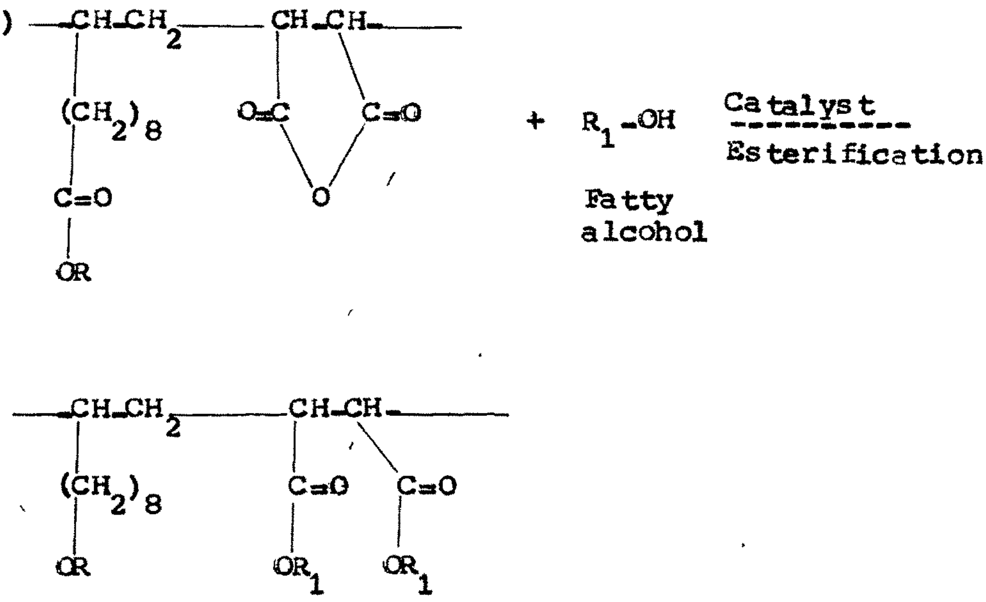
where R = straight chain even alkyl group containing C_2 to C_{18} and C_{22} ; C_8 is also as 2-ethyl hexyl.

(ii)



Anhydride copolymer

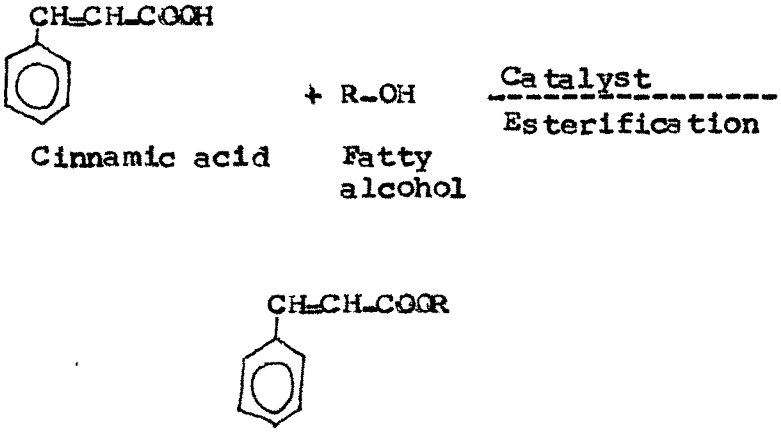
(iii)



Dimaleate ester

where R_1 = straight chain even alkyl group of C_{14} to C_{18} and C_{22}.

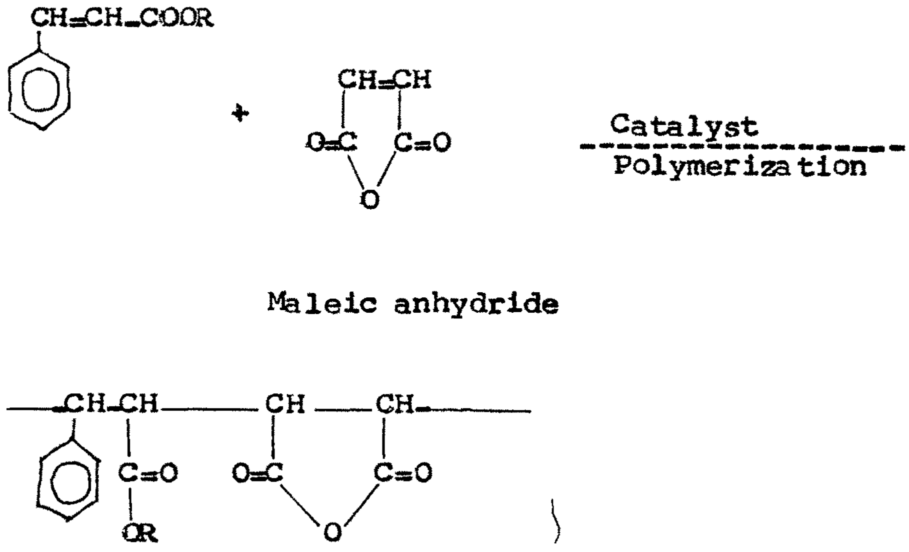
2. (i)



Ester

where R = C_1 to C_{18} and C_{22}

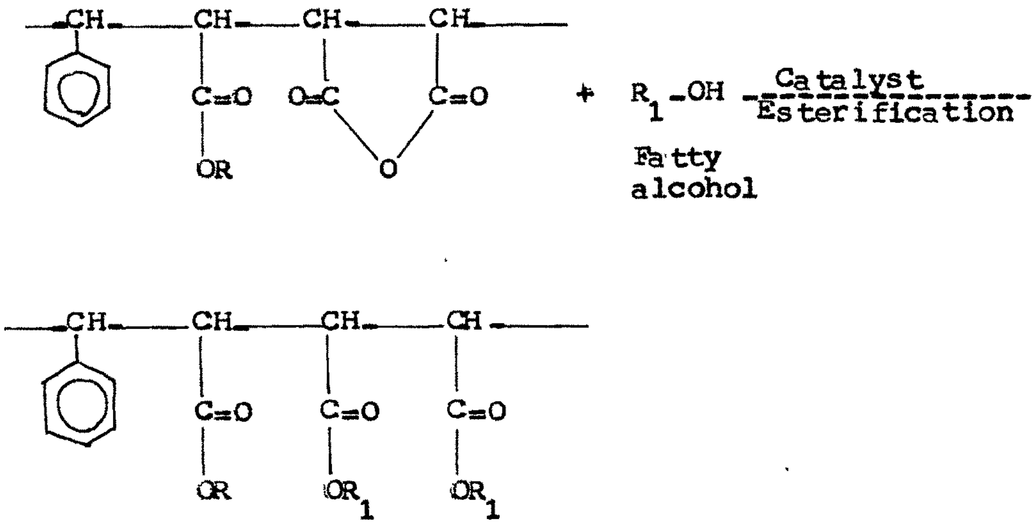
(ii)



Maleic anhydride

Anhydride copolymer

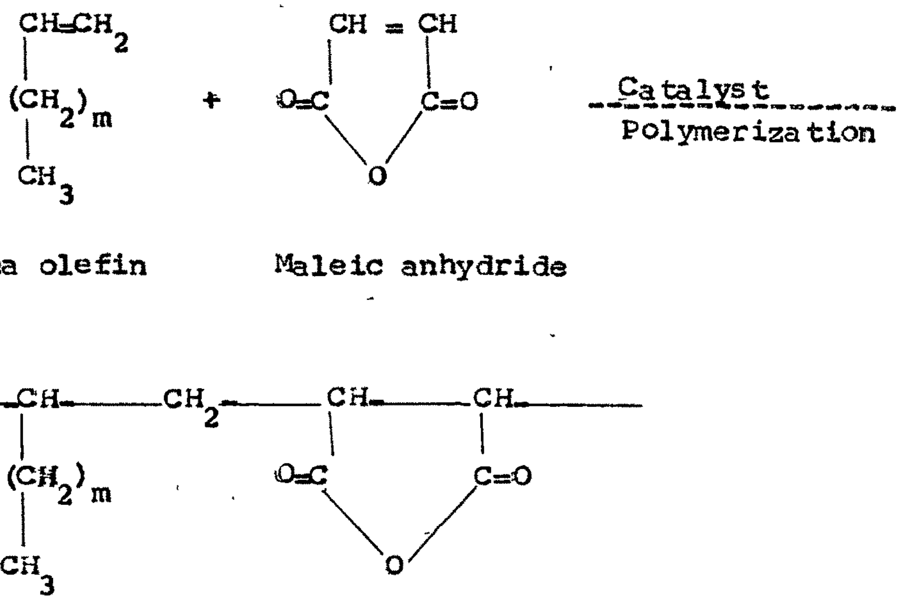
(iii)



Dimaleate ester

where R_1 = straight chain even alkyl group of C_{14} to C_{18} and C_{22}.

3. (i)

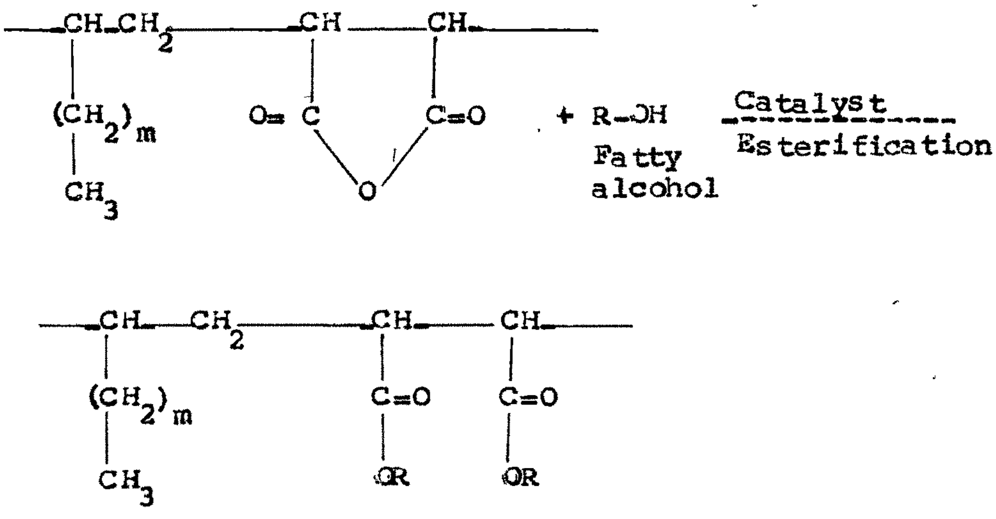


Alpha olefin — Maleic anhydride

Anhydride copolymer

where m = 11.67 and 17.94

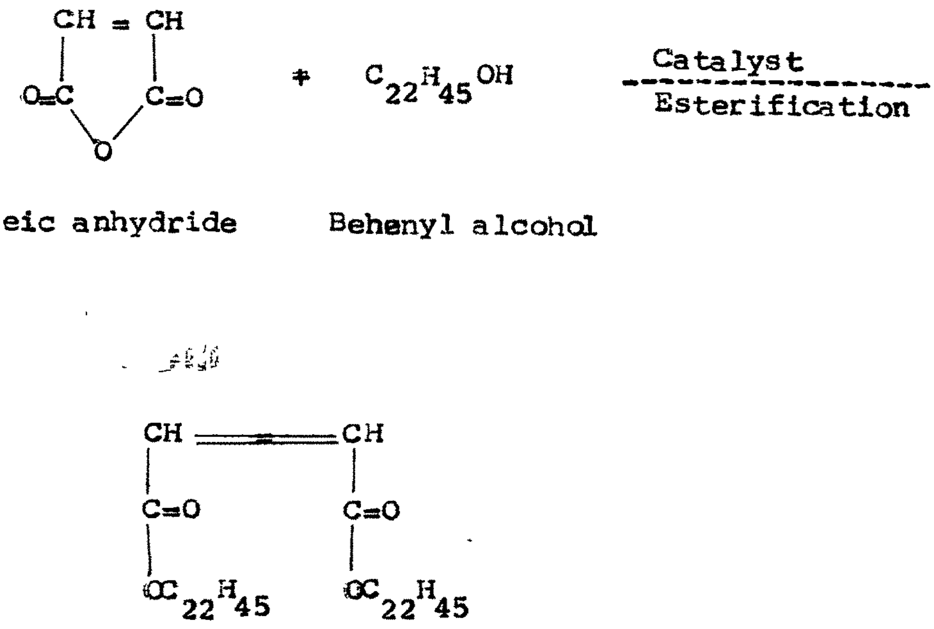
(ii)



Dimaleate ester

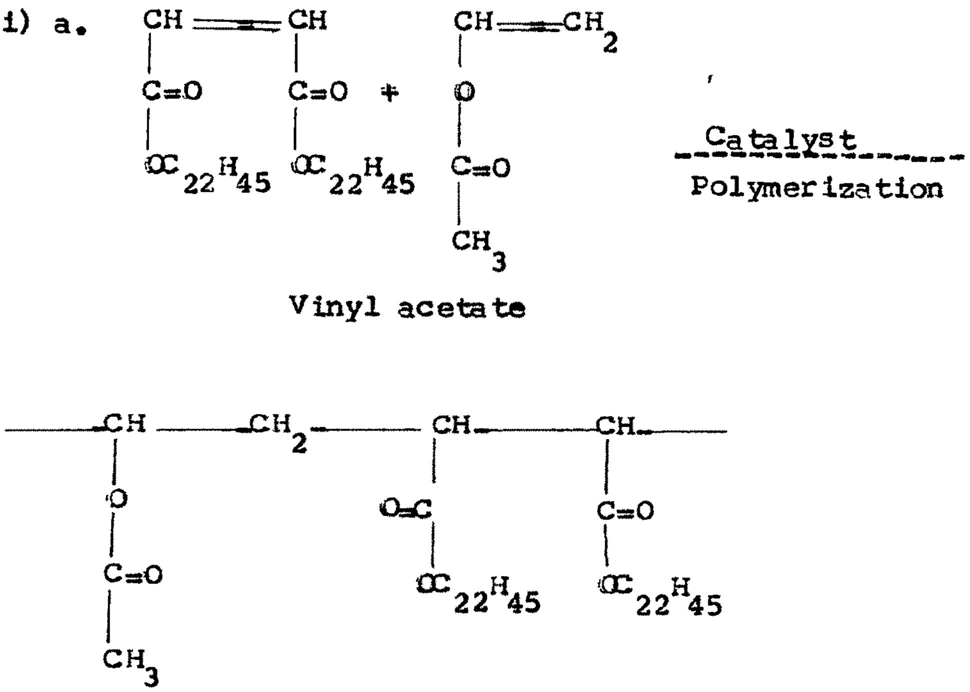
where R = straight chain even alkyl group of C_{14} to C_{18} and C_{22}.

4. (i)



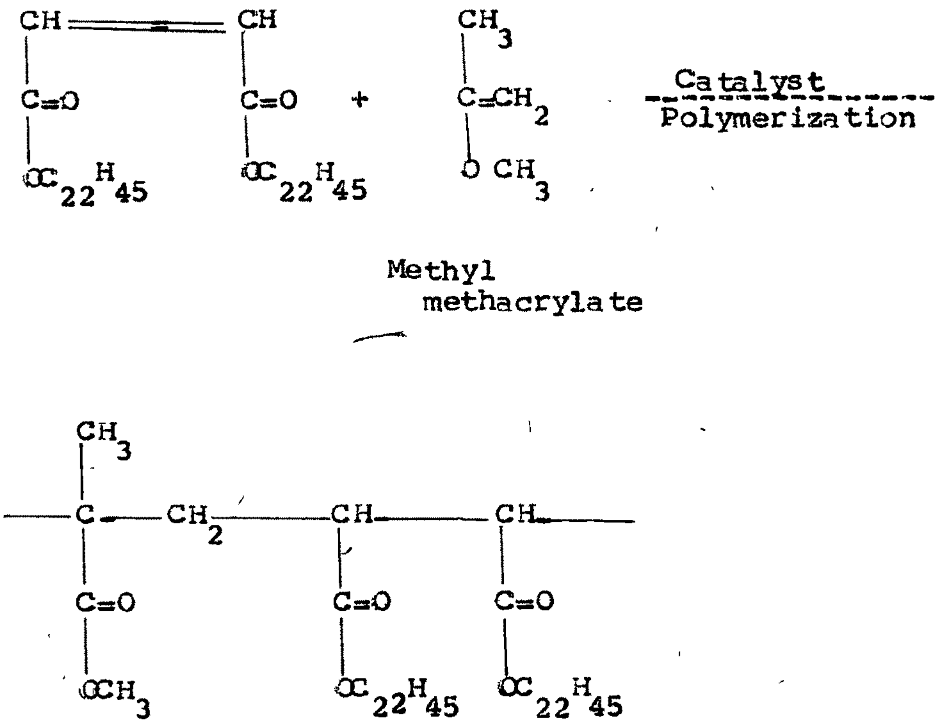
Dibehenyl maleate

(ii) a.



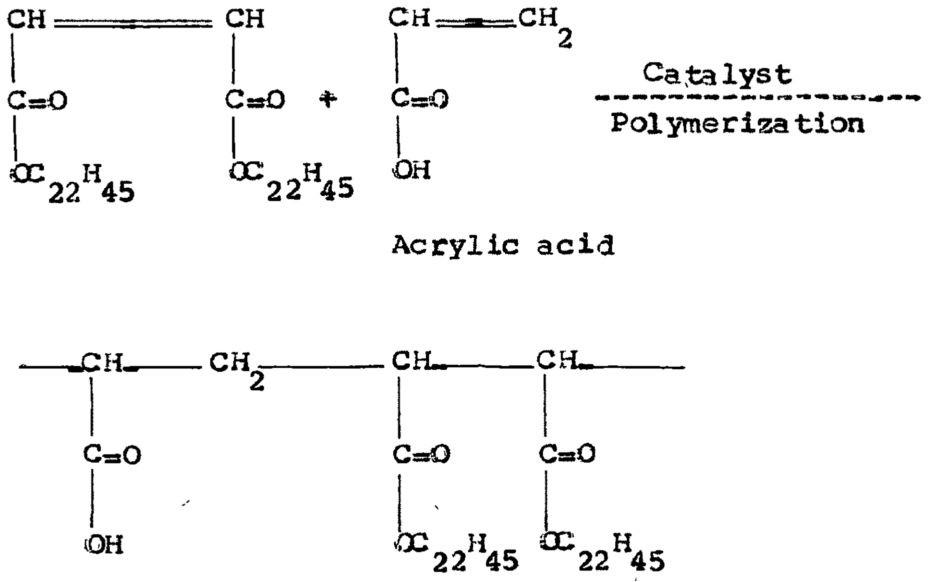
Copolymer

b.



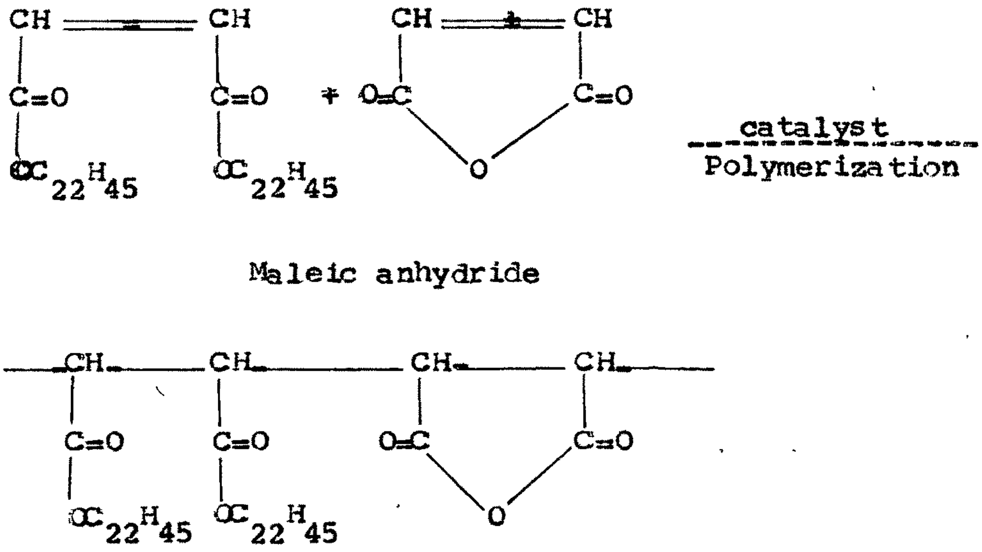
Copolymer

c.



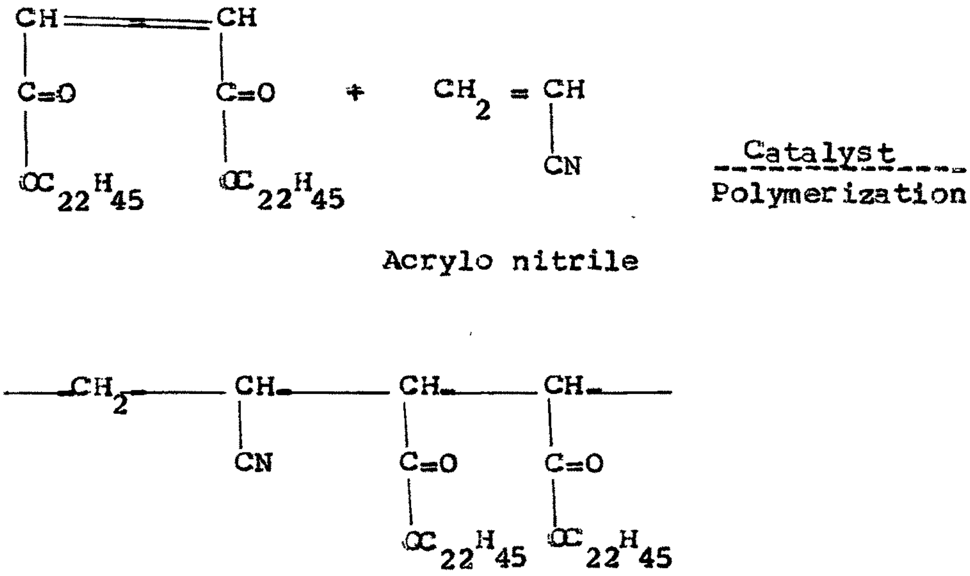
Copolymer

d.



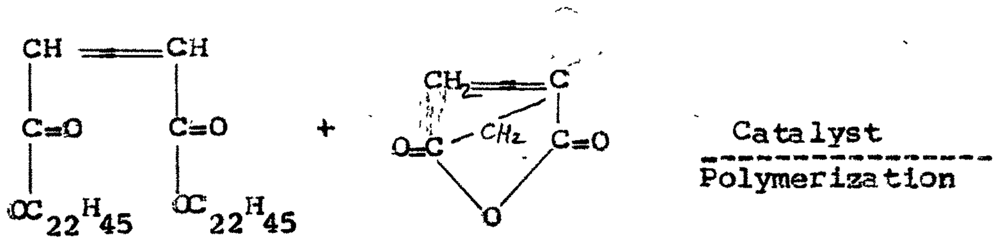
Anhydride copolymer

e.

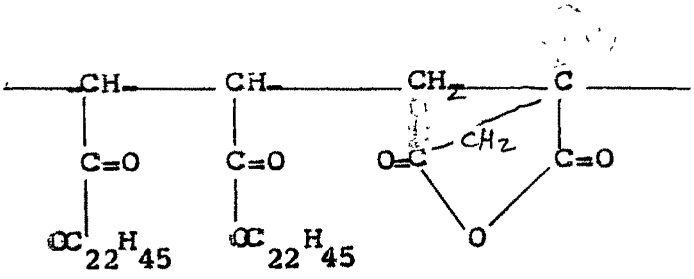


Copolymer

f.

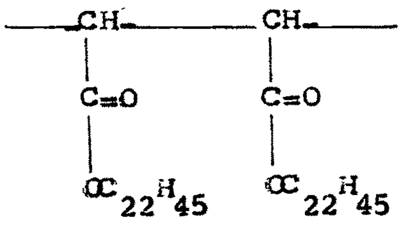


Itaconic
anhydride



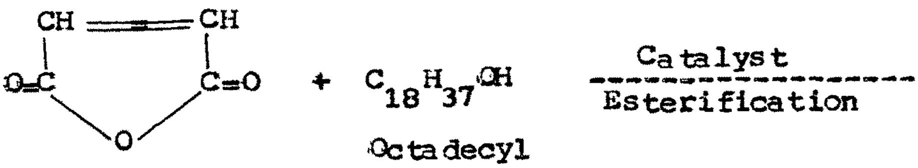
Copolymer

g.



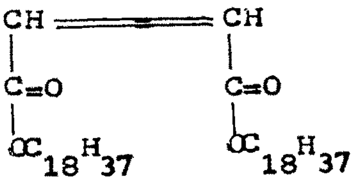
Poly dibehenyl maleate

5. (i)



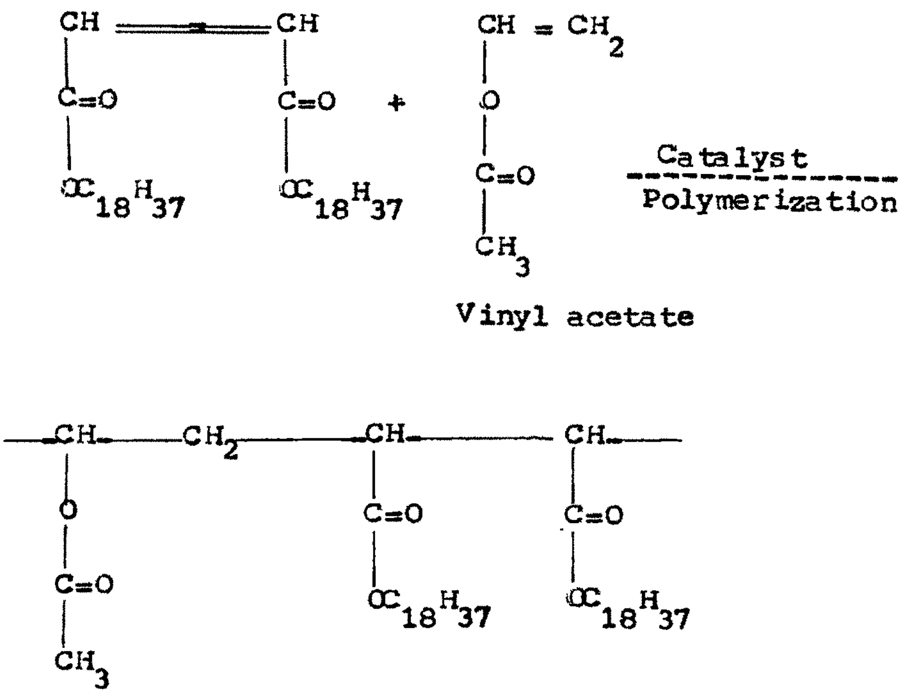
Maleic
anhydride

Octadecyl
alcohol



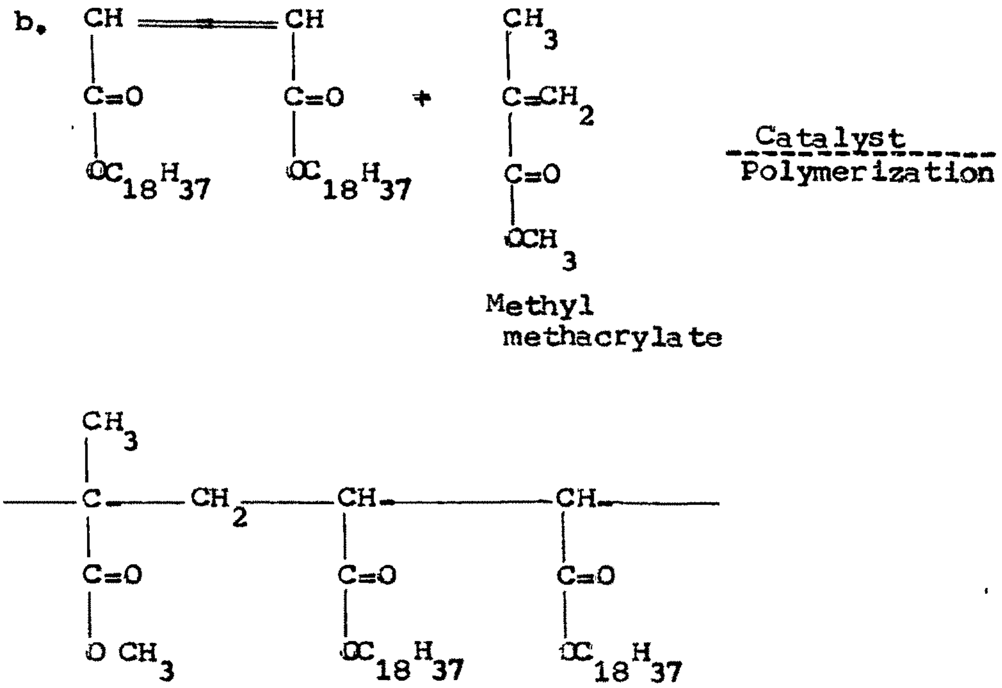
Dioctadecyl maleate

(ii) a.



