SUMMARY

SUMMARY

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

One hundred and eighteen new polymeric compounds have been synthesized in a planned sequence of variation in their basic polymer units. The synthesis is accomplished in an appropriate manner, setting proper conditions and establishing the standards for proper yields. Almost all of the newly synthesized compounds are copolymers except two of them which are homopolymers. Synthesis of monomers, co-polymerization and esterification of the copolymers thus obtained have been the main steps of the synthesis part. While the copolymers synthesized are now which impart the synthesis and the follow up characterization all the significance of a dissertation in a natural manner, the two prime objectives of the investigation are interalia (i) to explore the use of the polymeric

compounds newly synthesized as additives for pour depression activity for a host of crude oils collected from different oil fields of India and to assess further their impact on the rheological properties, and (ii) to find a correlation of the extent of pour depression and yield value characteristics with the molecular structure of the basic polymer units.

Of the total number of the new polymeric compounds, one hundred and six have been tested for their pour depression activity. As the experimental determination of the pour depression activity proceeded, the growing realization of a probable correlation with the molecular geometry of the copolymers suggested a drop out of about twelve of them outrightly, which was done, Not all the experimentally tested additives gave encouraging observations ; besides, recording of all such observations evidently was presenting an enormously expansive prospect in terms of the written number of pages. Therefore the results of some additives have been recorded and discussed in detail. Some of these additives have yielded excellent results in terms of pour depression while many others may be acclaimed as quite good. Some of these additives were chosen for

finding out their impact on the rheological behaviour of the crude oils.

The crude oils differ in their characteristics without any specific relevance to geographically. Unchanging regions, so much so that crude oils from different wells of the same field of the region would not be the same. Five crude oils from varying regions have been selected for the study, which are as follows :

(1) Bombay High (Western India), BH

(2) Nahorkatiya (Assam, Eastern India), Na

(3) Moran (Assam, Eastern India), Mo

(4) North Kadi (Gujarat), NK

(5) Amta (Gujarat), Am

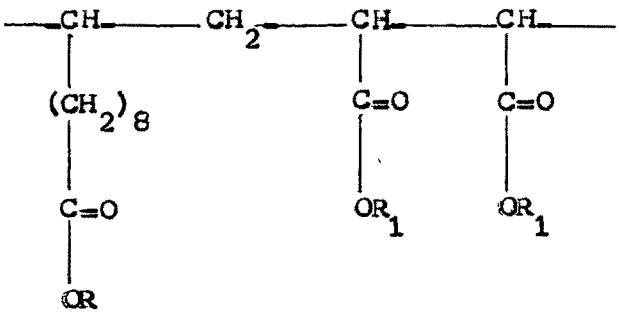
Pour points and rheological behaviour of these five crude oils have been determined during this investigation. Shear stress and shear rate properties of these five oils have been examined. All these aspects are included in the preliminary study and discussion. The pour points are high and the shear stress versus shear rate plottings indicate either

Bingham plastic or pseudoplastic characteristics at different temperatures. All of them are thus non-Newtonian fluids ; at high temperatures though, their near Newtonian behaviour is discernible. Table 1 gives in brief the varying characteristics of the five crude oils.

Sr. No.	Crude oil	Pour point °C	Nature below the pour point	Asphaltene %	Resin %	Wax %
1	BH	30	Mixed Bingham & pseudo-plastic	0.5	-	15
2	Na	30	"	2.4	-	13
3	Mo	27	"	0.9	-	11.5
4	NK	18	"	10.5	3.5	19.5
5	Am	6	"	8	3.9	13

The additives synthesized during the investigation fall under five different classes which differ from one another in their basic polymeric structure.

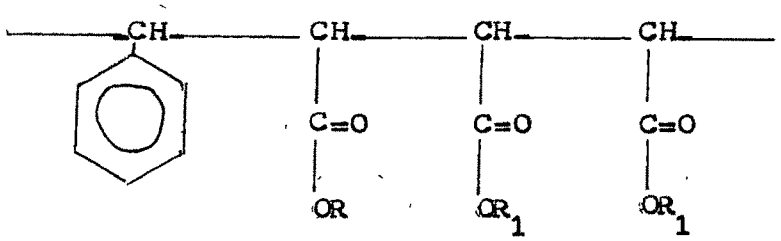
Class 1. Poly(alkyl Undecenoate-Co-dialkyl maleate) :



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

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

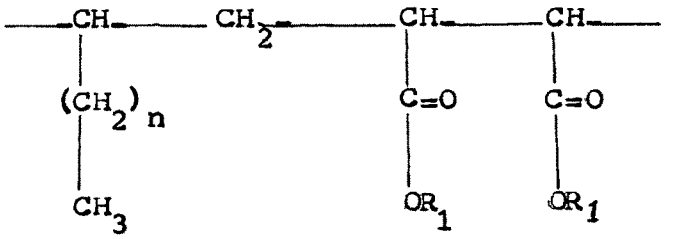
Class 2. Poly(alkyl cinnamate-Co-dialkyl maleate) :



where R = straight chain even alkyl group containing C_1 to C_{18} and C_{22}

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

Class 3. Poly(alpha-Olefin-Co-dialkyl maleate) :