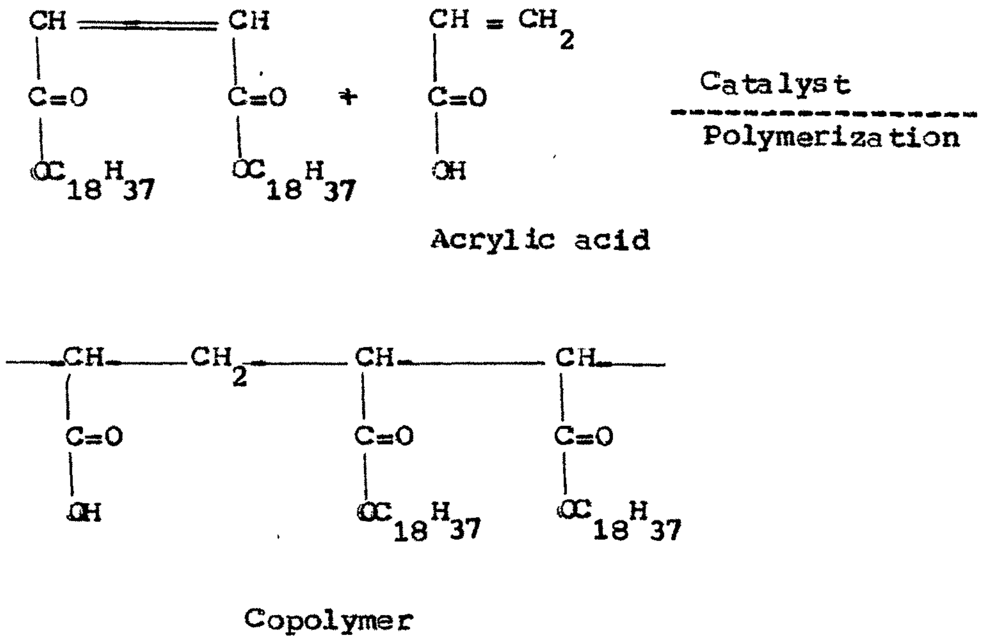
Copolymer

b.

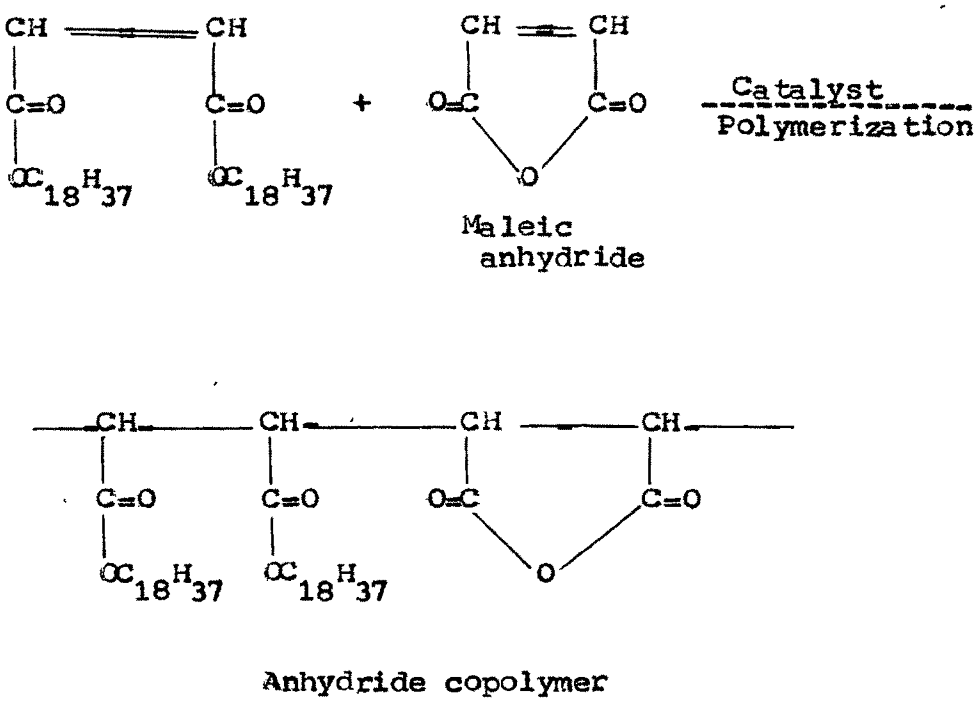


Copolymer

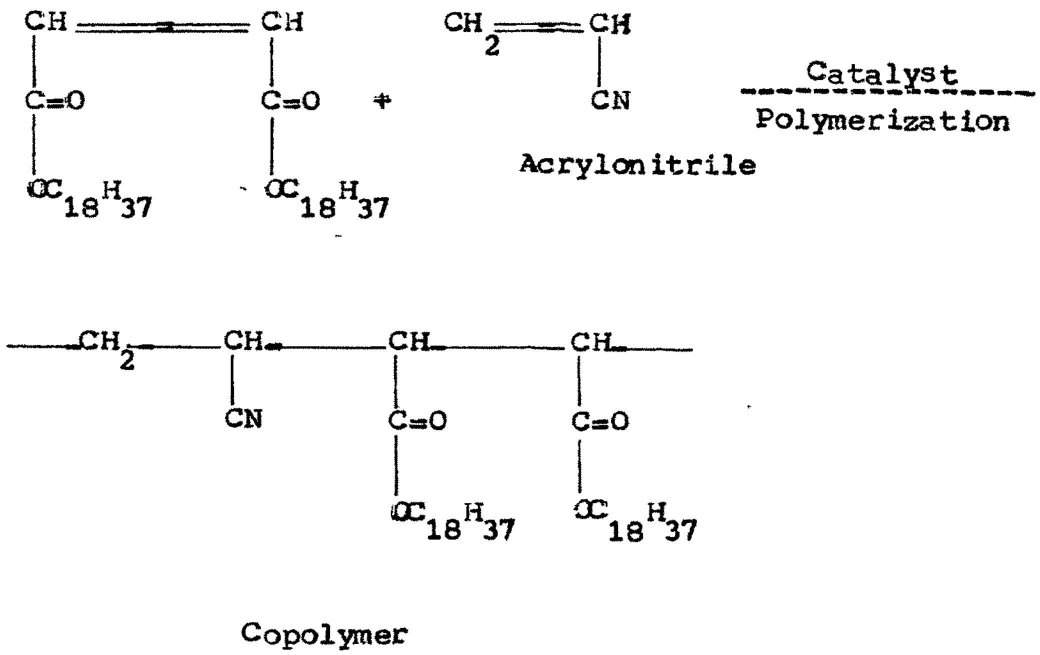
(c)


Catalyst
Polymerization
Acrylic acid
Copolymer

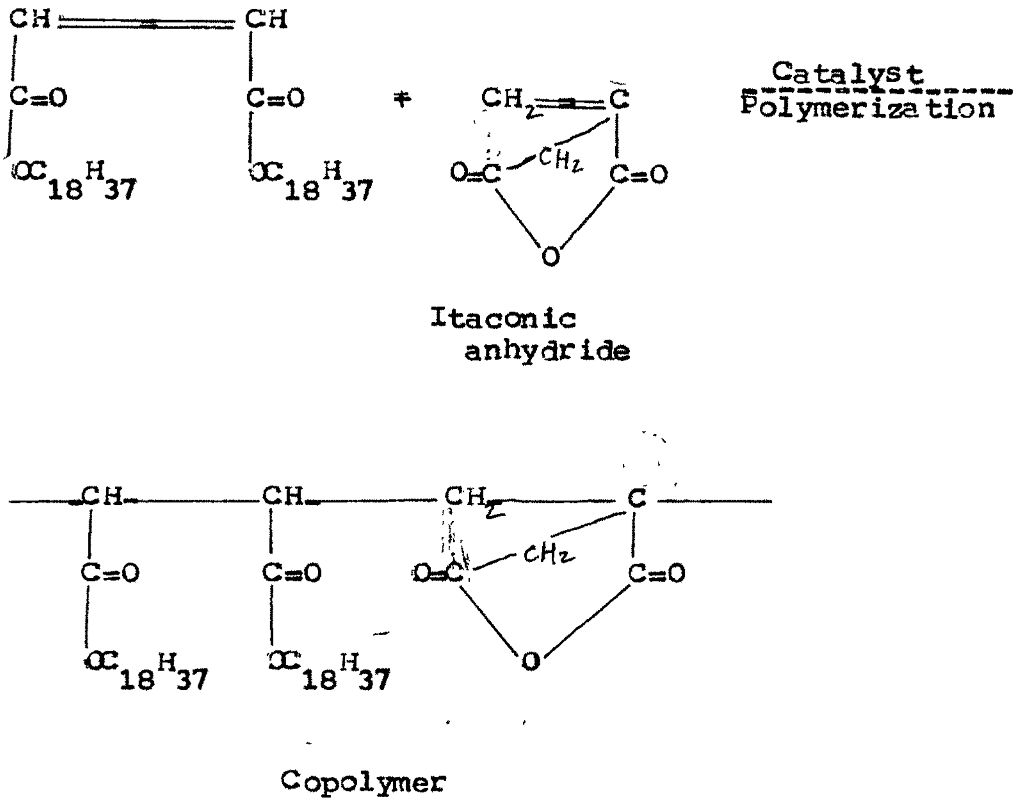
d.


Catalyst
Polymerization
Maleic anhydride
Anhydride copolymer

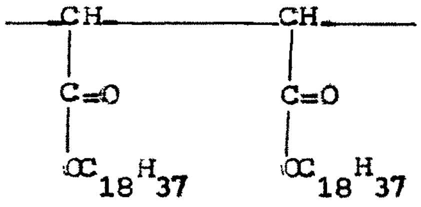
e.


Acrylonitrile
Catalyst
Polymerization
Copolymer

f.


Itaconic anhydride
Catalyst
Polymerization
Copolymer

(g)



$$-CH-CH-$$ with each CH bearing $C{=}O$ and $OC_{18}H_{37}$

Poly dioctadecyl maleate

For the product of the second step, the structural formula, as mentioned, is a most logical and scientifically reasonable derivation. The elemental analysis for all the products and IR spectroscopic studies for same products for the five classes of compounds have been carried out whose results (Tables 8, 10, 17, 19, 25, 26, 27, 33, 34, 36 and 37) completely agree with the depicted structural formulae. The anhydride copolymers were next, at the third step, esterified by the established procedure and the final products were obtained. Obviously, the structural depiction has to be that what is mentioned. Since the final polymeric products are as a result of 1:1 monomer ratio copolymerization system at the second stage, the study of the composition of the final products of the stage vs. monomer ratio was taken as of no consequence and hence this part of the study, which otherwise is an usual and normal part in the study of polymer synthesis, has been eliminated. Thus, the molecular structures of the basic unit of the polymers in all case of all the five classes, are as depicted above. It is visualized that in order that a polymeric derivative functions as an additive for the crude oils with the view to make them behave as Newtonian or near-Newtonian fluids at sufficiently low temperatures the following some structural specifications in a general sense should be associated with the polymer molecules.

(1) Sufficient number of pendant alkyl chains preferably straight ones, in a polymer basic unit.

(2) Sufficient length of the pendant straight alkyl chains in such cases.

(3) Poly ethylene segments in the polymer backbone itself.

(4) In some cases, the distance between the two pendant chains is effective in deciding the additive action.

Flow improving additives synthesized under this investigation are tried on Indian crude oils which are waxy in nature, hence such structural requirement of the additives as are necessary for dealing with the waxy nature are discussed at length in the above section. However, the asphaltene containing crude may not react to the additives in the same manner as the waxy ones. Variation in asphaltene content, even if the overall nature of the crude may be waxy, may cause variation in the results of the treatment of the crude oils on addition of these additives.

4.3 Efficiency of the Additives

The total 118 polymeric substances newly synthesized in this investigation, 93 have been tried variously for pour point depression activity and rheological changes with the five Indian crude oils. The 25 substances discarded from the study were thought to be the least effective on account of their primary structural characteristics.

In other words, 93 polymeric compounds have been investigated as potential additives for pour point depression activity. These 93 polymeric compounds have been found to be of some consequence and hence their pour point depression calculations are recorded in the Tables 46 to 52 meant for the purposes in the experimental section. It is quite interesting to discuss the effect of these 93 polymeric compounds from the view point of their functioning as additives.

The Bombay High (BH) operation which has the potential of turning out one of the biggest ever Indian source, has given crude oil of a different quality of the five different samples under consideration, the BH crude oil is the only one with the lowest asphaltene and resin content. Its pour point is also the lowest i.e. 30°C. Yet the non-Newtonian character of the BH crude oil is quite evident. From its rheogram (Fig. 14), it is clearly seen that as its natural pour point it has slight pseudo plastic character and that the non-Newtonian behaviour is sufficiently pronounced. However, at only 3°C higher, the Newtonian character is acquired by the BH crude oil. Since the average molecular weight character of the BH crude oils asphaltene content is not well established and also because this crude oil has higher wax content as compared to Nahorkatiya (Na) crude oil, a proposition for thermal conditioning is rather too risky to make, though theoretically it should be the easiest on account of a mere 5°C rise requirement above its pour point. Thus, a chemical additive could be perhaps a better alternative ; and the results of this investigation to seem to suggest that this is the surest way.

Of 93 products considered for this study, a large number has been attempted with the BH crude only. The first one to be discussed here is that which has given the best results as far as the BH crude is considered i.e. 22-22 UnMA, n-Docosylester of poly (n-docosyl undecylenate-co-maleic anhydride), has been tried in various proportions (Table 46) for observing the pour point depression in the case of BH crude. With just 100 ppm of 22-22 UnMA the pour point is depressed to the extent of 24°C and with rising proportion of the additive, the depression is further enhanced. With as low as 300 ppm the pour point depression is to the extent of 27°C. This at the laboratory scale does seem to be highly impressive ; as a matter of fact, this additive was one of the last to be tried, and with the unprecendented beautiful result, it gave a romantic experience.

The 22-22 UnMA additive could be represented structurally as follows :

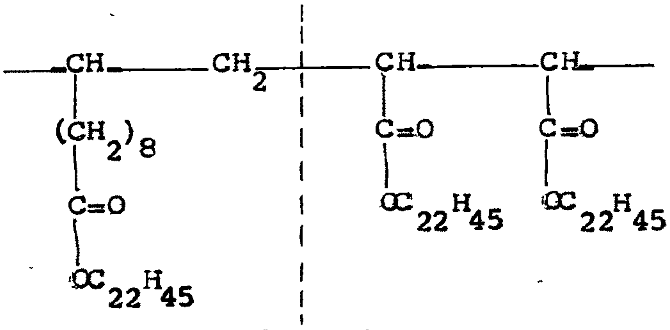


Fig. 21

In this basic polymer unit, there are three pendant chains of sufficient length. These three pendant chains could be classified into two groups - one which falls in the undecylenic ester segment (left of the dotted line), containing only one chain, and the other which is to the right of the dotted line falling in the maleic ester segment containing two chains. Now, a series of additives with decreasing lengths of the pendant chains in a definite sequence of two carbon atoms each time except in the first decreasing step down from C_{22} where it is of four carbon atoms, either to the right of the dotted line when the chain to its left has a fixed unchanging alkyl group, or to the left of the dotted line when the chain to its right has a fixed unchanging alkyl group, have been tried on the BH crude oil with a view to determine the effect of the chain length on the additive activity.

The 18-22 UnMA, where the two alkyl chains to the right of the dotted line have been shortened to the extent of 4 carbon atoms when that to the left of the dotted line (the alkyl chain length of 22 carbon atoms) is maintained unchanged, has a decreased effect on pour point depression of the BH oil as is evident from Table 46. With 100 and 200 ppm of the 18-22 UnMA, the effect of depression in this case is not noticeable, however, with 300, 500 and 1000 ppm of additive, it is sizeable but much less than that of the previous compounds. The 16-22 UnMA is still effective as pour point depressant, but to a lesser extent. The least effective compound in this series is 14-22 UnMA. This decreasing effect with decreasing alkyl chain length indicates two things (1) length of the alkyl chain plays an important role in pour point depression provided other factors are constant and (2) the shorterning of chain lengths by 8 carbon atoms is the limit in this case, beyond which pour depression is ruled out. Another important point that emerges is that within the consideration of the same additive its greater proportion has greater effect in pour point depression. It can be said thus that the larger the amount of the additive, the greater is the pour point depression.

The above discussion concerns the decreasing chain length consideration in the right hand sector of the basic polymer unit of the additive while the chain length of the left hand segment remained intact, a case now of a different series of the additive belonging, however, to the same class of polymeric substances where the alkyl chain length of the left hand sector to the dotted line decreases sequentially, while maintaining the alkyl chain lengths of the right hand sector of the dotted line, is taken up. The 22-18 UnMA is one such additive where the alkyl chain length at the left hand sector to the dotted line is shorter by 4 carbon atoms while those at the right hand segment are intact. Now, with this much change, the pour point depression effect is slightly altered as compared to that of the 22-22 UnMA compound with 100 ppm concentration of the 22-18 UnMA additive, the pour point of BH crude oil decreases to the same extent, but with its higher concentration of 200, 300, 500 and 1000 its effect is less. As a matter of fact the optimum effect with its rising concentration is obtained at 200 ppm level and then on it remains constant. When the effect of 22-18 UnMA additive is compared with that of the 18-22 UnMA (a cross sister compound) it is observed that 22-18 UnMA additive has much better pour depression effect than that of the cross sister 18-22 UnMA. This is so because in the case of 18-22 UnMA, the chain length shortening is no doubt of the same magnitude as of 22-18 UnMA, but there are two such chains in the right hand sector of the dotted line and hence the effective shortening is of 8C worth and not only 4C worth. Therefore 18-22 UnMA is less effective in pour point depression of BH crude than

22-18 UnMA additive. Continuing the discussion further, the effect of 22-16 UnMA additive is almost the same as that of 22-18 UnMA additive for 100 and 200 ppm concentrations, but with 300, 500 ppm, it becomes more effective than 22-18 UnMA, as the depression caused by it at this concentration level is to the extent of 30°C as compared to of 27°C in the case of 22-18 UnMA additive. This is surprizing that with greater shortening of the chain length, the effect is some what enhanced rather than decreased. However, it should be noted that its ' cross sister ' 16-22 UnMA, where the effective decrease in chain length by 4 carbon atoms is of 8 carbon worth since there are two such chains in question, is relatively very less effective in the pour point depression property. The next in the series 22-14 UnMA is less effective in pour point depression than 22-16 UnMA. Factually, as far as BH oil is concerned, the polymeric additives of this class where both chains belonging to the maleic ester segment are progressively getting decreased, the pour point depression effect becomes zero beyond 14-22 UnMA compoumd, whereas, in the ' cross sister ' series, where the alkyl chain belonging to the undecylenic ester part i.e. to the left of the dotted line, gets decreased progressively, the pour point depression effect is continued to be exhibited beyond

22-14 Un^{MA} and upto 22-2 Un^{MA} compound.

It may be said right at this stage that when two alkyl chains get shortened simultaneously, the pour point depression activity too is decreased greatly as compared to when only one alkyl chain length gets decreased at a time. By this consideration, taking the effect due to decrease in chain length to be equal, in the conditions as they are at this stage of the discussion, the pour point depression activity then would have continued up to C_6 alkyl length had there been only one chain at the right hand segment of the dotted line, instead of two. However, in the case of the ' cross sister ' series, the pour point depression activity is exhibited up to 22-2 Un^{MA} compound, up to two stages more in the decreasing sequence. In other words the entire series $22\text{-}\underset{\downarrow}{\underline{22}}$ Un^{MA} is more effective in pour point depression as compared to the $\underset{\downarrow}{\underline{22}}\text{-}22$ Un^{MA} (series (where $\overline{\downarrow}$ shows changing alkyl sector).

There may be other reasons why the $22\text{-}\underset{\downarrow}{\underline{22}}$ Un^{MA} series is more effective in pour point depression activity. Perhaps, the presence of $-(CH_2)_3-$ (eight methylene units) bunch in the pendant chain at the undecylenic ester segment, linked through $-\overset{O}{\overset{\|}{C}}-O-$

to the alkyl chain 'R', has its own contribution in pour point depression phenomenon. Linking through $-\overset{O}{\overset{\|}{C}}-O-$ group has an overall hampering effect, yet, the activity of eight methylene units attached to the backbone is not altogether eliminated due to $-\overset{O}{\overset{\|}{C}}-O-$ group's presence and that there is some ' residual effect ' of the $-(CH_2)_8-$ group that is added up in the pour point depression property.

Coming back to the 22-22 UnMA series of ester polymers, the entire series is quite effective in pour point depression function for the BH crude as is reported above, yet a patternised ' regularity ' is rather difficult to locate in the depression activity as the alkyl chain length is decreased progressively from C_{22} to C_2.

A plot of the extent of pour depression versus alkyl chain length of the undecylenic ester segment's pendant chain is given in Fig. 22(a). At the first sight it appears to be a mere zig-zag plot, but a closer look may bring out certain 'units' of regular variation as the alkyl chain length is decreased. It is drawn with the pour point values at 500 ppm concentration of the additive primarily because the pour point determination upto C_2 alkyl chain length was practically feasible. It is seen that from C_{22} length to C_{18} length of the alkyl chain of the poly (alkyl undecylenate-Co-maleic anhydride), the pour point depression is of lesser value i.e. to the extent of 3°C ; in this segment of the plot, the decrease in the alkyl chain length is of four carbon worth. With further decrease in the chain lengths equal to two carbon magnitude (C_{16}) the extent of pour point depression is again equal to that due to C_{22} chain length. From this point onwards in the decreasing sequence of the chain length the pour point depression value alternates up to C_{12} chain length. From C_{10} to C_8, there is a continuous decrease in the depression effect, that at C_6 being equal to that at C_8 and at C_{12} being equal to that at C_{14}. The depression value at C_2 is the same as that at C_4. The pour depression to the extent of 30°C is thus at C_{22}, C_{18}, C_{16}, C_{10}, C_8, C_4 and C_2 - the difference in the chain length being of 4 carbon, 2 carbon, 4 carbon, 2 carbon, 4 carbon and 2 carbon in the same sequence. The pour depression is the least i.e. 24°C at C_6 and C_8 the difference in the chain length being of 2 carbon. The medium pour depression value of 27°C is obtained at C_{12} and C_{14}

stages - the difference in the chain length being of 2 carbon. An overall pattern of decreasing pour point depression effect is thus that of a continuous decrease upto two stages followed by alternation to the next two stages and at last stage (i.e. at C_{16}, C_{18} and C_{22}) there is constant depression in pour point.

Similar pattern of the pour depression with decreasing chain length is observed with 300 ppm concentration of the said additive Fig. 22(b), with certain variations in the stages but without any marked change in the pattern. This effect is observed in the case of the series of ester polymers when only one chain undergoes a decreasing change. With its ' cross-sister ' series of the ester polymers, where two such chains simultaneously undergo a decreasing change in their lengths, a different pattern of pour depression is obtained Fig. 23. The pour depression study is obviously carried out in this case upto C_{14} homologue since for a homologue with C_{12} alkyl chain the pour depression is zero. In this case it is observed that the pour depression activity is continuously decreased without any ' sequence-alternation' pattern shown by its ' cross-sister ' polymer series. As the alkyl chain length decrease is simultaneously in

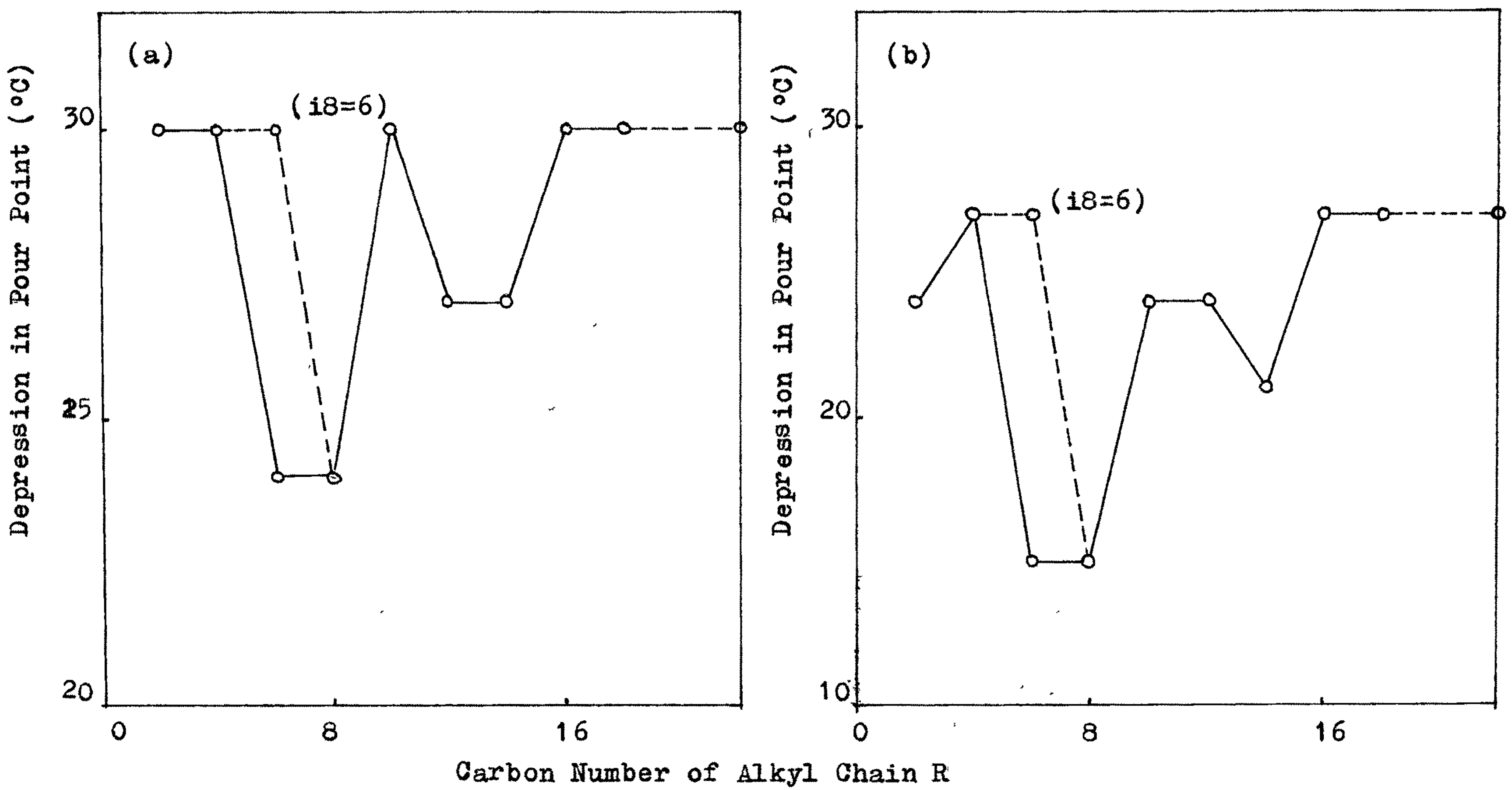


Fig. 22 : n-C_{22} Esters of R-UnMA in BH Oil vs. Pour Point Depression (°C)
(a) at 500 ppm (b) at 300 ppm

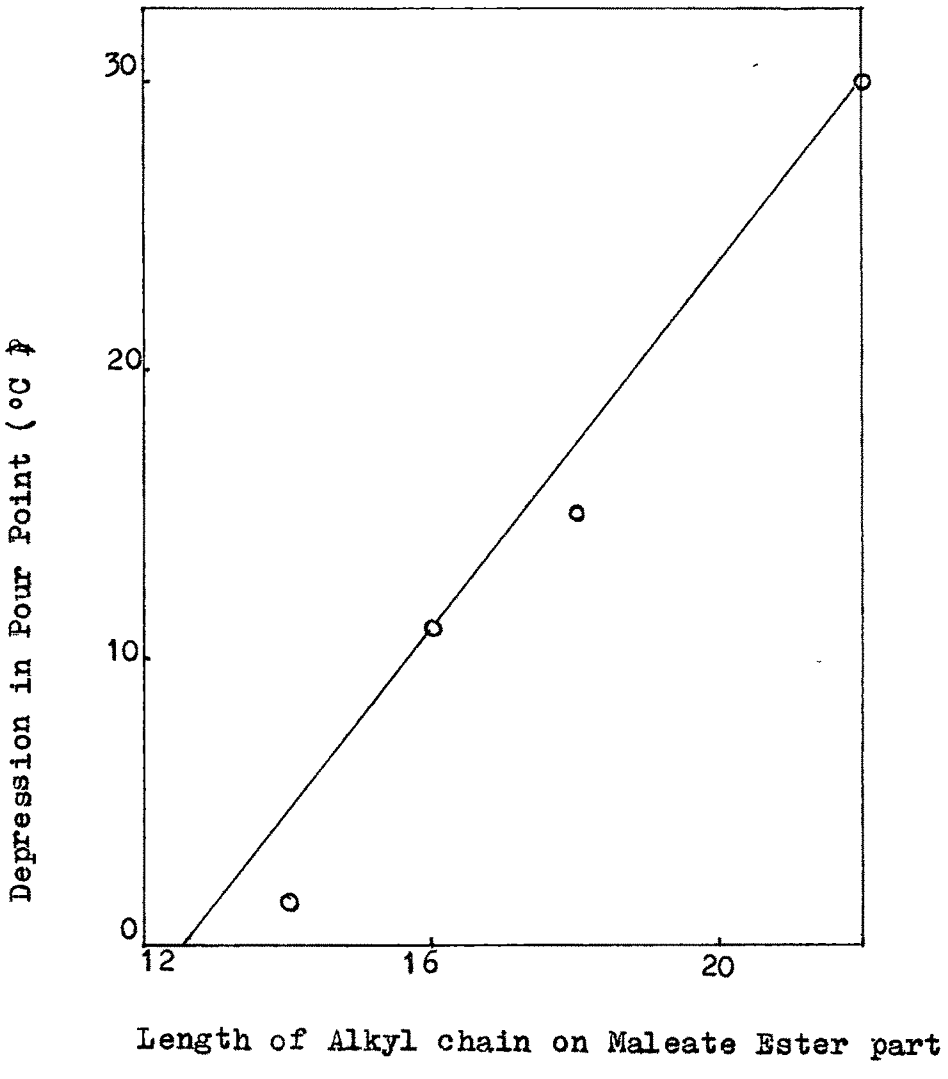


Fig. 23 : Poly(Dooosyl Undecylenate -co- Dialkyl Maleate) at 500 ppm in Bombay High Oil vs. Pour Point Depression

two chains, this continuous decreasing pattern is perhaps the most logical thing to happen. At C_{12} lengths, the depression activity is zero which means that there must be a certain minimum length of the alkyl chain in order for an additive to be able to function as pour point depressant and that in this case it turns out to be C_{14}.

Thus it is interesting to note that both series of the ester polymers in consideration are very good pour depressants even with very less concentration i.e. 100 ppm. The additive with full alkyl chain lengths (all the three) i.e. poly (n-docosyl undecylenate-Co-didocosyl maleate) in 100 ppm concentration only transforms the BH crude oil from a normally high pour point of 30°C to a mere 6°C pour point - a depression of 24°C with such a small amount of the depressant is something really noteworthy of.

When the additive 22-22 UnMA is replaced by 18-22 UnMA in the case of Na, Mo, crude oils, the pour depression activity is also decreased, though the activity is still quite marked. With 500 ppm concentration, the extent of pour depression is of 18°, 18°C respectively for Na and Mo oils. The 16-22 UnMA compound is effective by and large in its pour depression activity. The extent of pour depression is of 9° and 9° in Na and Mo crude respectively. The decreasing pour depression activity can be attributed to the decreasing ($\underset{\downarrow}{22}$-22 UnMA) alkyl chain length ; the activity decreases faster since two alkyl chains get shortened simultaneously progressively as one passes from 22-22 UnMA to 16-22 UnMA.

Taking into consideration 22-$\underset{\downarrow}{\underline{22}}$ UnMA changing series where $\overline{\downarrow}$ shows decreasing alkyl chain length in the undecylenic ester sector to the left of the dotted line Fig. 21 of the basic polymer unit, the additive activity for pour depression is less than the 22-22 UnMA additive. The 22-18 UnMA ester polymer shows the extent of depression, with its 500 ppm concentration in the Na and Mo crude oils, as 24° and 27°C respectively. The 22-16 UnMA compounds follows suit with the extent of depression being 24° and 24°C respectively. The next 22-14 UnMA ester polymer shows depression by 21° and 18°C respectively. Table 100 shows the extent of depression for the decreawing series. With increasing asphaltene and resin content, the extent of depression in the pour points decreases with decreasing chain length.

Table 100

Extent of Pour Depression at 500 ppm

Crude oil	22-22 UnMA	C_{18}	C_{16}	C_{14}	C_{12}	C_{10}	C_8	C_{18}	C_6	C_4	C_2
Na	30	24	24	21	21	24	18	27	24	24	30
Mo	33	27	24	18	18	21	21	27	24	30	33

The 22-22 UnMA series of ester polymers, the entire series is quite effective in pour point depression function for Na and Mo crude. A plot of the extent of pour depression versus alkyl chain length of the undecylinic ester segment's pendant chain is given in Fig. 24 and 25. At the first sight it appears to be a mere zig-zag plot, but a closer look may bring out certain 'units' of regular variation as the alkyl chain length is decreased. It is drawn with the pour point values at 500 and 300 ppm concentration for Na crude and at 500 and 200 ppm concentration of the additive for Mo crude oil. It is seen that from C_{22} length to C_{18} length of the alkyl chain of the poly(alkyl undecylenate-Co-maleic anhydride), the pour point depression is of lesser value i.e. to the extent of 6°C in this segment of the plot, the decrease in the alkyl chain length is of four carbon worth. With further decrease in the chain lengths equal to two carbon magnitude (C_{16}) the extent of pour point depression is of 24°C i.e. equal to C_{18} chain length. From C_{16} to C_{14} chain length there is decrease in depression effect and this effect is equal at C_{12}. Then after C_{12} chain length there is increase in depression effect upto C_{10} chain length. After C_{10} chain length there is decrease in depression

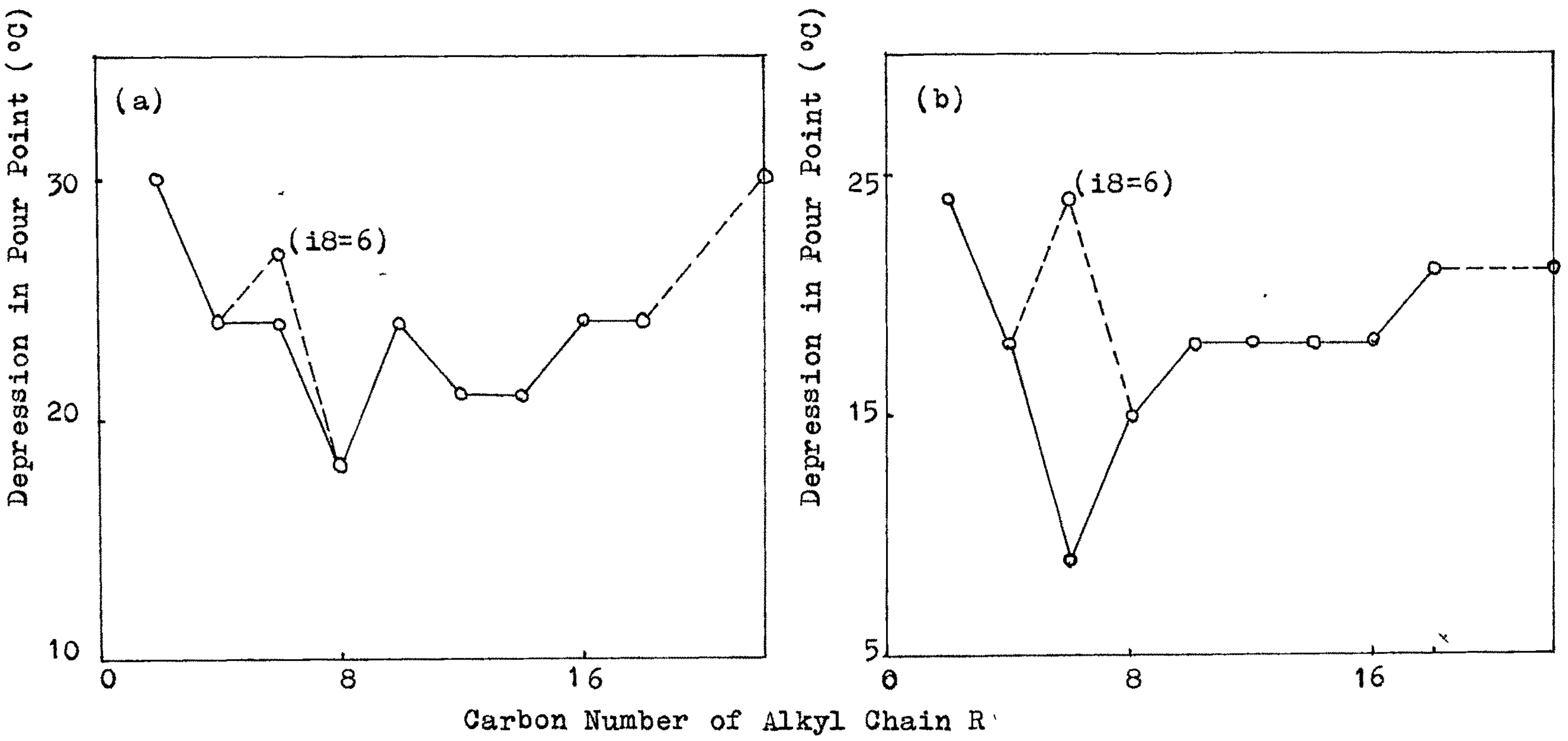


Fig. 24 :n-C_{22} Esters of R-UnMA in Na Oil vs. Depression in Pour Point (°C)
(a) at 500 ppm (b) at 300 ppm

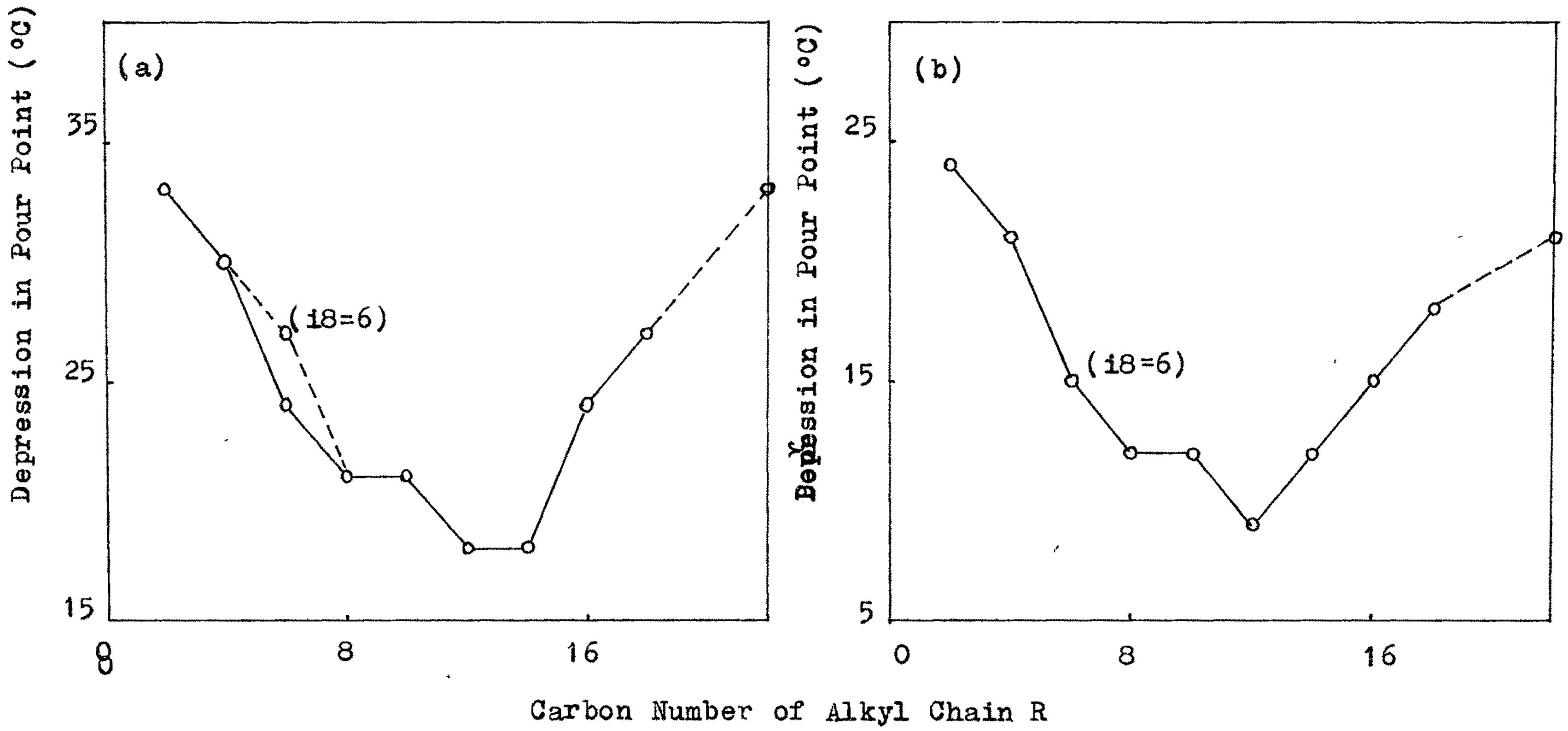


Fig. 25 : n-C_{22} Esters of R-UnMA in Mo Oil vs. Depression in Pour Point (°C)
(a) at 500 ppm (b) at 200 ppm

effect upto C_8 chain length. After C_8 chain length there is continuous increase in the depression effect at C_6, C_4 and C_2. An overall pattern of decreasing pour point depression effect is thus upto three stages followed by alternation to the next three stages. An overall increasing pour point depression effect is thus up to two stages. Thus a zig-zag pattern of pour depression effect is exhibited by this additive with Na crude oil.

Almost a similar pattern of the pour depression with decreasing chain length is observed with 300 ppm concentration of the said additive Fig. 24(b). Just as in the case of BH crude oil, the 22-22 UnMA compound is plotted against the extent of pour point depression Fig. 26. The plot obtained follow the BH pattern in Na crude oil also.

The next group of substances synthesized and studied under this investigation is of n-alkyl esters of poly(n-alkyl cinnamate-Co-maleic anhydride) a class which has certain similarities incorporated on account of maleic anhydride segment of the basic polymer unit, to the class I, and certain distinguishing character as is evidenced by the presence of aromatic ring.

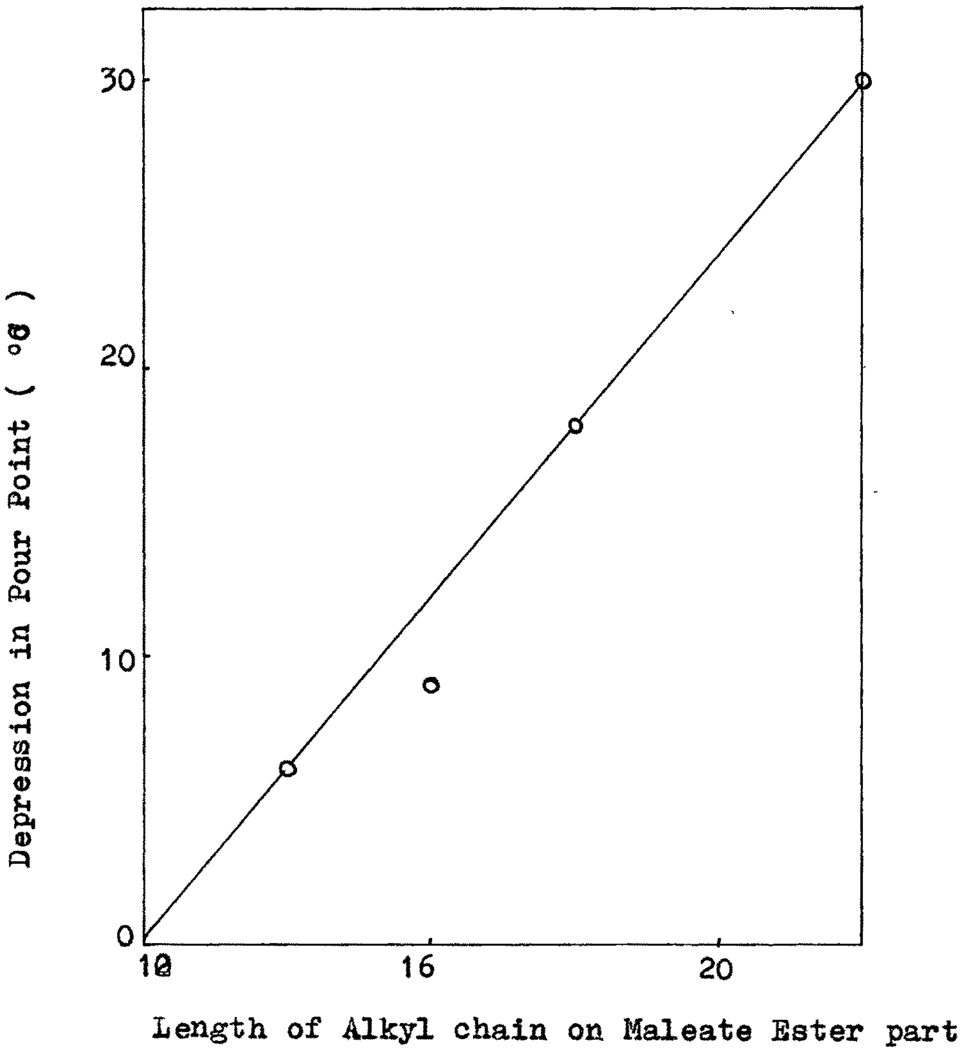


Fig. 26 : Poly (Docosyl undecylenate - co - Dialkyl Maleate) at 500 ppm in Nahorkatia Oil vs. Pour Point Depression

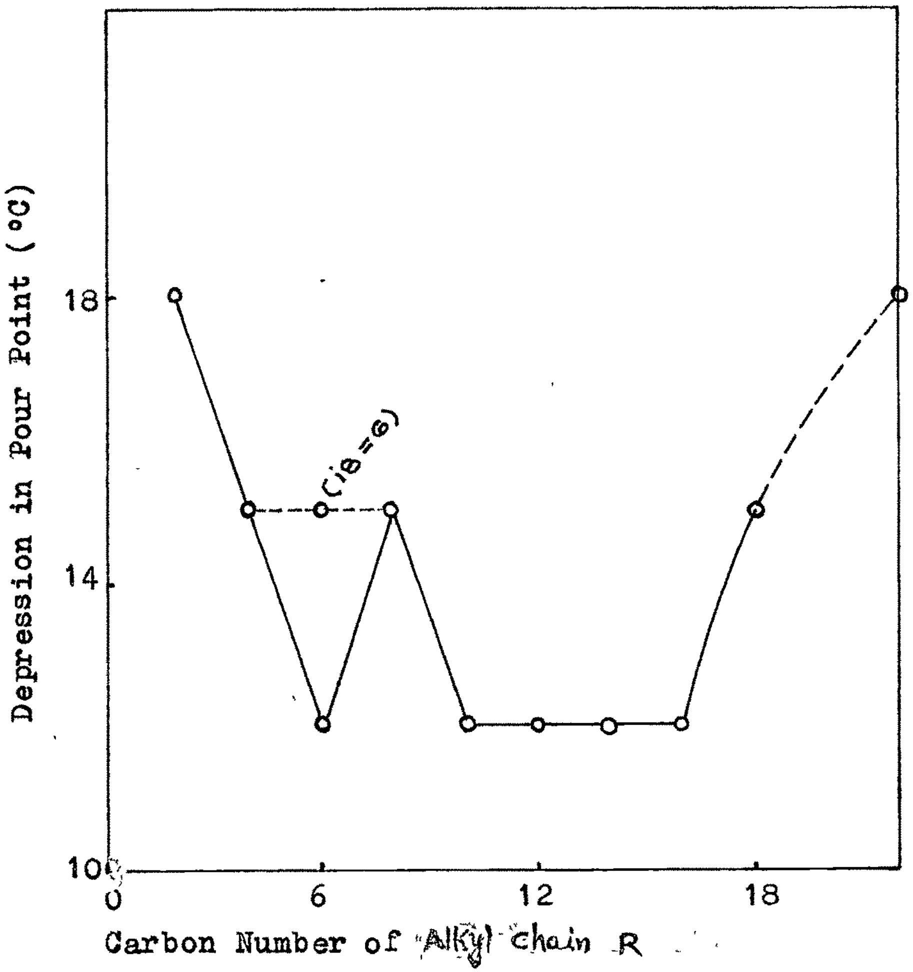


Fig. 27 : n-C_{18} Ester of R-UnMA in Mo Oil vs. Pour Point Depression at 500 ppm Dosage

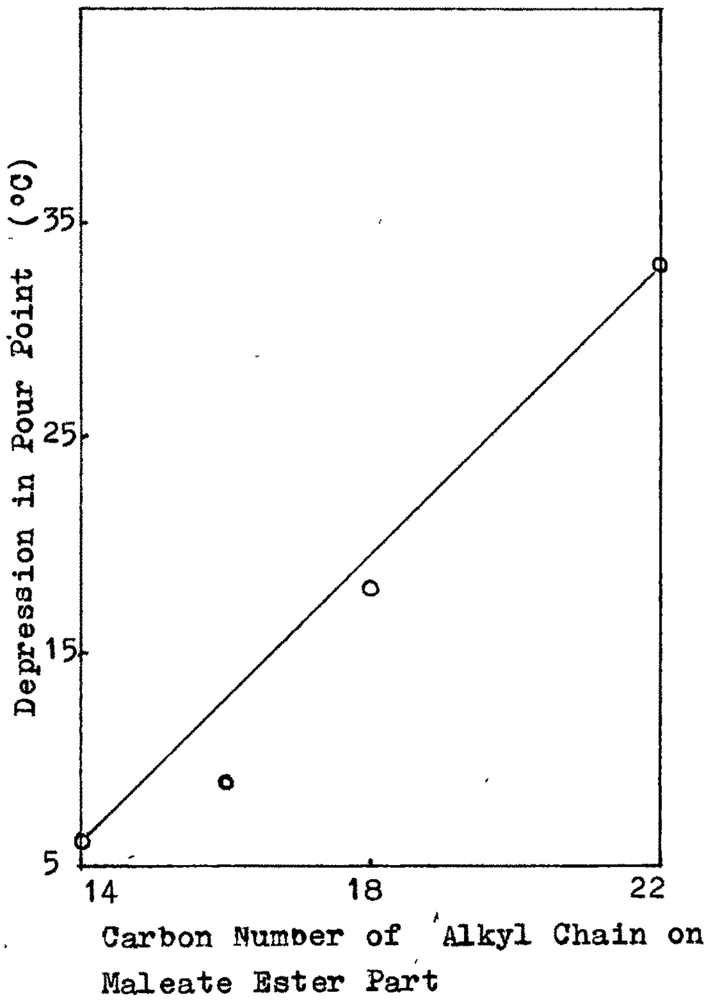


Fig. 28 : Poly(Docosyl Undecylenate-co-Dialkyl Maleate) at 500 ppm in Mo Oil vs. Pour Point Depression

From among this class of polymeric substances, all have been checked as possible additives for pour point depression, however, the results of 44 of them are recorded in Table 46, 48, 50. Since other results were not much encouraging.

Here again, the effect of BH crude is discussed first. The 22-22 CMA compound shows pour depression activity with 100 ppm concentration though it is much less as compared to its counter part 22-22 UnMA of the class I polymeric additives. The pour depression effect is increased as ppm concentration of the additive is increased. Pour depression with 100 ppm is 21°C, this rises to 21°C, 24°C, 27° and 30°C as the concentration is raised to 200, 300, 400 and 500 ppm respectively. The maximum effect is with the maximum concentration of the additive. The next compound in the series is 18-22 CMA, where the two pendant alkyl chains are shortened by 4 carbon atoms each, its pour depression activity on BH crude oil, surprisingly is slightly more as compared to the 22-22 CMA member of the series. The pour depression as shown is 18°, 24° and 24°C for 300, 400 and 500 ppm concentration of the additive.

With higher concentration of course, the activity is a little bit still higher. The third compound in the series is 16-22 CMA ; the alkyl chain lengths are further shortened by 2 carbon each. The overall activity is decreased with the shortened chains, however, with a very high concentration of 1000 ppm, the pour depression is of 18° a depression achieved by just 300 ppm concentration of the previous compound. However, the decreased effect in pour depression is quite discernible with shortening of the chain lengths.

The ' cross sister ' series of polymeric substances of this class, where the alkyl chain length with variation in the cinnamate sector only provides again an interesting behaviour. In Table 101 below are given the pour depressions against the pendant chain lengths, for the BH crude oil. While the extent of depression is quite high in almost all the homologues of this series, the variation in the chain length is not followed for pour depression by any regular pattern-decreasing or increasing, though a sort of alternating behaviour is somewhat manifested, but here too since the difference in the pendant chain length in the first two members is that of 4 carbons, and then the difference in the pendant chain length is of 2 carbons, at last the difference is of one carbon.

Table 101

Pour Depression °C for BH crude oil at 500 ppm concentration

22-22 CMA	18 CMA	16 CMA	14 CMA	12 CMA	10 CMA
30°	27°	21°	24°	24°	18°

8 CMA	6 CMA	4 CMA	2 CMA	1 CMA
21°	18°	18°	21°	18°

From Tables 46, 48 and 50, it should also, however, be noted that the extent of pour depression is quite high with as less as 200 ppm concentration as well when the alkyl chain length is sufficiently good. Fig. 29(a) and (b) shows the plot of the alkyl chain length Vs. pour depression for the BH crude oil at 500 ppm and 300 ppm concentration of the additive. The highest depression of 30°C is found with 22 carbons ; the medium effect is at 12 and 14 carbons, the less effect is at 1, 2, 4, 6, 8 and 10 carbons. At 300 ppm

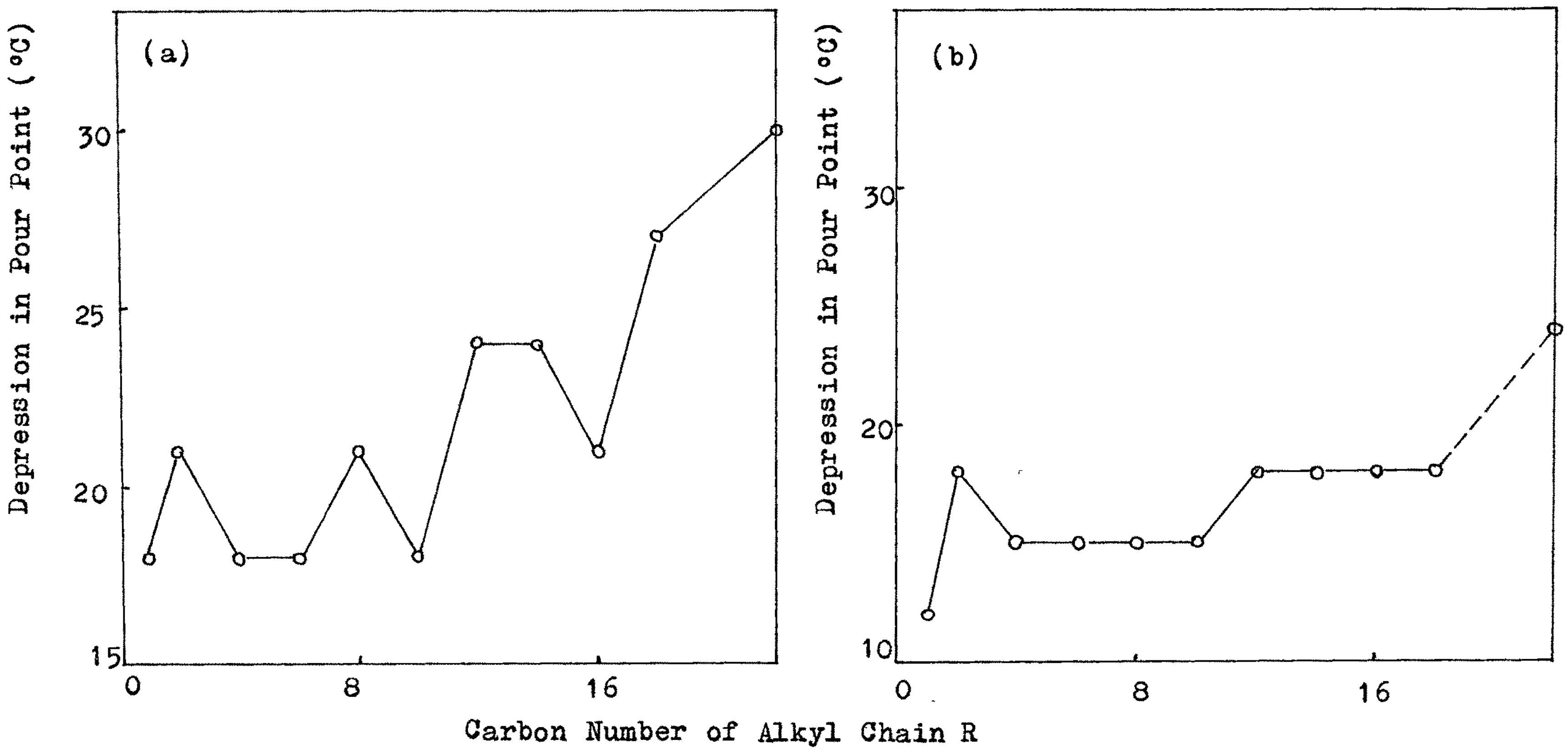


Fig. 29 : n-C_{22} Esters of R-CMA vs. Depression in Pour Point (°C) in BH Oil
(a) at 500 ppm (b) at 300 ppm

concentration of the additive, the highest effect is of 24° at 22 carbon, the medium effect is of 18° and 15° at 18, 16, 14, 12 and 10, 8, 6, 4 carbons respectively. It is surprising to find that with as short a chain length as 2 carbons, the pour depression is of 18°C.

The basic polymer unit of this class of polymeric derivatives has all plus points, theoretically at least, to exhibit maximum pour depression. It possesses not only three pendent chains like the previous class, it has also an aromatic unit attached to the polymer backbone chain. The aromatic unit should be adding to the pour depression effect as a matter of fact, due to adsorption both during and after crystallization. Yet, when the $22\text{-}\underset{\downarrow}{\underline{22}}$ UnMA and $22\text{-}\underset{\downarrow}{\underline{22}}$ CMA additives are compared, at least the first five in the decreasing sequence of chain length, they manifest an interesting deviation from the expected behaviour. The data as recorded in Table 102 is self revealing.

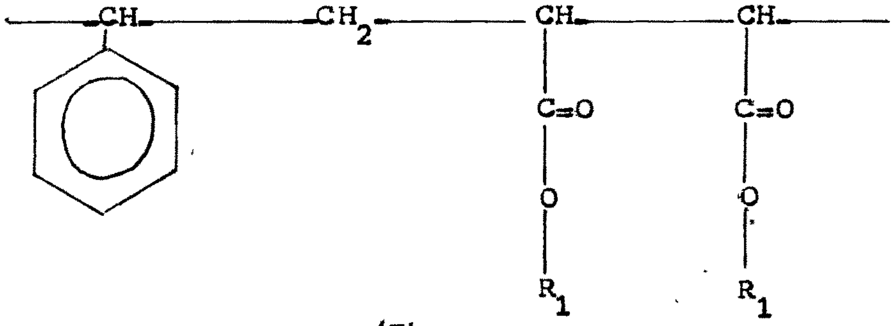
Table 102

Comparative statement of Pour Depression °C BH Crude Oil : 500 ppm concentration of the additive

	22-22	22-18	22-16	22-14	22-12
UnMA	30°	30°	30°	27°	27°
CMA	30°	27°	21°	24°	24°

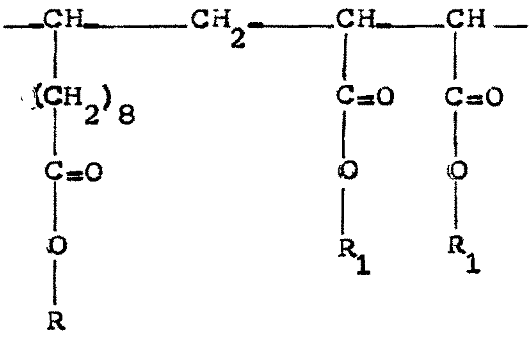
	22-10	22-8	22-18	22-6	22-4	22-2
UnMA	30°	24°	30°	24	30	30
CMA	18°	21°	-	18°	18°	21°

The overall pour depression effect is more in the UnMA series than the CMA series though that at 22-22, 22-18, 22-14 and 22-12 carbons the effect in both series is either equal or almost equal. As mentioned above, the high expectation was in the case of CMA series as compared to the UnMA. The structural difference between these two basic polymer unit is that of an aromatic ring present in the cinnamate sector (III). Polymeric unit such as 22 ester of styrene maleic anhydride copolymer (I) has been reported to be quite effective in pour depression in the case of a sufficiently waxy

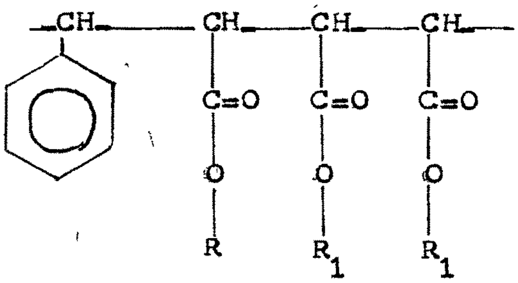


(I)

crude oil (223-225) and the evidence, as discussed a little earlier, coming forth from this investigation, again for a sufficiently waxy crude oil, for a basic polymer unit as represented by 22-22 UnMA (II) provides a good pour depression activity.



(II)



(III)

By comparing the three polymer basic units in question, the most apparent thing that strikes the right note in this case is the intervening alkyl chain. It is seen that when the aromatic ring is present as a ' pendant chain ' at a distance of one carbon atom from the other two chains, or a pendant chain replaces the aromatic unit maintaining the same distance from the other two pendant chains, besides the individual homopolymeric units represented in the copolymers, pour depression activity is quite pronounced (453). But, as is the case, in a copolymer of two homopolymer basic units when three pendant chains and an aromatic unit are positioned side by side without leaving any distance, the pour depression activity is hampered to some extent despite all the four pendant units being individually conducive to pour depression phenomenon. While this fact is quite apparent, other factors such as molecular weight of polymers cannot be ruled out from a consideration of a possible contribution to the effect.

A plot of the pour depression of the $\underset{\downarrow}{\underline{22}}$-22 CMA homologues versus the number of carbon atoms of the alkyl chains in the ' maleic ' sector of the basic polymer unit yields Fig. 30 and 31 in BH and Na crude oil respectively. The highest effect of pour depression is at C_{22} carbon, then the effect decreases upto C_{14} carbon.

The effectivity of the additives synthesized in this investigation besides the pendant alkyl chain lengths, has a relationship with low asphaltene and resin content - a view so formed because of the results of the previous class of the ester-polymers ; almost a parallel behaviour is exhibited by this class II ester-polymers. Their effectivity on the Bombay High crude oil is quite admirable, but when they are tested for the other four crude oils, the effectivity seems to be going down as the asphaltene and resin content increases but to a limit. Nahorkatia (Na) crude oil which has the lowest asphaltene and resin content amongst the ' medium ' asphaltene and resin containing group of the crude oils selected for the study, but whose asphaltene and resin content is higher than that of the BH crude oil, shows quite a good pour depression with a number of the homologues of the CMA series of ester-polymers. However the effect is limited to a small number of the homologues. Fig. 32 and 33. The plot is of nC_{22} ester of R-CMA Vs. pour point depression.at 500 and 300 ppm in Na and Mo crude oil. In this plot the highest effect of pour depression is

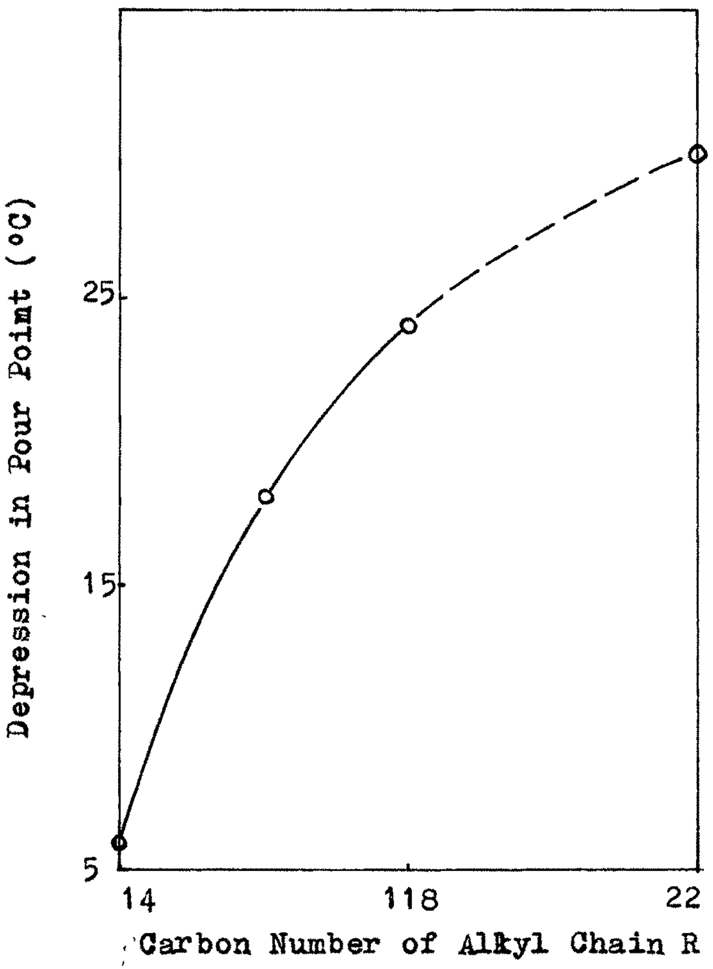


Fig. 30 : n- Alkyl Esters of 22-CMA in BH Oil at 500 ppm vs. Pour Point Depression

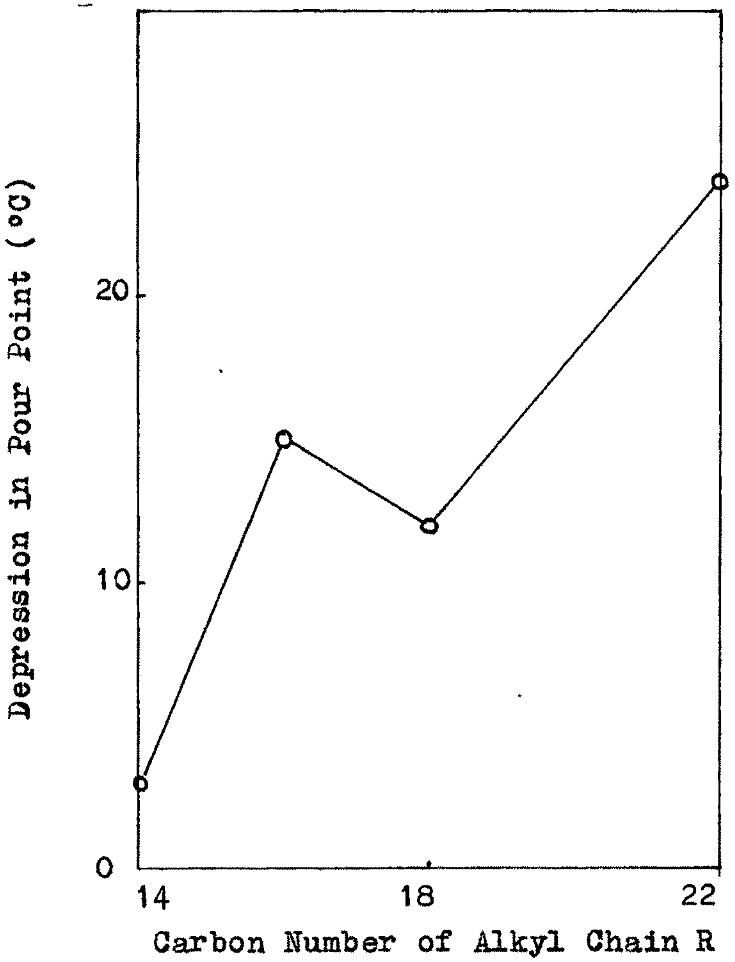


Fig. 31 : n- Alkyl Esters of 22-CMA in Na Oil at 500 ppm vs. Pour Point Depression

at C_{16}, C_{14} and C_{12} carbon of 27°C. The lowest effect of pour depression is at C_{10}, C_8, C_6, C_4, C_2 carbon of 18°C. At 300 ppm concentration of additive the pour point depression at highest level is at C_{16}, C_{14} and C_{12} carbon of 21°C, and less effect of pour depression is at C_6, C_4 and C_2 carbon of 12°C.

Table 103

Extent of Pour Depression °C Na Crude Oil - 500 ppm additive

22 ester	-22 CMA	-18CMA	-16 CMA	-14CMA	-12CMA	-10 CMA
	24°	24°	27°	27°	27°	18°

22 ester	-8 CMA	-6CMA	-4 CMA	- 2 CMA	-1 CMA
	18°	18°	18°	18°	12°

18 ester	-22 CMA	-18 CMA	-16 CMA	-14 CMA	-12 CMA	-10 CMA
	12°	3°	3°	3°	3°	0°

18 ester	-8 CMA	- 6CMA	-4 CMA	-2 CMA	-1 CMA
	0°	0°	0°	3°	0°

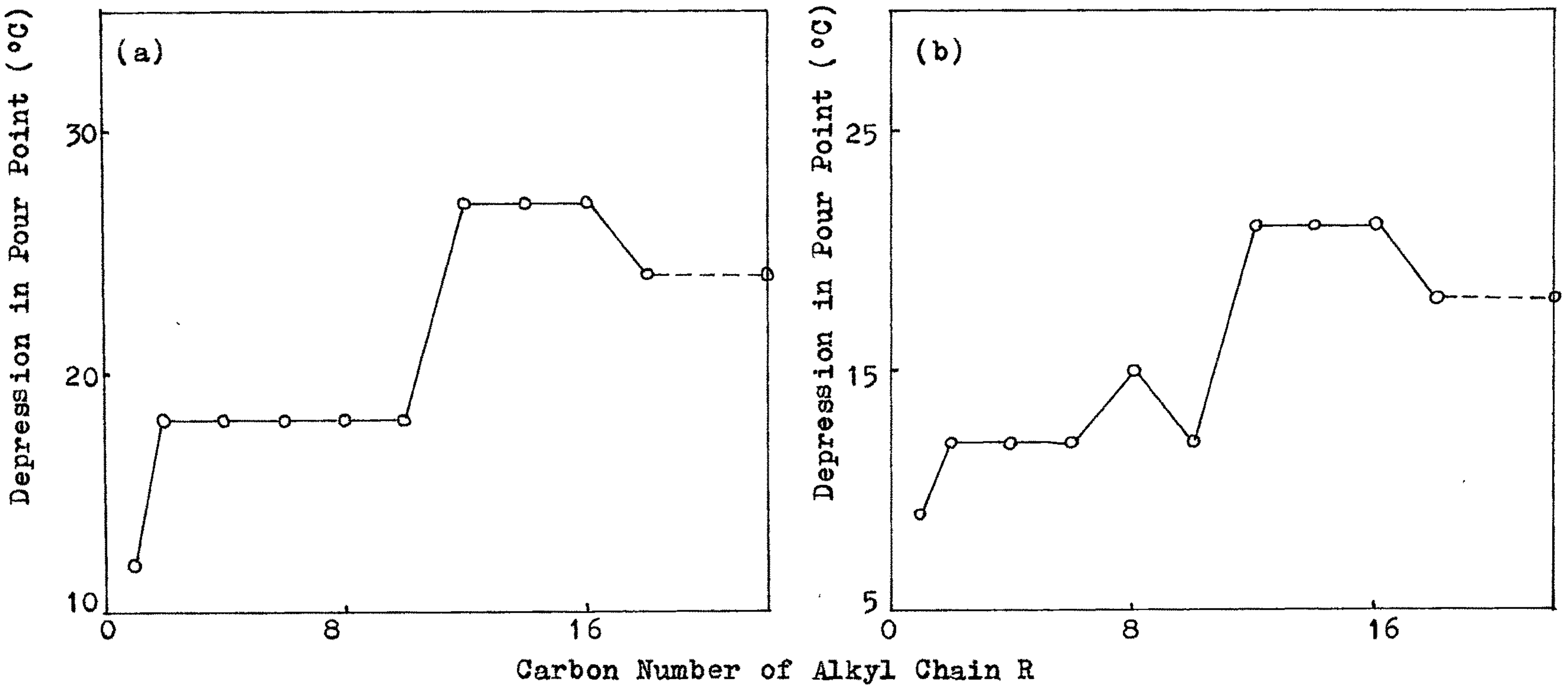


Fig. 32 : n-C_{22} Esters of R-CMA vs. Depression in Pour Point (°C) in Na Oil
(a) at 500 ppm (b) at 300 ppm

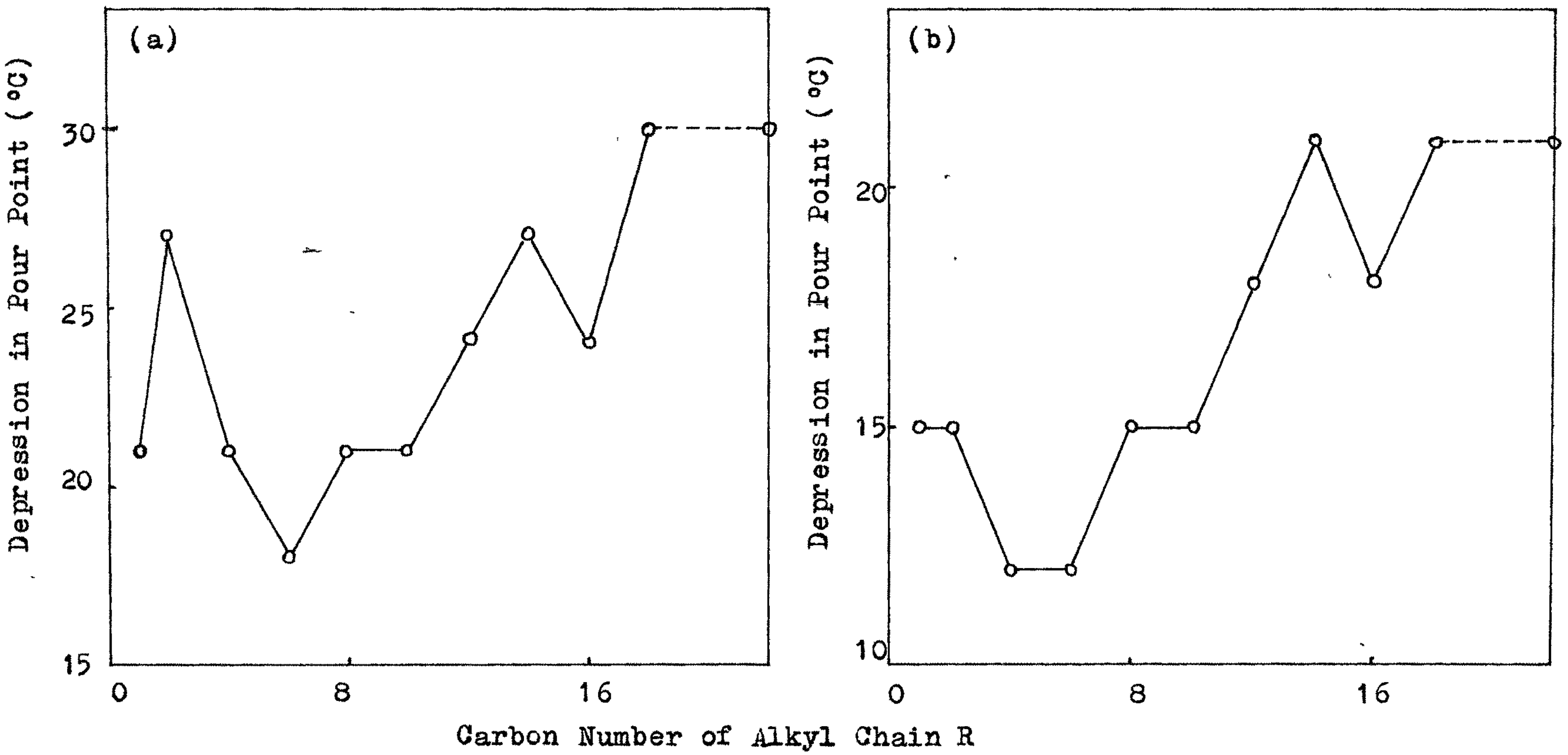


Fig. 33 : n-C_{22} Esters of R-CMA vs. Depression in Pour Point (°C) in Mo oil
(a) at 500 ppm (b) at 300 ppm

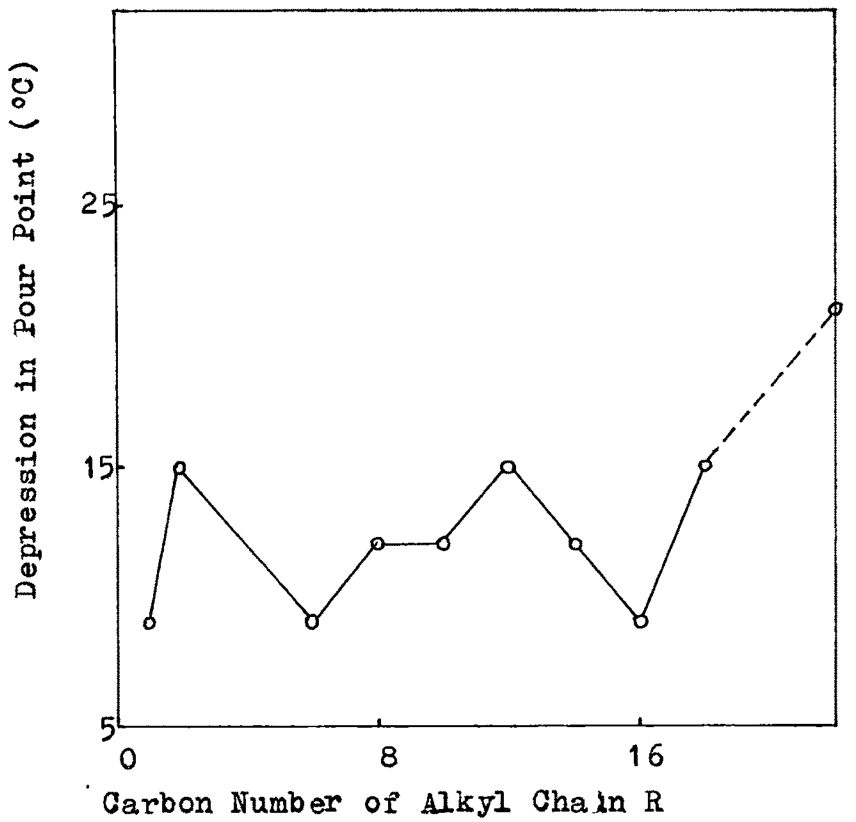


Fig. 34 : n-C$_{18}$ Ester of R-CMA vs. Depression in Pour Point (°C) in Mo Oil at 500 ppm

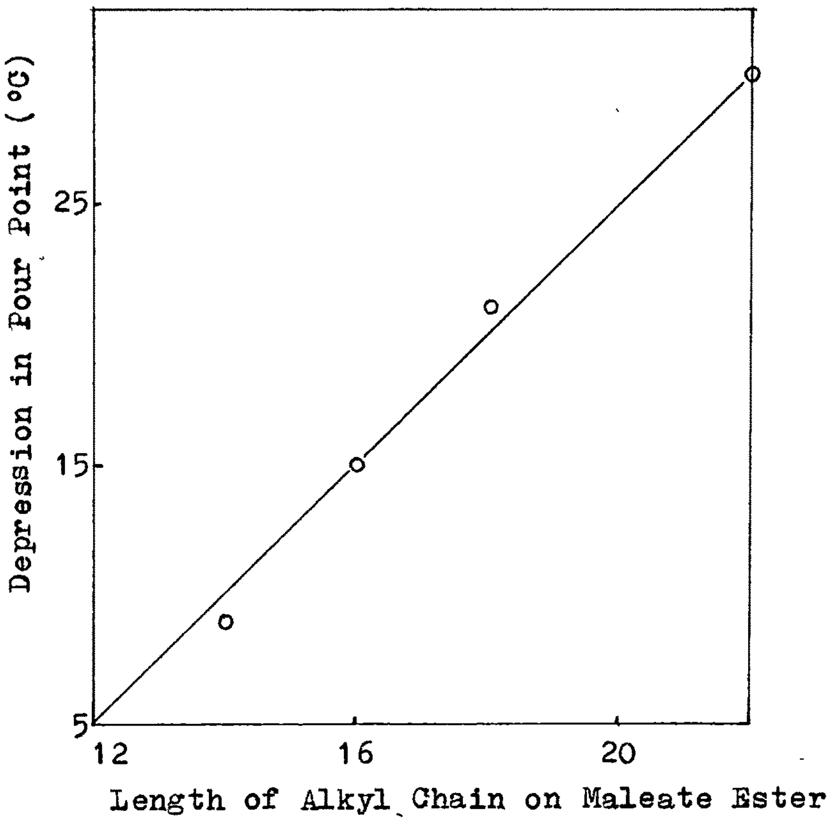


Fig. 35 :Poly(Docosyl-Cinnamate-co-Dialkyl Maleate) vs. Depression in Pour Point (°C) in Mo Oil at 500 ppm

Table 104

Extent of Pour Depression at 500 ppm °c in

Na crude oil.

22-22 CMA	18-22 CMA	16-22 CMA	14-22 CMA
24°	12°	15°	3°

From Table 103 and 104, the veracity of the view could be easily established ; about 21 homologues with varying alkyl chain lengths are found to be effective of course the effectivity is also varying with the increase or decrease in the pendant alkyl chain lengths.

Table 106

Extent of Pour Point Depression at 500 ppm

in Moran Crude Oil

22-22 CMA	18-22 CMA	16-22 CMA	14-CMA
30°	21°	15°	12°

Table 105

Pour Depression °C of 22 esters of R-CMA

500 ppm additive in Moran Crude Oil

22 ester	-22 CMA	-18 CMA	-16 CMA	-14 CMA	-12 CMA	-10 CMA
	30°	30°	24°	27°	24°	21°

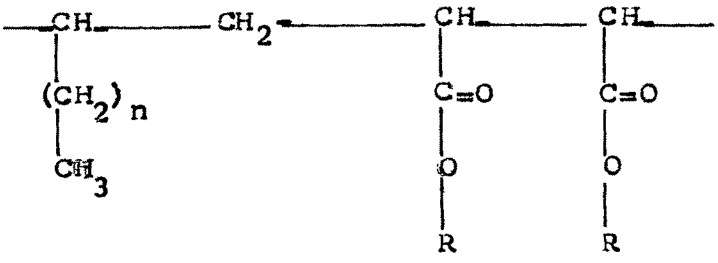
22 ester	-8 CMA	-6 CMA	-4 CMA	-2 CMA	-1 CMA
	21°	18°	21°	27°	21°

18 ester	-22 CMA	-18 CMA	-16 CMA	-14 CMA	-12 CMA	-10 CMA
	21°	15°	9°	12°	15°	12°

18 ester	- 8CMA	-6 CMA	-4 CMA	-2 CMA	-1 CMA
	12°	9°	12°	15°	9°

The data given in Tables 105 and 106 clearly indicate the good effect of the various homologues of the cinnamate ester-polymer series (class II) additives, on pour depression of Moran crude oil at 500 ppm concentration.

The class III of the additives newly synthesized under this investigation differ from those of the class I in one vital respect and that is the pendant alkyl chain belonging to the α-olefin sector of the basic polymer unit in the class III series, is directly attached to the polymer backbone carbon, without the $-(CH_2)_8COO-$ group as an interlinking unit as in the case for the class I additives at the undecylenic ester sector (Fig. 36). The absence of the interlinking unit $-(CH_2)_8COO-$ decreases the pendant alkyl chain to that extent in an overall manner. This being the only structural difference in the basic polymer units of the two classes I and III, a direct comparison can be more fruitful.



$$-CH(-(CH_2)_n-CH_3)-CH_2-CH(-C(=O)-O-R)-CH(-C(=O)-O-R)-$$

Fig. 36

Table 107

Pour point depression of nC_{22} esters of poly(alpha olefin-Co-maleic anhydride) at 500 ppm, °C.

22 Ester of	Crude oils				
	BH	Na	Mo	NK	Am
PA-15(1)	30°	24°	30°	18°	6°
PA-15(2)	30°	24°	30°	-	-
PA-21(1)	24°	21°	30°	18°	6°
PA-21(2)	27°	24°	30°	-	-

In Table 107 is recorded the extent of pour depression for all the five crude oils under consideration. It is a observed that when the alkyl chains in the ' maleic ' sector of the basic polymer unit are with the length of 22 carbons, the extent of depression is quite good. The BH crude treated with PA-15(1), (2) and PA-21(1), (2) has a pour point reduced to 0° and 3° respectively at 500 ppm concentration i.e. the extent of pour depression at 500 ppm is of 30° and 27° respectively. The effect of this additive on other crudes i.e. Na, Mo NK and Am at 500 ppm concentration is certainly not that high as in the case of BH crude ; this fact again is a pointer to the role of the low, medium and high asphaltene and resin contents indicating thereby some kind of relationship between the extent of asphaltene and resin content and the nature of the basic polymer units under consideration with respect to the pour depression activity.

Table 108

Pour point depression nC_{18} esters of poly(alpha olefin-Co-maleic anhydride) at 500 ppm, °C.

nC_{18} Ester of	Crude oils		
	BH	Na	Mo
PA-15(1)	3^o	0^o	12^o
PA-15(2)	3^o	3^o	12^o
PA-21(1)	3^o	0^o	12^o
PA-21(2)	3^o	0^o	9^o

Table 109

Pour point depression nC_{16} esters of poly (alpha olefin-co-maleic anhydride) at 500 ppm °C

nC_{16} Ester of	Crude oils		
	BH	Na	Mo
PA-15(1)	3°	0°	3°
PA-15(2)	0°	0°	0°
PA-21(1)	0°	0°	3°
PA-21(2)	0°	0°	3°

The n C_{18} and nC_{16} esters of PA-15 (1), (2) and PA-21(1), (2) are less effective as pour depressants. The data given in Table 108 and 109.

Table 110

Comparison of pour point depression of nC_{22} esters of 22 UnMA, 22 CMA, PA-15 and PA-21 at 500 ppm °C

Ester	Crude oils		
	BH	Na	Mo
22-22 UnMA	30°	30°	33°
22-22 CMA	30°	24°	30°
22-PA 15	30°	24°	30°
22-PA 21	27°	21°	30°

An interesting view emerges from a comparative study of the pour depressing activity of the better homologues of all the three classes examined as additives. In Table 110 are given the extent of pour depressions for 22-22 UnMA (class I), 22-22 CMA (class II), 22-PA 15, and 22-PA 21 (class III). From the data it is observed that the effect of pour depression is good and having the similar effect of pour depression in each crude oil i.e. in BH, Na and Mo crude oils. The 22-22 UnMA and 22-PA are quite comparable structurally in the sense that both have three pendent alkyl chains and that there is a ' pace ' worth one carbon atom in the polymer back bone chain between the undecylenic ester part chain or alpha olefin part chain and the two pendant chains at the maleate segment of the basic polymer unit. While the presence of three pendant chains is to be viewed as significant from the point of view of their good pour depressing activity, the ' pace ' should be taken as an important factor from the ' hindrance ' point of view, since the 22-22 CMA compound has an alkyl chain at the cinnamate sector but quite adjacent to the chains of the maleate part and this very fact seems to have a retarding effect in the pour depressing activity. The effect of pour depressant is fruitful.

Pour depression versus n-C_{22} ester of poly(alpha-olefin-co-maleic anhydride) of the basic polymer unit are plotted in Fig. 37, 38 and 39. Fig. 37 for BH crude oil at 500 ppm concentration, Fig. 38 for Nahorkatia crude at 500 ppm concentration and Fig. 39 for Mo crude oil at 500 ppm concentration. The plot for BH crude oil shows a pour depression of 30°C at PA-15(1) and (2), and that of 27°C, 24°C at PA-21(1), (2) respectively. The highest effect of pour depression is at PA-15, while the lowest effect of pour depression is at PA-21. The plot for Nahorkatia crude oil shows a pour depression of 24°C at PA-15(1), (2) and PA-21(2) i.e. the plot runs parallel to the alpha olefin alkyl chain axis. The lowest effect of pour depression of 21°C at PA-21(1). The plot for Mo crude oil shows a pour depression of 30°C at PA-15 and PA-21 i.e. the plot runs parallel to the alkyl chain axis.

Under the fourth and fifth category of the polymeric derivatives only seven compounds of each category are synthesized ; these vary only in parts, in a definite manner - the variation being in a sequence. The idea is to find out the variations in their effectivity as additives (pour point depressants) against the small changes in their molecular structure and to assess the overall utility.

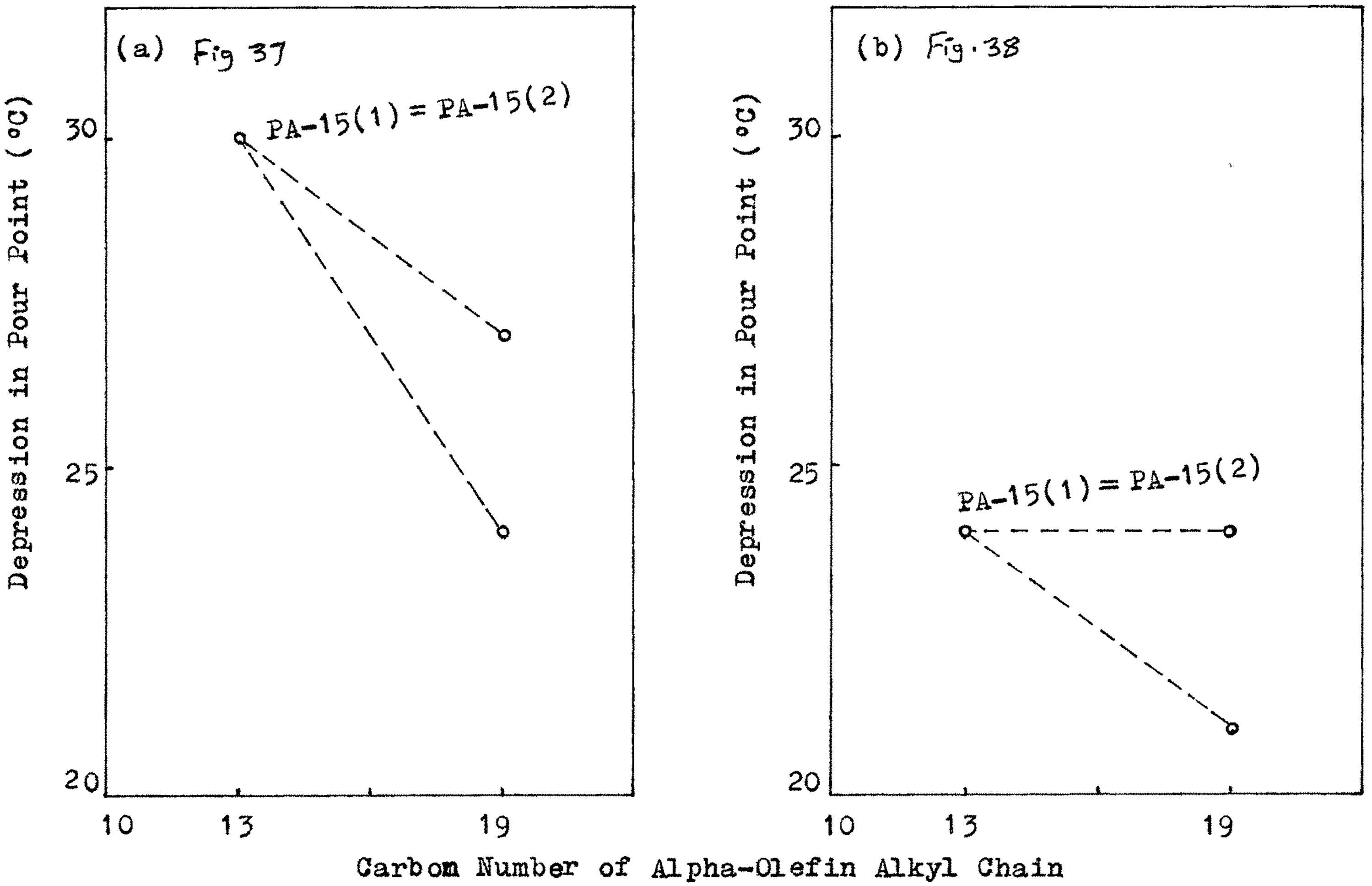


Fig. 37 : n-C_{22} Esters of Poly(Alpha-Olefin -co- Maleic Anhydride vs.
& 38 Depression in Pour Point at 500 ppm
(a) in BH Oil & (b) in Na Oil

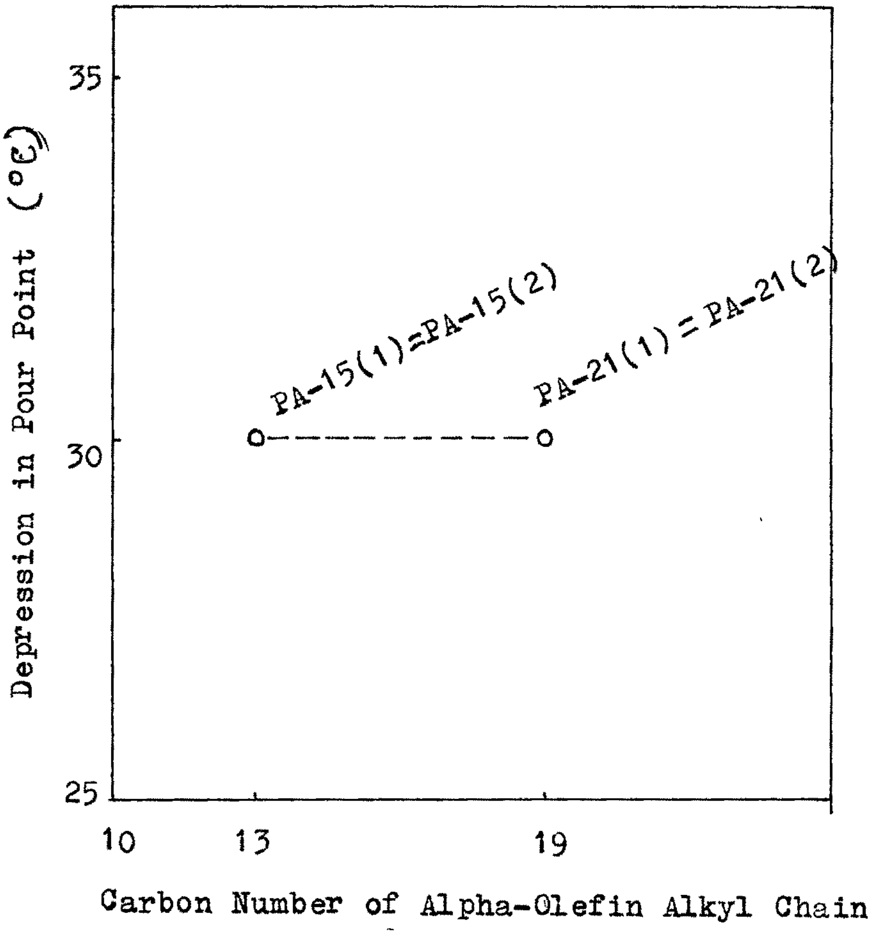


Fig. 39 : n-C_{22} Esters of Poly(Alpha-Olefin -co-Maleic Anhydride) in Mo Oil at 500 ppm vs. Depression in Pour Point

In these seven compounds of each class, the two pendant alkyl chains at the maleate sector of the basic polymer unit are the same and have the same chain length. Even the polymer backbone chain can be said to be the same in all these compounds except in the PDBM (poly dibehenyl maleate) and PDODM (poly dioctadecyl maleate) derivatives where the basic polymer unit will have only two carbons in the its back bone chain. The third pendant chain belonging to the co-monomer sector may be taken as ' chains ' in the case of DBM-VAc and DBM-MMA only because of the presence of an alkyl group and a methyl ester group respectively in these compounds. In the other four compounds viz., DBM-AA, DBM-IA, DBM-MA and DBM-AN, the attached part in the co-monomer sector are 'groups' only while in the seventh compound the comonomer sector itself is absent. Same description for DODM series.

Table 111

Depression in pour point at 500 ppm concentration -$^{\circ}C$

Additive	Crude oils				
	BH	Na	Mo	NK	Am
DBM-VAc	24°	21°	27°	18°	6°
DBM-MMA	21°	18°	24°	-	-
DBM-AA	24°	24°	24°	-	-
DBM-MA	24°	24°	27°	-	-
DBM-IA	27°	27°	27°	-	-
DBM-AN	21°	21°	27°	-	-
Poly DBM	24°	27°	27°	-	-

Taking the best additive action first into consideration the polymer DBM-IA (poly dibehenyl maleate-co-itaconic anhydride) which is the fifth compound of this class it shows the effect of pour depression maximum out of this class. The effectivity of pour depression in BH crude is $27^{\circ}C$, in Na crude is $27^{\circ}C$ and in Mo crude is $27^{\circ}C$. In Mo crude it shows the 100% depression. (Table 111). The two dimensional wax crystals are reduced to the three dimensional fine crystal size particles due to the penetration activity of the pendant chains of the additive compound into the waxy part followed by cocrystallization and subsequent loss of the interconnecting linking system responsible for giving rise to a jelly formation. The additive action for the proportionally higher asphaltene and resin bearing crudes viz; NK and Am is not mentioned in the Table 111 because these polymer additives are less effective for pour depressing properties.

The extent of pour depression by the compound DBM-VAc is quite impressive at 500 ppm concentration. It is a copolymer with only two pendant alkyl chains per basic polymer unit. The next copolymer of this class i.e. DBM-MMA is quite similar to this compound, with the small difference at the comonomer sector there being one more methyl group attached to the fourth carbon of the basic polymer unit and a slight difference in the pattern of linking of the O atom there at in the case of the copolymer DBM-MMA. With such a small difference, the pour depression activity of this compound is quite reduced of that of the compound DBM-VAc.

On copolymerization of the DBM with MA and IA the extent of pour depression in BH, Na and Mo crude is good. The reduction in the extent of pour depression thus has to be directly linked with the copolymerized unit i.e. maleic anhydride and itaconic anhydride. The extent of pour depression by the compound DBM-AA is quite good. The carboxyl group attached at the comonomer sector, as a part of the acrylic group is not a pendant chain and therefore does not participate in the cocrystallization forces besides the fact that the third carbon atom of the polymer backbone of the basic polymer unit is without any attached ' group ' or ' pendant chain '.

The extent of pour depression by the compound DBM_AN in BH and Na crude is less as campare to other compound. But the effectivity in Mo crude is fruitful. The effect of pour depression by the compound Poly DBM in BH, Na and Mo crude is good.

Table 112

Depression in pour point at 500 ppm concentration -°C

Additive	Crude oils				
	BH	Na	Mo	Nk	Am
DODM_VAc	21°	18°	21°	18°	6°
DODM_MMA	18°	18°	18°	-	-
DODM_AA	18°	18°	21°	-	-
DODM_MA	21°	21°	21°	-	-
DODM_IA	24°	24°	21°	-	-
DODM_AN	18°	18°	21°	-	-
Poly DODM	24°	21°	27°	-	-

From the Table 112 the best additive action first into consideration the polymer DODM-IA (poly dioctadecyl maleate-co-itaconic anhydride) which is the fifth compound of this class, which shows the effect of pour depression maximum out of this class V. The extent of pour depression in BH, Na and Mo crude for this compound is 24°, 24° and 21°C respectively. The less effective additive of this class is DODM-MMA, it shows the extent of pour depression in BH, Na and Mo crude oil as 18°, 18° and 18° respectively. The remaining five compound of this class shows the quite good effectivity for pour depression. This class is less effective for NK and Am crude, so the results are not mentioned in the Table 112. Only the additive DODM-VAc tested with NK and Am crude, it shows the effectivity of pour depression 9°C.

So far the discussion about the class IV and V additives has been confined to the BH, Na and Mo oils only in a way. By and large, these additives are less effective relatively in the case of the rest of the oils i.e. NK and Am oils. Fig. 40 to 43.

The extent of pour depression at various ppm concentration for BH, Na and Mo oils are given in Tables 113, 114.

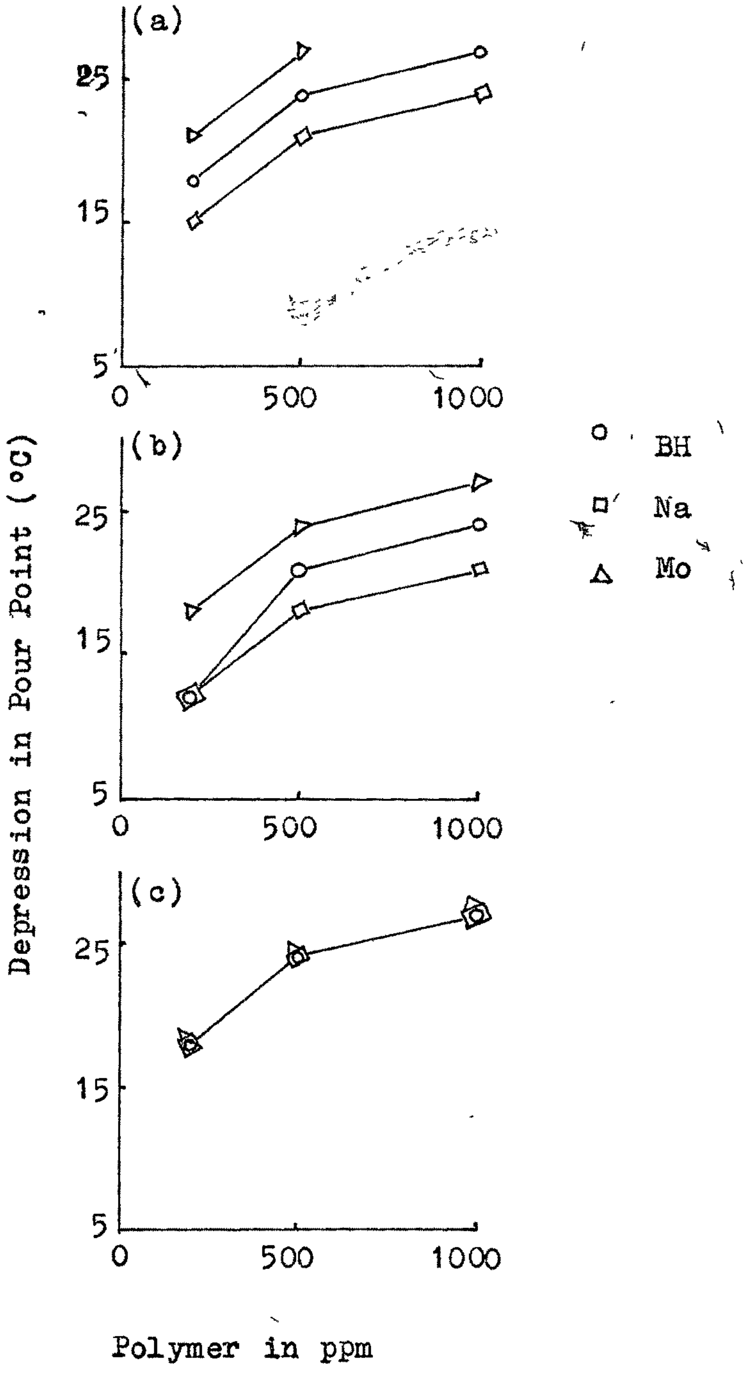


Fig. 40 : Depression in Pour Point (°C) vs. Polymer in ppm for (a) DBM-VAc (b) DBM-MMA (c) DBM-AA

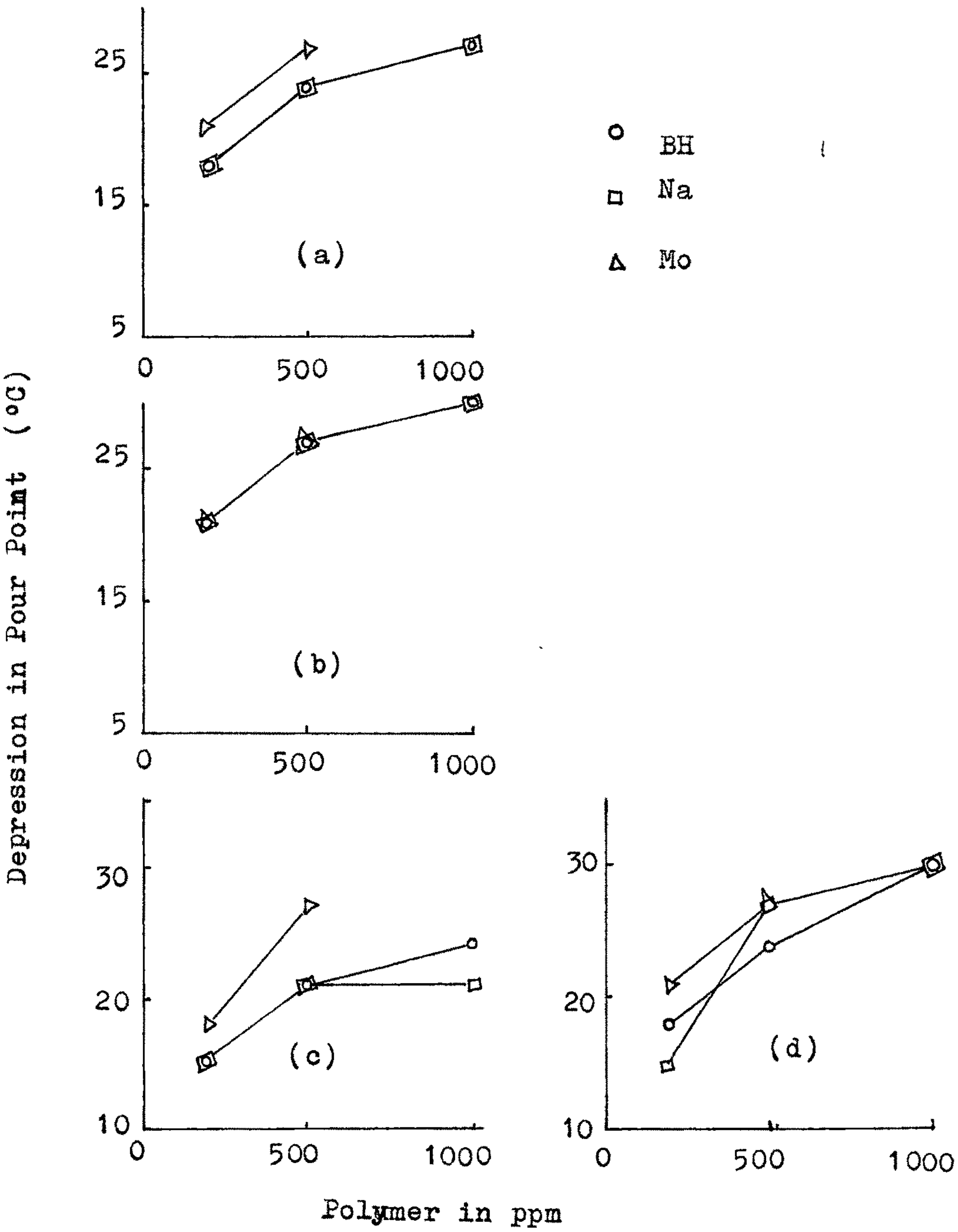


Fig. 41 : Depression in Pour Point (°C) vs. Polymer in ppm for (a) DBM-MA (b) DBM-IA (c) DBM-AN (d) Poly(DBM)

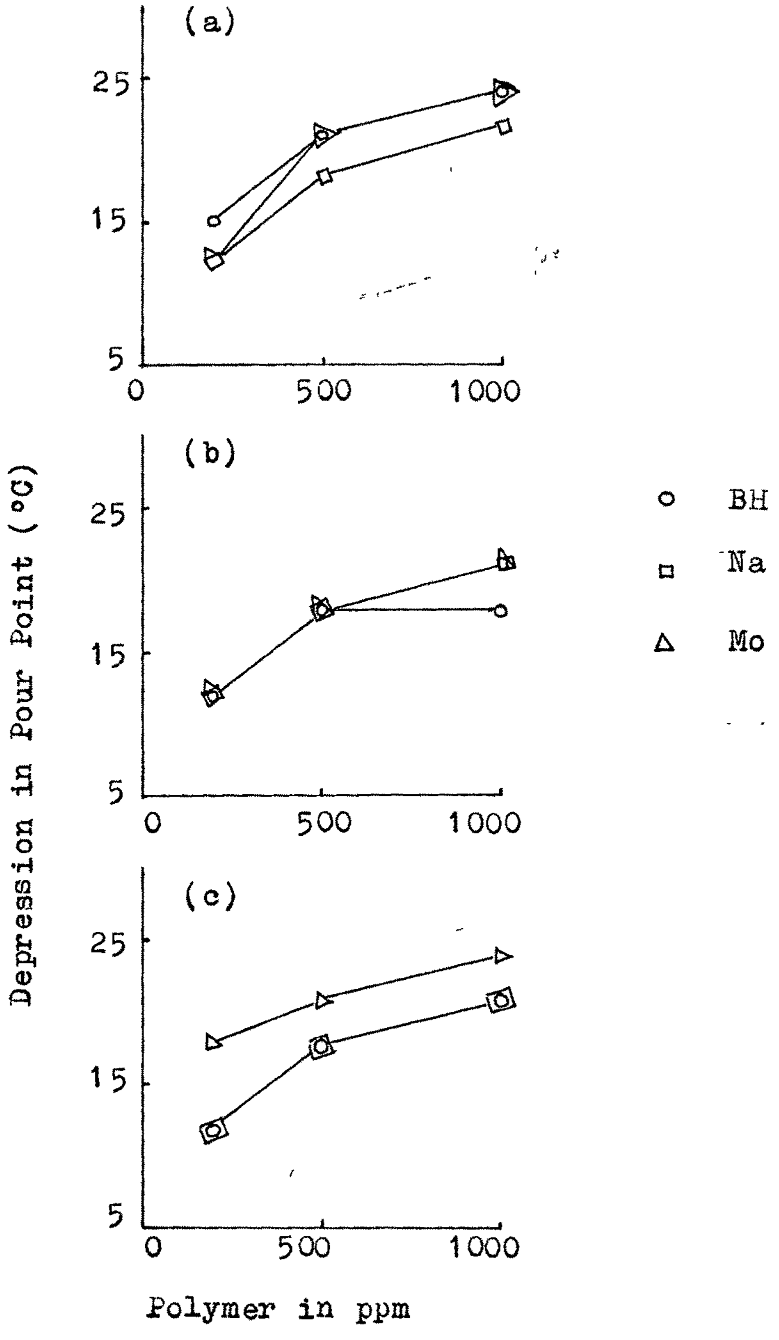


Fig. 42 : Depression in Pour Point (°C) vs. Polymer in ppm for (a) DODM-VAc (b) DODM-MMA (c) DODM-AA

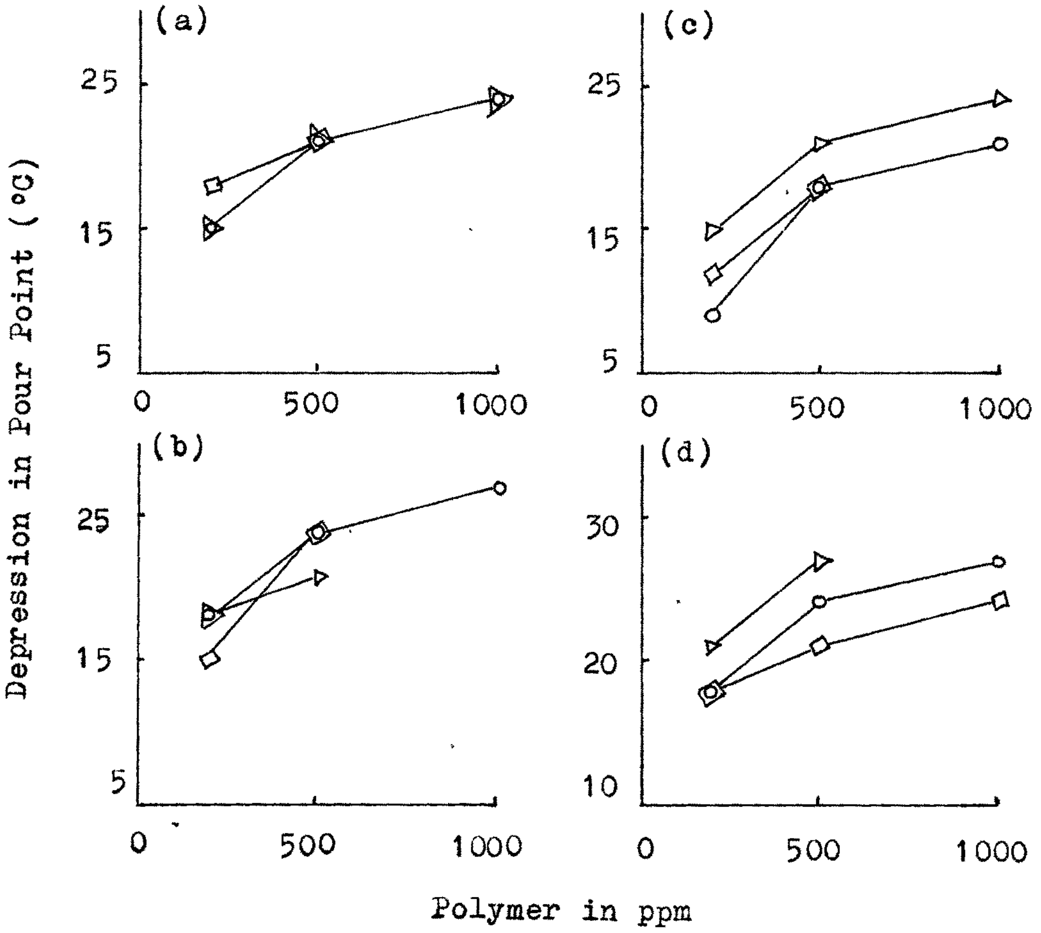


Fig. 43 : Depression in Pour Point (°C) vs. Polymer in ppm for (a) DODM-MA (b) DODM-IA (c) DODM-AN (d) Poly(DODM)

⊙ BH ⊡ Na ◬ Mo

Table 113

Extent of pour depression : BH oil, -°C and Na oil -°C

	Additive Code	BH oil				Na oil			
		100	200	300	500	100	200	300	500
1.	22-2 UnMA	21	24	24	30	15	21	24	30
2.	22-4 UnMA	21	24	27	30	12	12	18	24
3.	22-6 UnMA	9	15	15	24	6	6	9	24
4.	22-8 UnMA	9	9	15	24	6	9	15	18
5.	22-18 UnMA	18	21	27	30	6	18	24	27
6.	22-10 UnMA	18	21	24	30	9	15	18	24
7.	22-12 UnMA	18	21	24	27	9	15	18	21
8.	22-14 UnMA	18	18	21	27	15	15	18	21
9.	22-16 UnMA	21	24	27	30	15	18	18	24

cont....

Table 113 cont....

10.	22-18 UnMA	21	24	27	30	18	18	21	24
11.	22-22 UnMA	24	27	27	30	18	21	21	30
12.	22-2 CMA	15	18	18	21	9	12	12	18
13.	22-4 CMA	12	15	15	18	6	6	12	18
14.	22-6 CMA	12	12	15	18	6	12	12	18
15.	22-8 CMA	15	15	15	21	12	15	15	18
16.	22-10 CMA	12	12	15	18	12	15	18	18
17.	22-12 CMA	12	12	18	24	18	18	21	27
18.	22-14 CMA	12	15	18	24	15	18	21	27
19.	22-16 CMA	12	15	18	21	18	18	21	27
20.	22-18 CMA	12	15	18	24	12	15	18	24
21.	22-22 CMA	21	21	24	30	15	18	18	24
22.	22-PA 15(1)	21	24	27	30	12	15	18	24

cont....

Table 113 cont...

23.	22-PA 15(2)	18	21	24	30	15	18	18	24
24.	22-PA 21(1)	15	18	18	24	15	18	18	21
25.	22-PA 21(2)	18	21	24	27	12	15	15	24
26.	DBM_VAc	18	18	21	24	12	15	18	21
27.	DBM_MMA	12	12	15	21	12	12	15	18
28.	DBM_AA	18	18	21	24	15	18	18	24
29.	DBM_MA	15	18	21	24	15	18	21	24
30.	DBM_IA	21	21	24	27	18	21	24	27
31.	DBM_AN	15	15	18	21	12	15	15	21
32.	Poly_DBM	15	18	18	24	15	15	21	27
33.	DODM_VAc	12	15	15	21	9	12	15	18
34.	DODM_MMA	9	12	12	18	9	12	12	18

cont....

Table 113 cont...

35.	DODM_AA	12	12	15	18	9	12	12	18
36.	DODM_MA	12	12	18	21	15	18	18	21
37.	DODM_IA	18	18	21	24	15	15	18	24
38.	DODM_AN	9	9	12	18	9	12	12	18
39.	Poly DODM	18	18	21	24	15	18	18	21

Table 114

Extent of pour depression : Mo oil -°C.

Additive code			Mo oil			
			100	200	300	500
1.	22-2	UnMA	21	24	27	30
2.	22-4	UnMA	18	21	21	30
3.	22-6	UnMA	9	15	15	24
4.	22-8	UnMA	9	12	12	21
5.	22-18	UnMA	6	15	21	27
6.	22-10	UnMA	9	12	15	21
7.	22-12	UnMA	9	9	15	18
8.	22-14	UnMA	9	12	12	18
9.	22-16	UnMA	15	15	18	24
10.	22-18	UnMA	18	18	21	27
11.	22-22	UnMA	18	21	27	33
12.	22-2	CMA	12	15	21	27
13.	22-4	CMA	12	12	15	21
14.	22-6	CMA	9	12	15	18
15.	22-8	CMA	12	15	15	21
16.	22-10	CMA	15	15	18	21
17.	22-12	CMA	15	18	18	24
18.	22-14	CMA	18	21	21	27

cont...

Table 114 cont...

19.	22-16 CMA	15	18	18	24
20.	22-18 CMA	21	21	24	27
21.	22-22 CMA	21	21	24	30
22.	22-PA 15(1)	18	21	21	30
23.	22-PA 15(2)	21	24	27	30
24.	22-PA 21(1)	21	21	24	30
25.	22-PA 21(2)	21	21	27	30
26.	DBM-VAc	18	21	21	27
27.	DBM-MMA	15	18	21	24
28.	DBM-AA	18	18	21	24
29.	DBM-MA	15	21	21	27
30.	DBM-IA	18	21	21	27
31.	DBM-AN	18	18	21	27
32.	Poly DBM	18	21	21	27
33.	DODM-VAc	12	12	18	21
34.	DODM-MMA	9	12	15	18
35.	DODM-AA	15	18	21	21
36.	DODM-MA	15	15	18	21
37.	DODM-IA	15	18	21	21
38.	DODM-AN	15	15	18	21
39.	Poly DODM	18	21	24	27

It is viewed as proper to highlight the additive function of such ester polymers from the lot newly synthesized and studied under this investigation which have, at their 500 ppm concentration exhibited atleast a 50% activity in depressing the pour points of BH, Na and Mo crude oils. About 39 of the additives have shown good activity and their depressions in percent are noted for the BH and Na crudes in Table 115 and for Mo crude in Table 116.

At a glance, the activity is maximum at 500 ppm concentrations. For a 50% and above efficiency in pour depression, as far as BH crude is concerned, there are as many as 25 depressants at 100 ppm concentration, 31 at 200 ppm, 37 at 300 ppm and 39 at 500 ppm concentration. The BH crude has a wax content of typical nature, besides it has the least asphaltene content. However, the study has thrown good light on pour depression efficiency. As far as Na crude concerned, the picture is as like, for 50% and above efficiency in pour depression, there are 18 depressants at 100 ppm concentration, 28 at 200 ppm, 32 at 300 ppm, and 39 at 500 ppm concentration.

At 500 ppm, those which give a 100% pour depression efficiency are 10 for BH crude. There are about other 16 of them giving 80-90 percent efficiency at 500 ppm. At 500 ppm concentration which give a 100% pour depression efficiency are 2 for Na crude. There are about other 19 of them giving 80-90 percent efficiency at 500 ppm concentration.

Table 115

% Pour Depression at various ppm dosages

Additive			Bombay High Oil				Nahorkatia Oil			
			100	200	300	500	100	200	300	500
1.	22-2	UnMA	70	80	80	100	50	70	80	100
2.	22-4	UnMA	70	80	90	100	40	40	60	80
3.	22-6	UnMA	30	50	50	80	20	20	30	80
4.	22-8	UnMA	30	30	50	80	20	30	50	60
5.	22-18	UnMA	60	70	90	100	20	60	80	90
6.	22-10	UnMA	60	70	80	100	30	50	60	80
7.	22-12	UnMA	60	70	80	90	30	50	60	70
8.	22-14	UnMA	60	60	70	90	50	50	60	70
9.	22-16	UnMA	70	80	90	100	50	60	60	80

cont...

Table 115 cont...

10.	22-18	UnMA	70	80	90	100	60	60	70	80
11.	22-22	UnMA	80	90	90	100	60	70	70	100
12.	22-2	CMA	50	60	60	70	30	40	40	60
13.	22-4	CMA	40	50	50	60	20	20	40	60
14.	22-6	CMA	40	40	50	60	20	40	40	60
15.	22-8	CMA	50	50	50	70	40	50	50	60
16.	22-10	CMA	40	40	50	60	40	50	60	60
17.	22-12	CMA	40	40	60	80	60	60	70	90
18.	22-14	CMA	40	50	60	80	50	60	70	90
19.	22-16	CMA	40	50	60	70	60	60	70	90
20.	22-18	CMA	40	50	60	90	40	50	60	80
21.	22-22	CMA	70	70	80	100	50	60	60	80
22.	22-PA 15(1)		70	80	90	100	40	50	60	80
23.	22-PA 15(2)		60	70	80	100	50	60	60	80

cont....

Table 115 cont.....

24.	22-PA 21(1)	50	60	60	80	50	60	60	70
25.	22-PA 21(2)	60	70	80	90	40	50	50	80
26.	DBM-VAc	60	60	70	80	40	50	60	70
27.	DBM-MMA	40	40	50	70	40	40	50	60
28.	DBM-AA	60	60	70	80	50	60	60	80
29.	DBM-MA	50	60	70	80	50	60	70	80
30.	DBM-IA	70	70	80	90	60	70	80	90
31.	DBM-AN	50	50	60	70	40	50	50	70
32.	Poly DBM	50	60	60	80	50	50	70	90
33.	DODM-VAc	40	50	50	70	30	40	50	60
34.	DODM-MMA	30	40	40	60	30	40	40	60
35.	DODM-AA	40	40	50	60	30	40	40	60
36.	DODM-MA	50	50	60	70	50	60	60	70
37.	DODM-IA	60	60	70	80	50	50	60	80
38.	DODM-AN	30	30	40	60	30	40	40	60
39.	Poly DODM	60	60	70	80	50	60	60	70

Table 116

% Pour Depression at various ppm dosages

Addative			Moran oil			
			100	200	300	500
1.	22-2	UnMA	77.8	88.9	100	100
2.	22-4	UnMA	66.7	77.8	77.8	100
3.	22-6	UnMA	33.4	55	55	88.9
4.	22-8	UnMA	33.4	44.5	44.5	77.8
5.	22-18	UnMA	22.2	55.	77.8	100
6.	22-10	UnMA	33.4	44.5	55	77.8
7.	22-12	UnMA	33.4	33.4	55	66.7
8.	22-14	UnMA	33.4	44.5	44.5	66.7
9.	22-16	UnMA	55	55	66.7	88.9
10.	22-18	UnMA	66.7	66.7	77.8	100
11.	22-22	UnMA	66.7	77.8	100	100
12.	22-2	CMA	44.5	55	77.8	100
13.	22-4	CMA	44.5	44.5	55	77.8
14.	22-6	CMA	40	50	60	70
15.	22-8	CMA	44.5	55	55	77.8
16.	22-10	CMA	55	55	66.7	77.8
17.	22-12	CMA	55	66.7	66.7	88.9
18.	22-14	CMA	66.7	77.8	77.8	100
19.	22-16	CMA	55	66.7	66.7	88.9

cont..

Table 116 cont..

20.	22-18 CMA	77.8	77.8	88.9	100
21.	22-22 CMA	77.8	77.8	88.9	100
22.	22-PA 15(1)	66.7	77.8	77.8	100
23.	22-PA 15(2)	77.8	88.9	100	100
24.	22-PA 21(1)	77.8	77.8	88.9	100
25.	22-PA 21(2)	77.8	77.8	100	100
26.	DBM-VAc	66.7	77.8	77.8	100
27.	DBM-MMA	55	66.7	77.8	88.9
28.	DBM-AA	66.7	66.7	77.8	88.9
29.	DBM-MA	55	77.8	77.8	100
30.	DBM-IA	66.7	77.8	77.8	100
31.	DBM-AN	66.7	66.7	77.8	100
32.	Poly DBM	66.7	77.8	77.8	100
33.	DODM-VAc	44.5	44.5	55	77.8
34.	DODM-MMA	33.4	44.5	55	66.7
35.	DODM-AA	55	66.7	77.8	77.8
36.	DODM-MA	55	55	66.7	77.8
37.	DODM-IA	55	66.7	77.8	77.8
38.	DODM-AN	55	55	66.7	77.8
39.	Poly DODM	66.7	77.8	88.9	100

These 39 additives have shown good activity for Mo crude also and their depressions in percent are noted in Tables 115, 116. The activity is maximum at 500 ppm concentrations. For a 50% and above efficiency in pour depression is concerned, there are 27 depressants at 100 ppm, 32 depressants at 200 ppm, 37 at 300 ppm and 39 depressants at 500 ppm concentration. At 500 ppm concentration, those which give a 100% pour depression efficiency are 19 depressants.

It is further interest to note that at the same concentration, the efficiency is more marked if the pendant alkyl chain lengths are of 22 carbons for all the three of them.

Fourty such compounds as additives are subjected to the rheological study and the observations are recorded in Tables 53 to 99. The 35 5A (with SR-12 gear box) Fann Viscometer has been used for the purpose. Apparent viscosity plastiv viscosity and yield value are the properties taken into consideration. Plottings of plastic viscosity vs. temperature and yield value Vs. temperature (Fig. 44 to 61 respectively).

When the intra jelly like structure is broken down sufficiently by the additives, then the hindrances

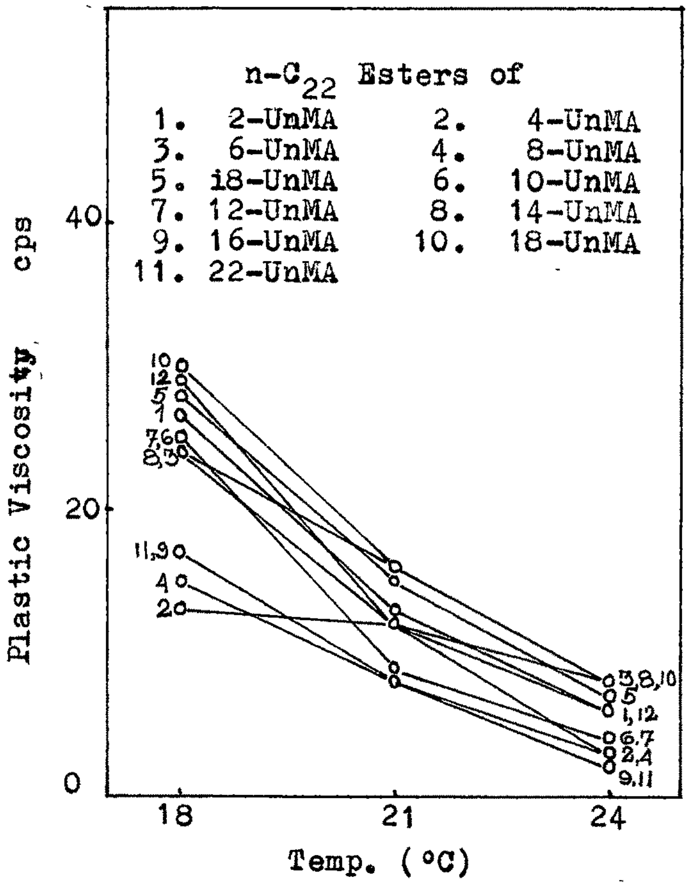


Fig. 44 : BH Oil: Temp. vs. Plastic Viscosity. n-C_{22} Esters of R-UnMA at 500 ppm

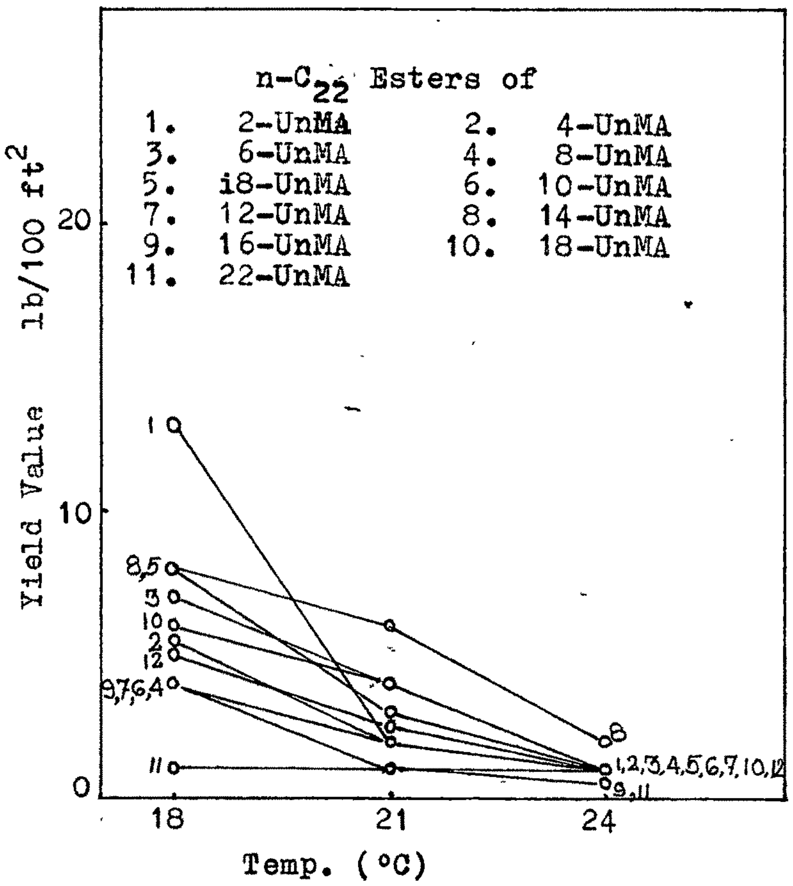


Fig. : BH Oil :Temp. vs. Yield Value n-C_{22} Esters of R-UnMA at 500 ppm

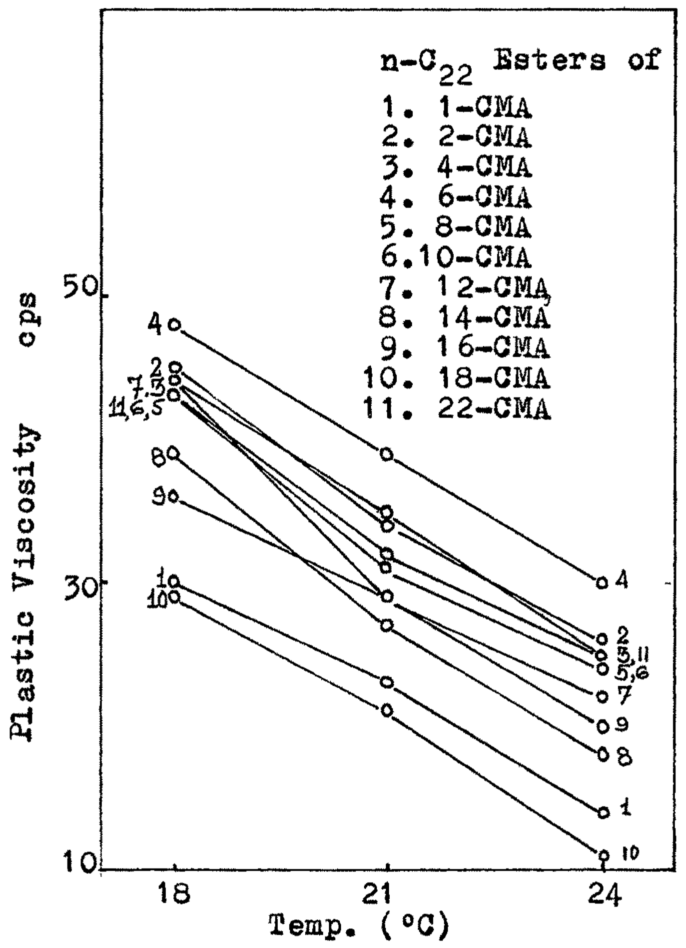


Fig. 45 : BH Oil: Temp. vs. Plastic Viscosity. n-C_{22} Esters of n-CMA at 500 ppm

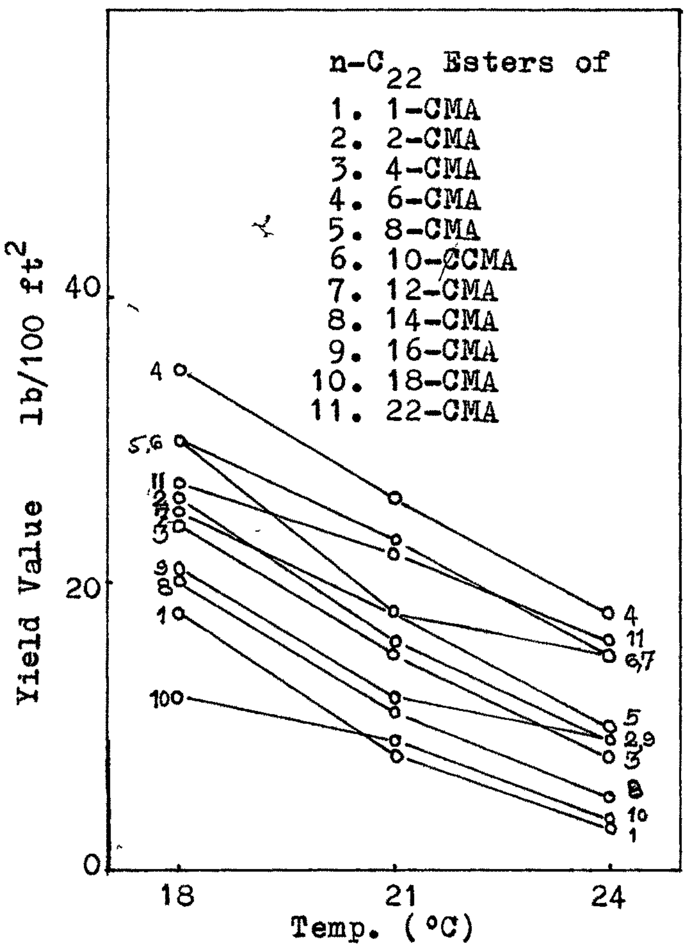


Fig. : BH Oil: Temp. vs. Yield Value n-C_{22} Esters of R-CMA at 500 ppm

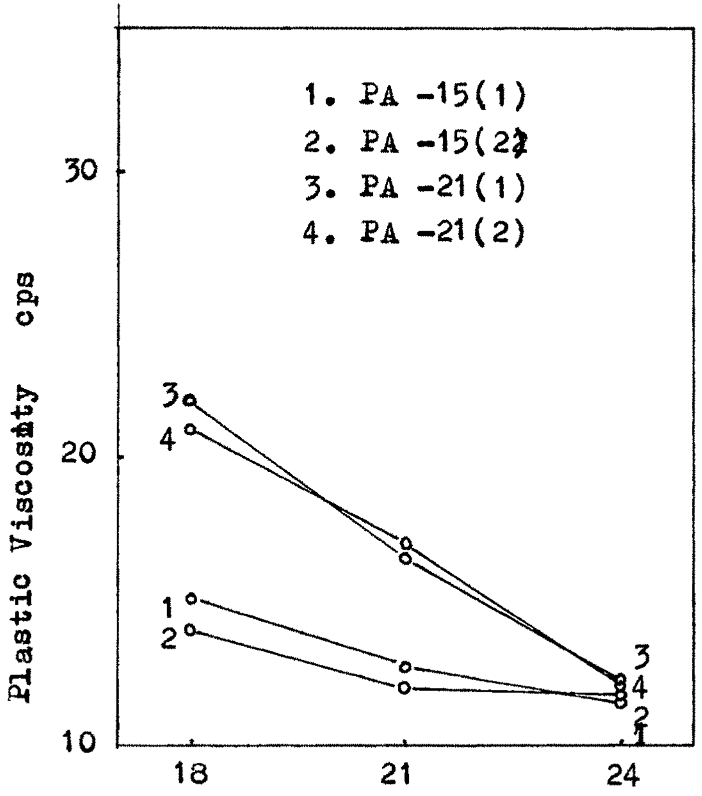


Fig. 46 : BH Oil: Temp. vs. Plastic Viscosity n-C_{22} Esters of PA at 500 ppm

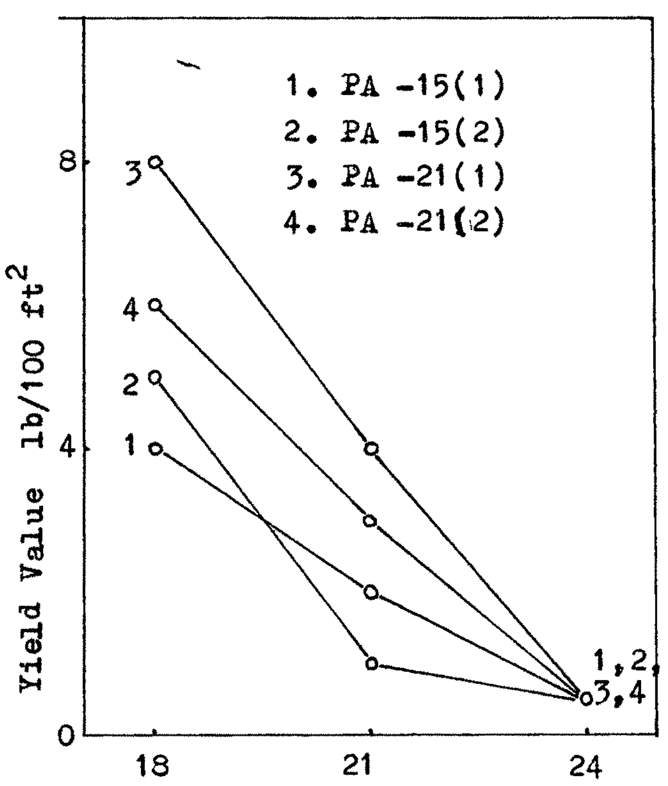


Fig. : BH Oil: Temp. vs. Yield Value n-C_{22} Esters of PA at 500 ppm

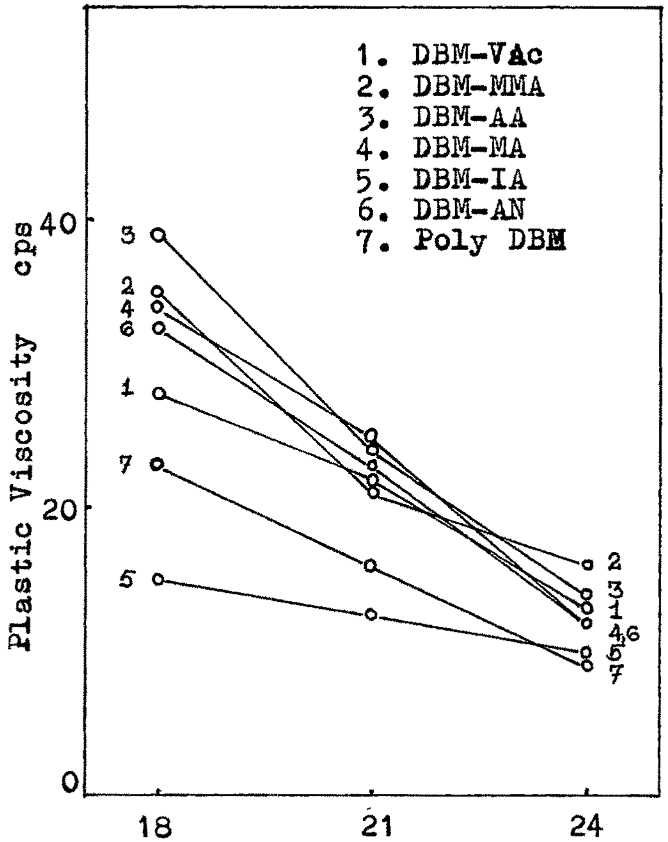


Fig. 47 :BH Oil: Temp. vs. Plastic Viscosity. Copolymers of DBM-VAc and so on at 500 ppm

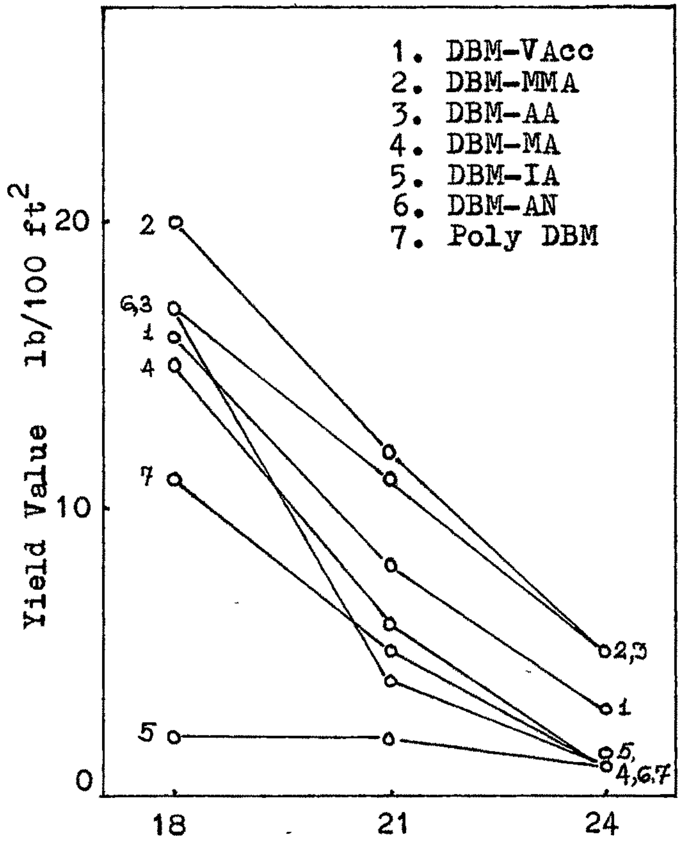


Fig. : BH Oil : Temp. vs. Yield Value Copolymers of DBM-VAc and so on at 500 ppm

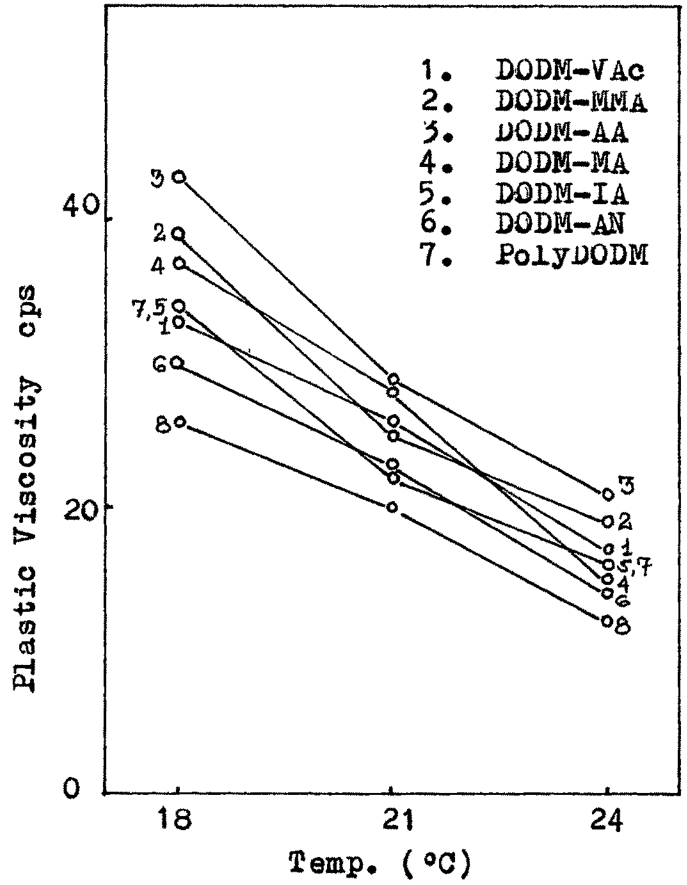


Fig. 48: BH Oil: Temp. vs. Plastic Viscosity. Copolymers of DODM-VAc and so on at 500 ppm

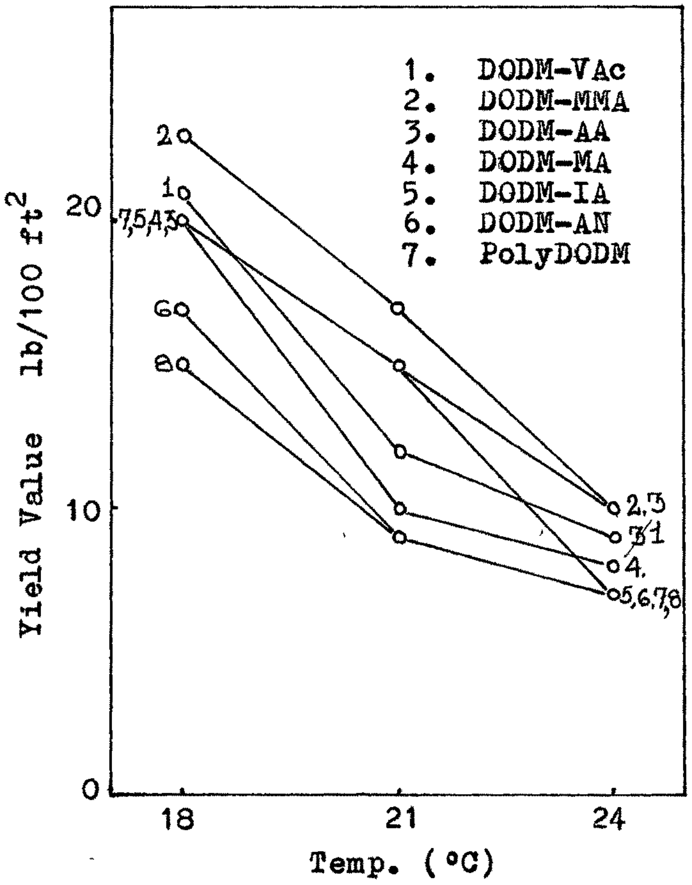


Fig. : BH Oil: Temp. vs. Yield Value Copolymers of DODM-VAc and so on at 500 ppm

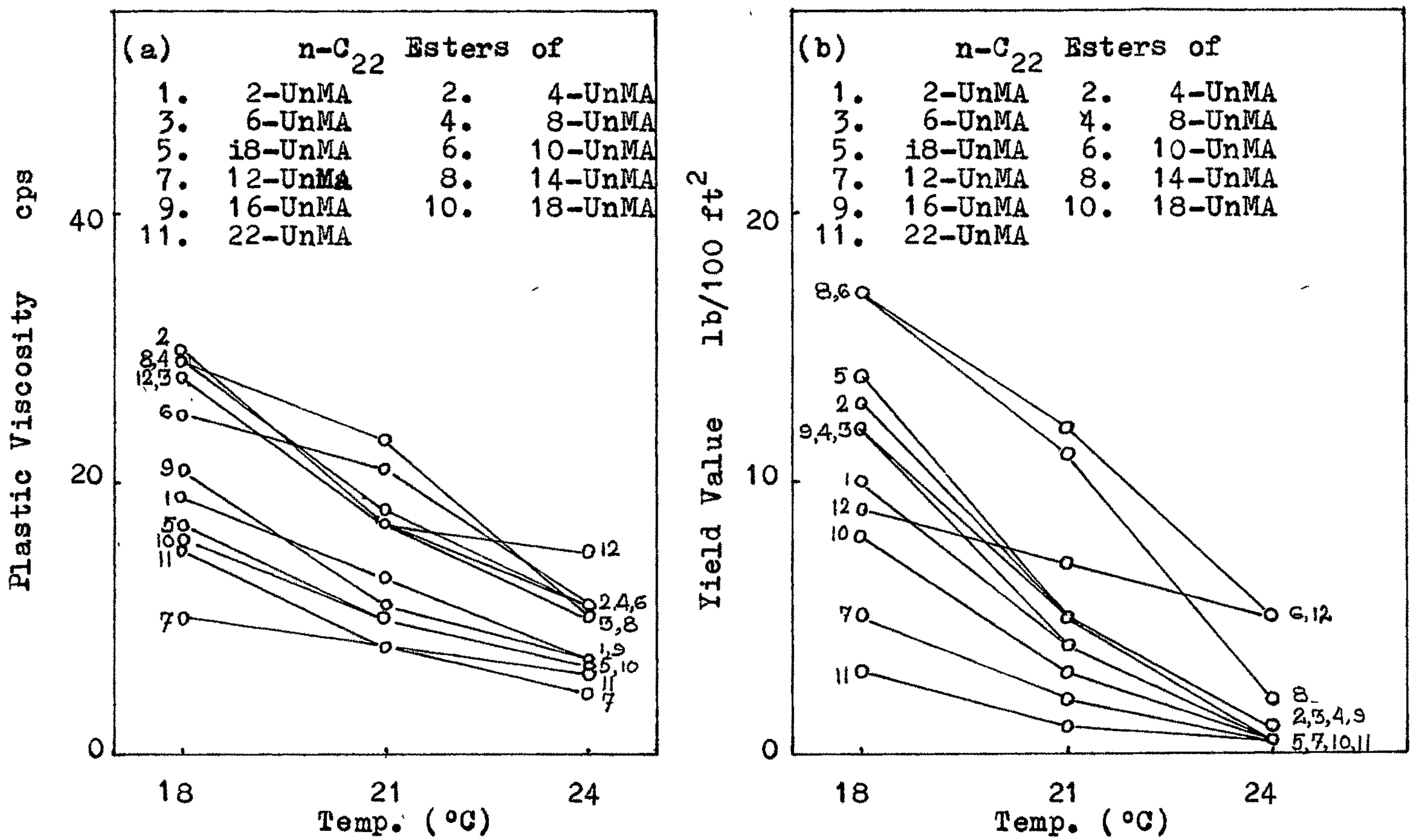


Fig. 49 : Na Oil : (a) Temp. vs. Plastic Viscosity (b) Temp. vs. Yield Value n-C_{22} Esters of R-UnMA at 500 ppm

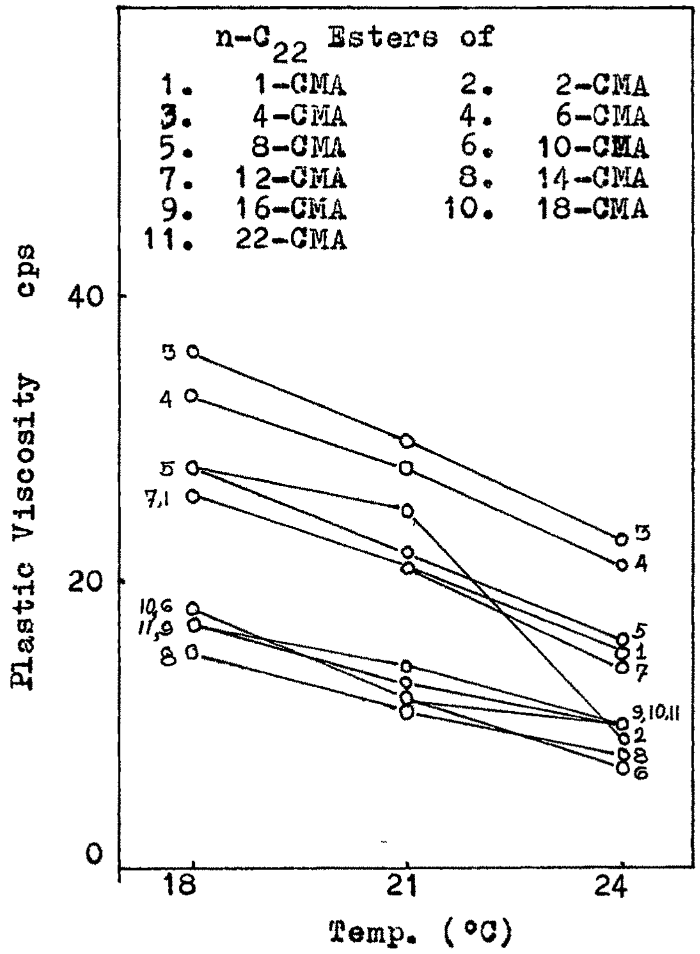


Fig. *50* : Na Oil :Temp. vs. Plastic Viscosity. n-C_{22} Esters of R-CMA at 500 ppm

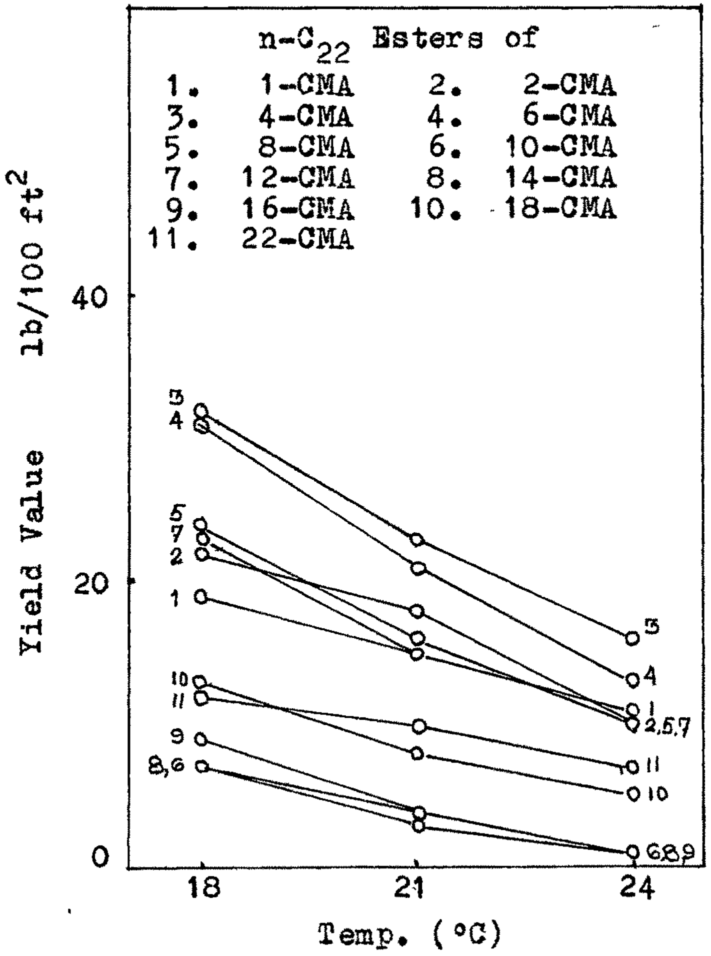


Fig. : Na Oil: Temp. vs. Yield Value n-C_{22} Esters of R-CMA at 500 ppm

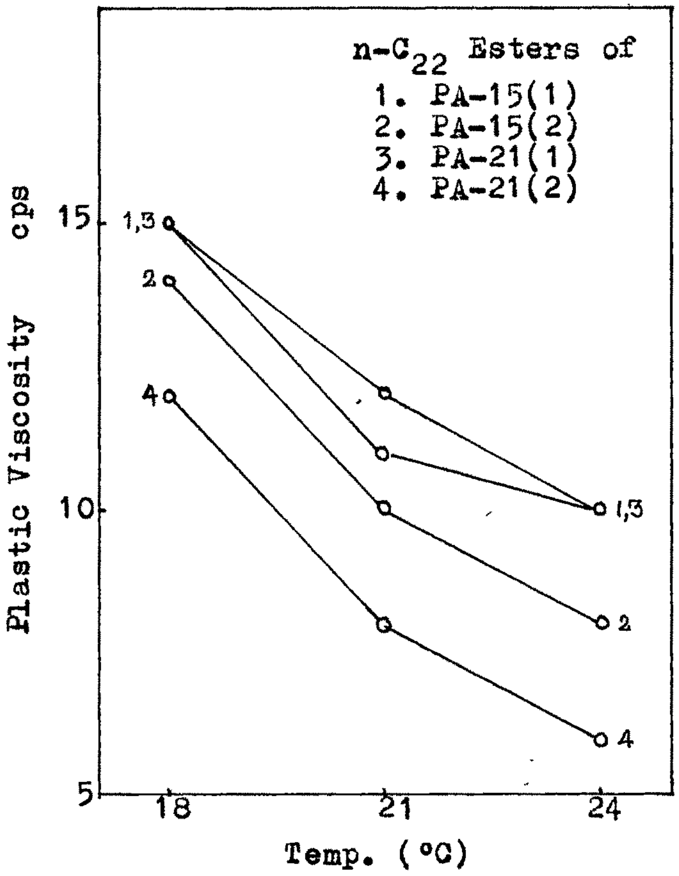


Fig. 51 : Na Oil: Temp. vs. Plastic Viscosity. n-C_{22} Esters of PA at 500 ppm

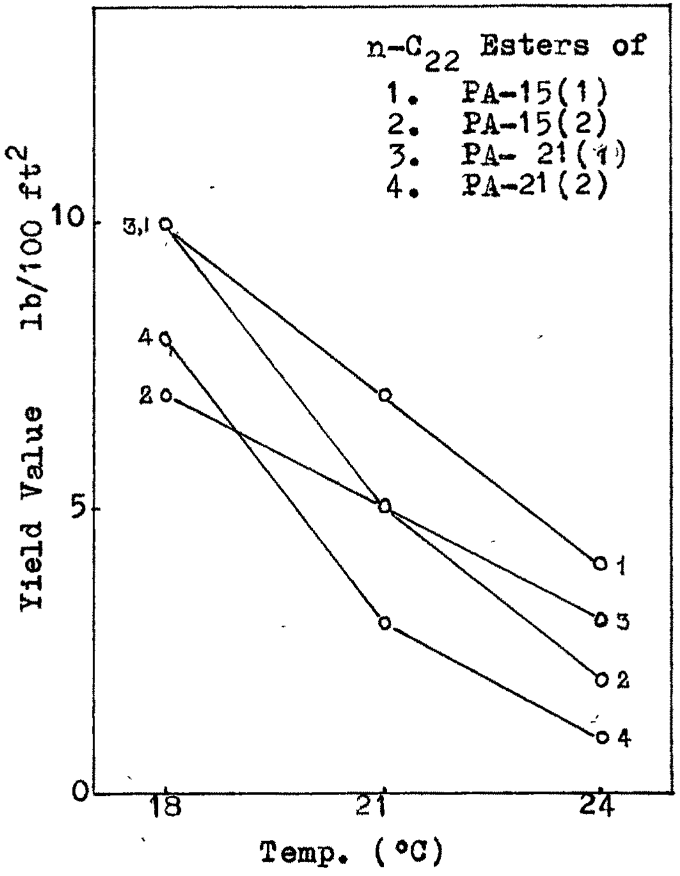


Fig. : Na Oil: Temp. vs. Yield Value n-C_{22} Esters of PA at 500 ppm

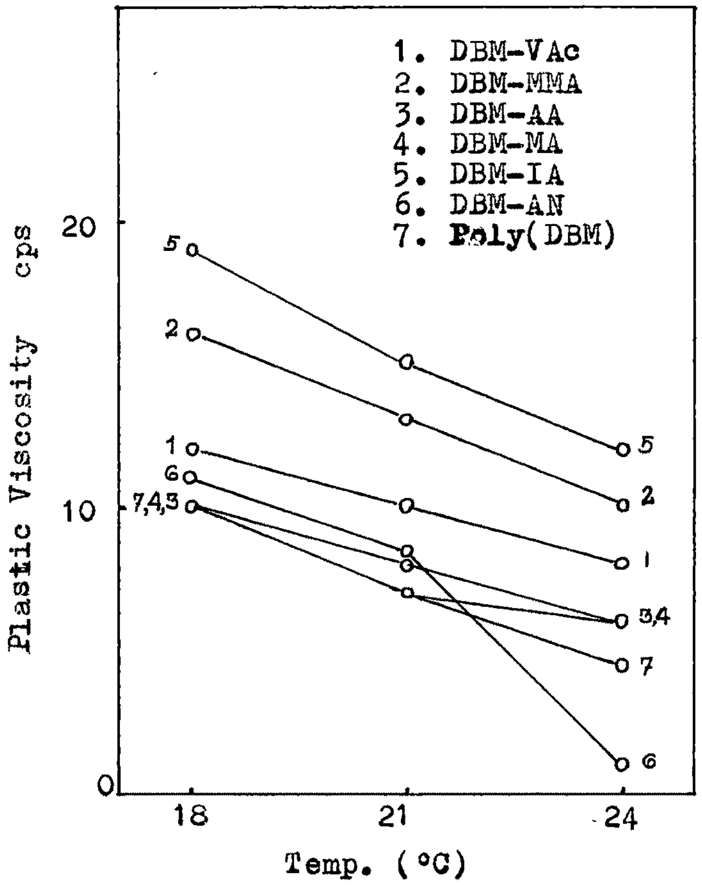


Fig. 52 :Temp. vs. Plastic Viscosity Na Oil. Copolymers of DBM-VAc and so on at 500 ppm

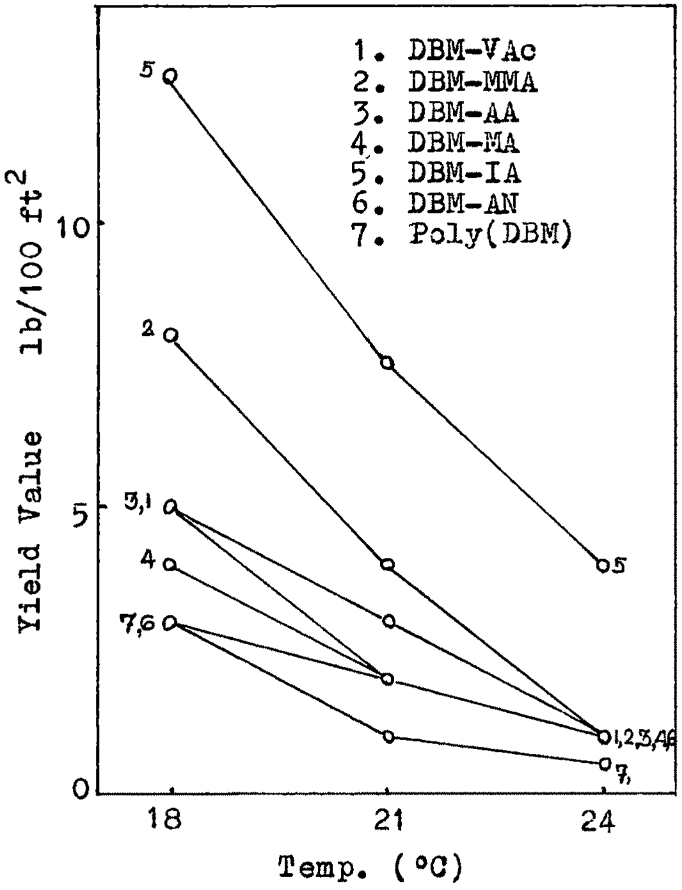


Fig. :Na Oil: Temp. vs. Yield Value Copolymers of DBM-VAc and so on at 500 ppm

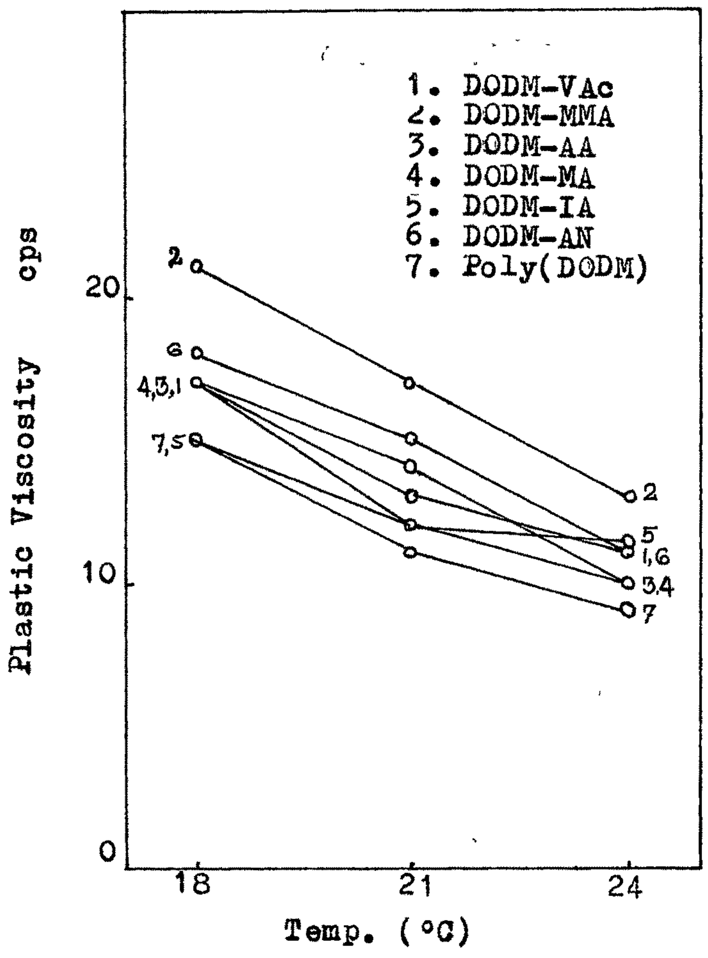


Fig. 53 : Na Oil:Temp. vs. Plastic Viscosity. Copolymers of DODM-VAc and so on at 500 ppm

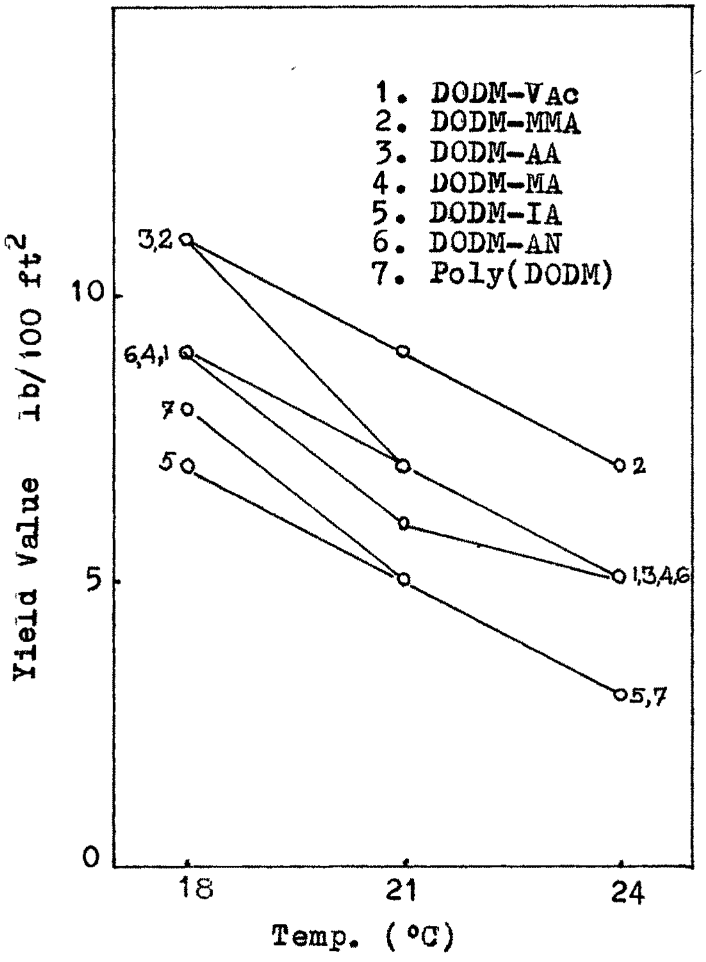


Fig. : Na Oil: Temp. vs. Yield Value Copolymers of DODM-VAc and so on at 500 ppm.

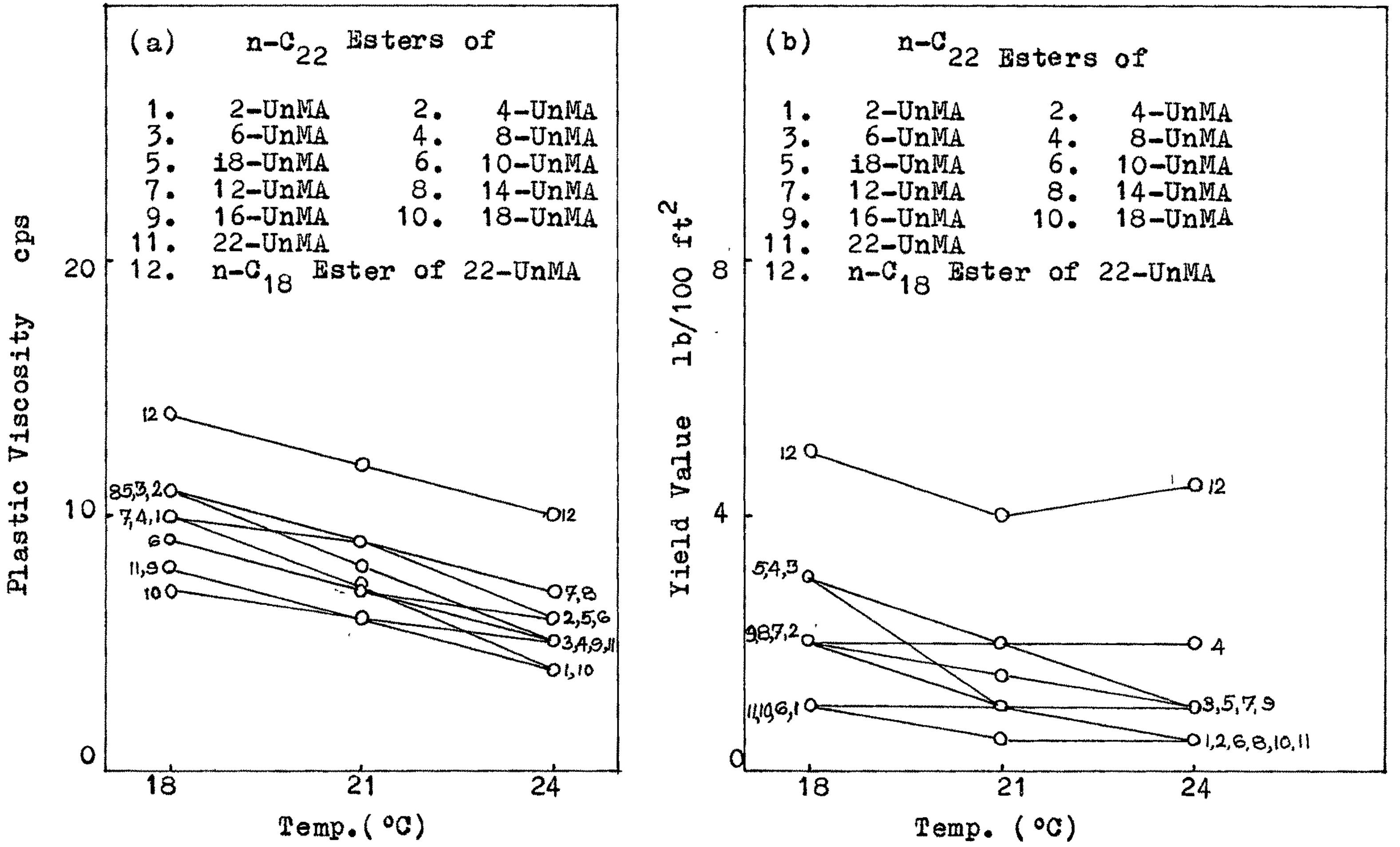


Fig. 54 : Mo Oil: n-C_{22} Esters of R-UnMA at 500 ppm. (a) Temp. vs. Plastic Viscosity (b) Temp. vs. Yield Value

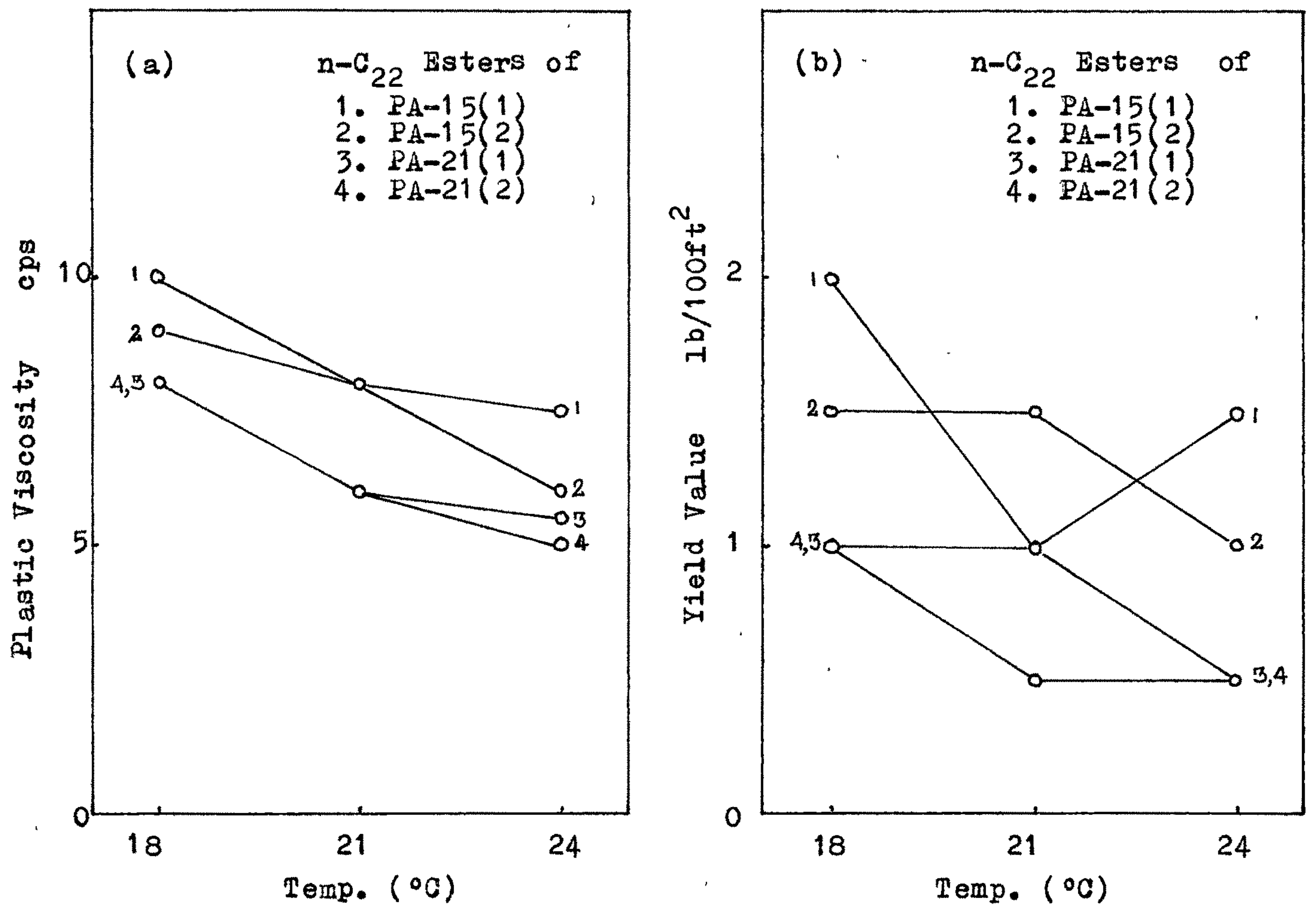


Fig. 56 : Mo Oil: (a) Temp. vs. Plastic Viscosity (b) Temp. vs. Yield Value n-C_{22} Esters of PA at 500 ppm

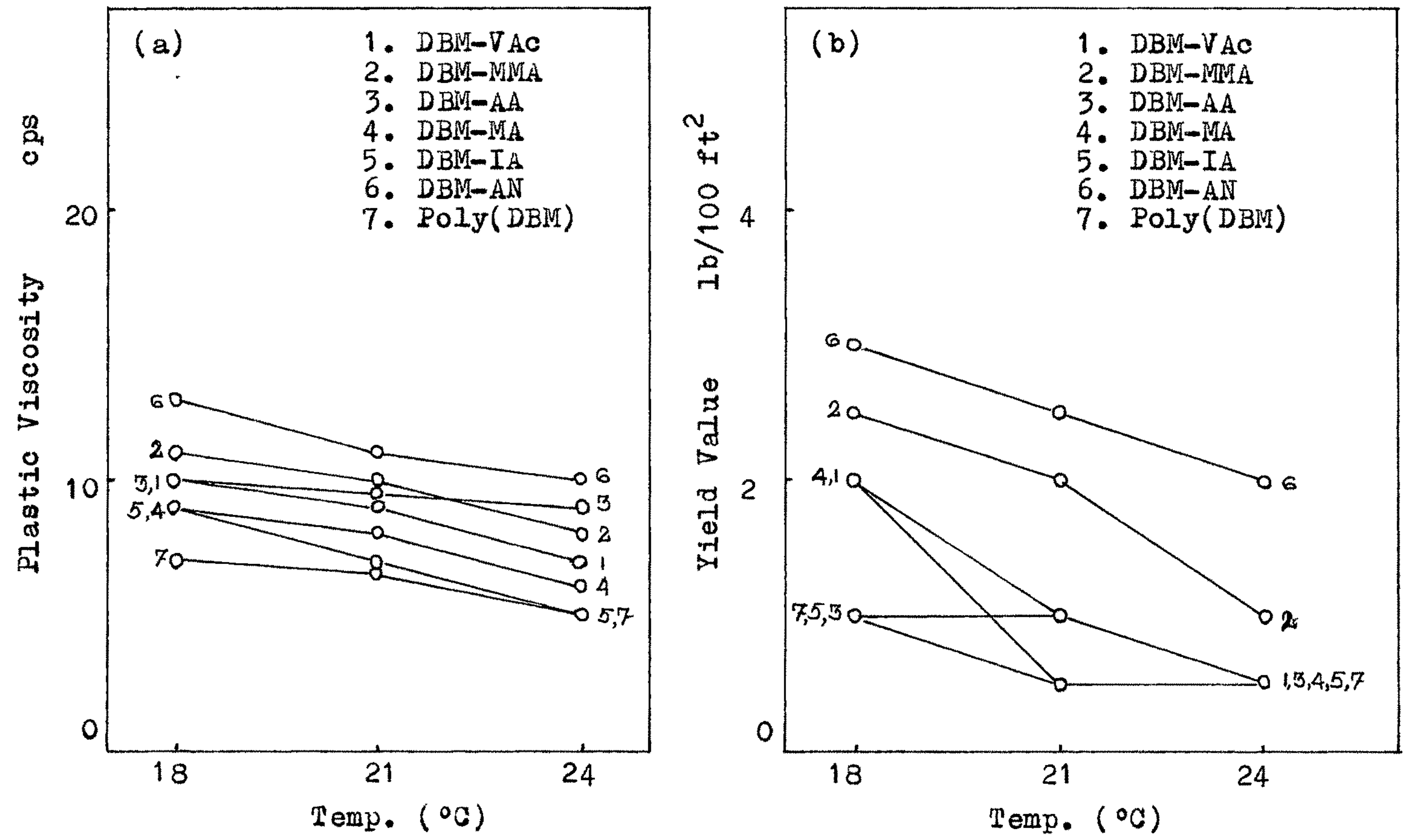


Fig. 57 : Mo Oil: (a) Temp. vs. Plastic Viscosity (b) Temp. vs. Yield Value Copolymers of DBM-VAc and so on at 500 ppm

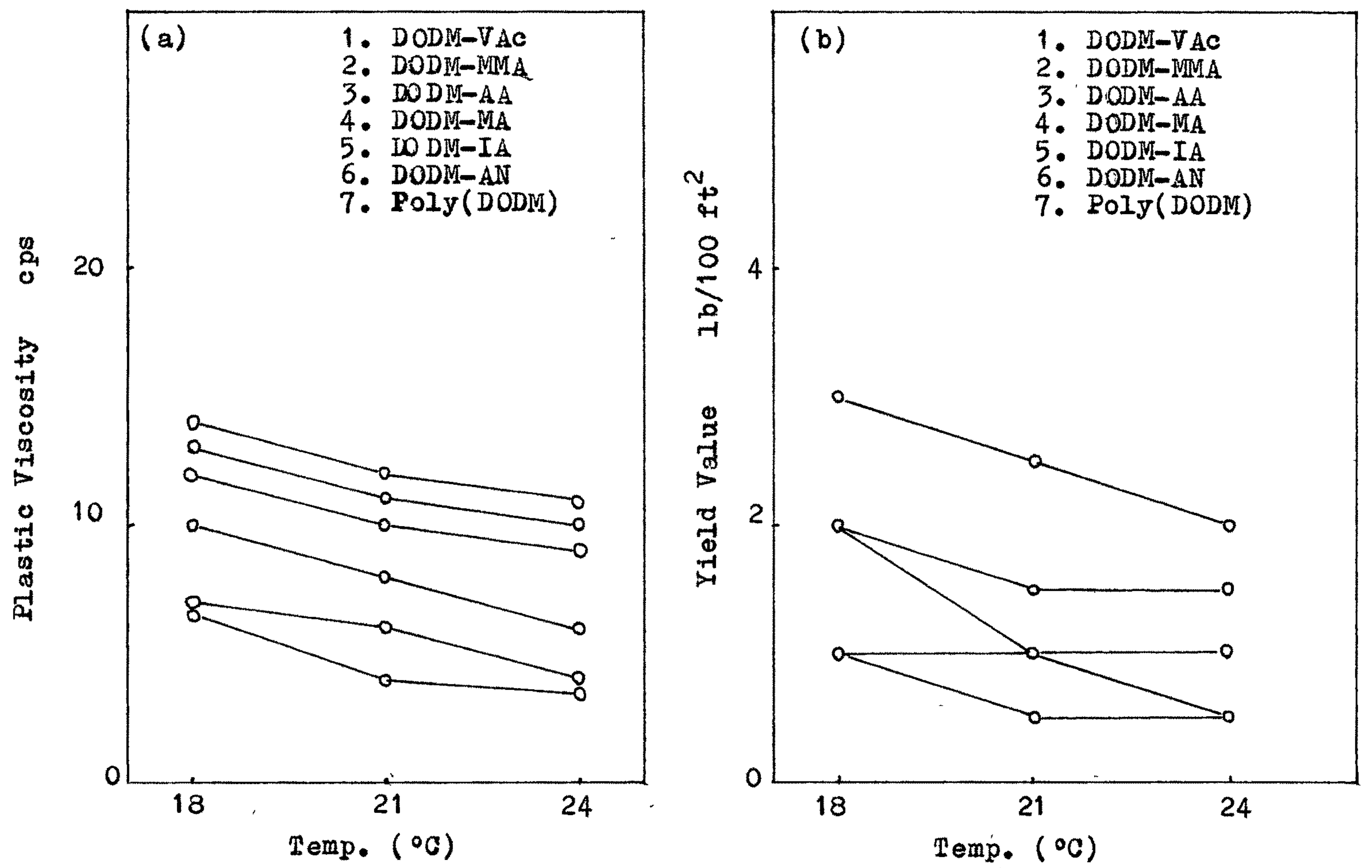


Fig. 58 : Mo Oil:(a) Temp. vs. Plastic Viscosity (b) Temp. vs. Yield Value Copolymer's of DODM-VAc and so on at 500 ppm

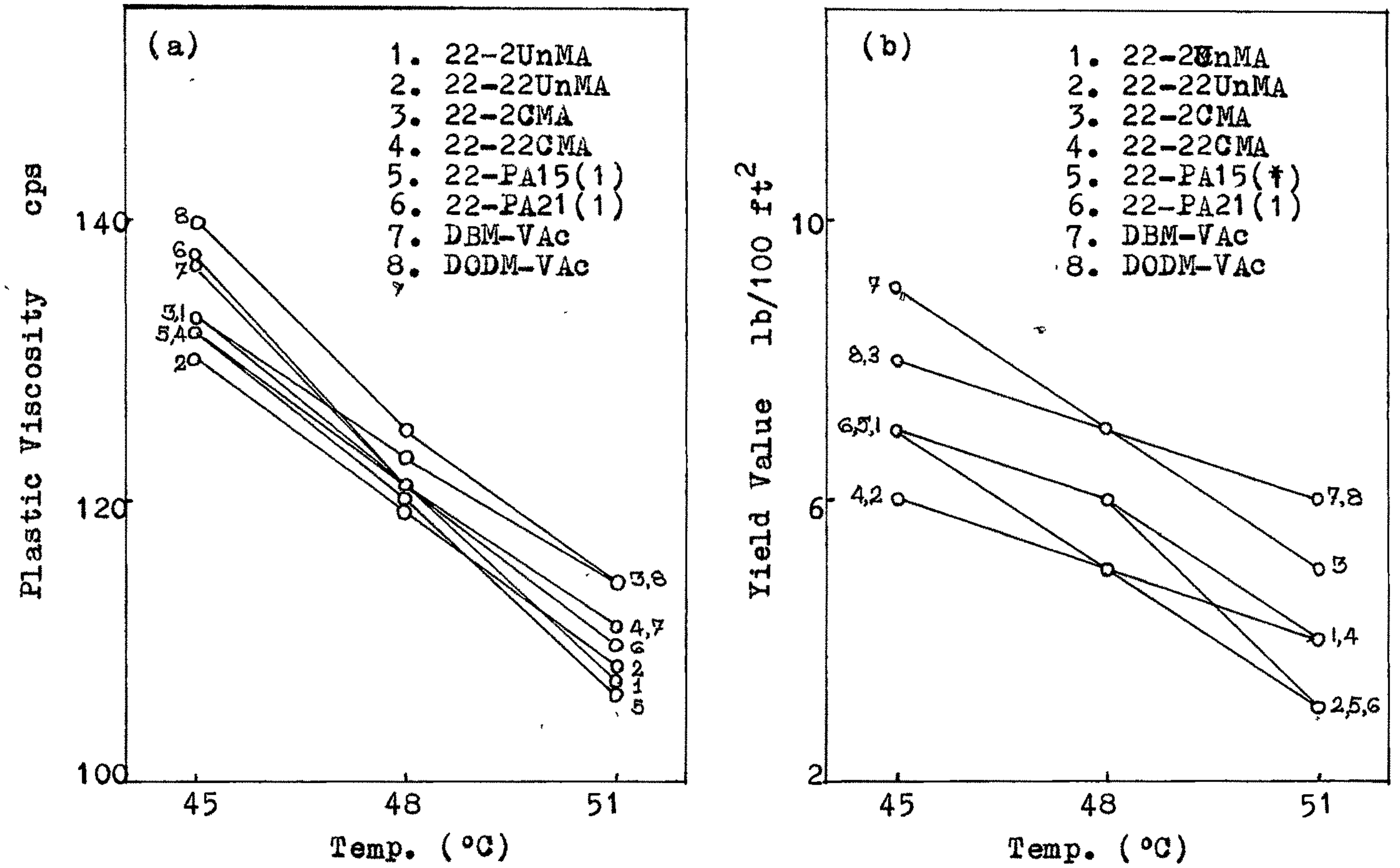


Fig. 59 : NK Oil : n-C_{22} Esters of Copolymers at 500 ppm
(a) Temp. vs. Plastic Viscosity (b) Temp. vs. Yield Value

pendant alkyl chains occurs, the effectivity of pour-point depression becomes almost zero with the chains shortening to 14 carbons.

(3) The pour-point depression activity is well maintained, even with a pendant alkyl chain length ~~worth~~ of just 2 carbons in the anhydride sector of the basic copolymer unit, provided the other two pendant alkyl chains remain unlatered.

(4) When all the three pendant alkyl chains of the copolymers diminish their lengths simultaneously, the pour depression activity experiences a steep fall.

(5) The alkyl pendant chain length of 22 carbons attached to the other segment of a copolymer should, however, be constant in order that the pour depression function remains operative.

(6) When four pendant chains are attached adjacent to each other, the pour depression activity of the moiety is hampered to some extent but as soon as the hindrance is immunized with adequate decrease in the other two chain lengths, the copolymer regains its pour-point depression efficiency.

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offset ?

(7) On homopolymerization, the polymer unit with two pendant chains of sufficient length is devoid of any hindrance effect though all the pendant alkyl chains in the repeating units are adjacent to each other ; the pour -point depression activity is quite superior.

(8) ~~The~~ crude oil cont~~ents~~ains adphaltene and resin, which ~~it~~ play a definite role in affecting the impact of the additives on pour -point ~~depression~~ ; it can be said that the pendant alkyl chains probe deeper into their counterparts ~~of~~ in the two dimensional gel- ~~jelly~~ like waxy portion of the crude oils and initiate a process of co-crystallization forming three dimensional crystals of microfine size. This leav~~ing~~es no scope for a ~~jelly~~ gel formation, which essentially would result in~~to~~ the breaking off of the original gel- jelly like structure of the crude oil ; hence, ~~as a result~~ the pour-point depression.

(9) The effect of the additives is quite specific in terms of waxy and other parts of the crude oil. An additive which is the best for the BH, Na and Mo crude is not found effective for NK and Am crude oil.

(10) The best pour depressants are not necessarily the best ' yield value ' reducers from the rheological point of view.

(11) The rheologically best additives may be only better as pour depressants and vice-versa. Rheologically improvement caused by these additives is also impressive as far as the BH, Na and Mo crude concern though relative~~ly~~ their impact on pour-point depression is ~~a little bit~~ slightly superior to ~~that~~ their effect on other ~~the~~ rheological propert~~y~~ies.

(12) Most of the additives have shown remarkable effect in converting the non-Newtonian BH, Na and Mo crude oils to near-Newtonian or almost Newtonian ~~fluids concerning the~~ shear rate/shear stress ~~relationship view point~~ behavior.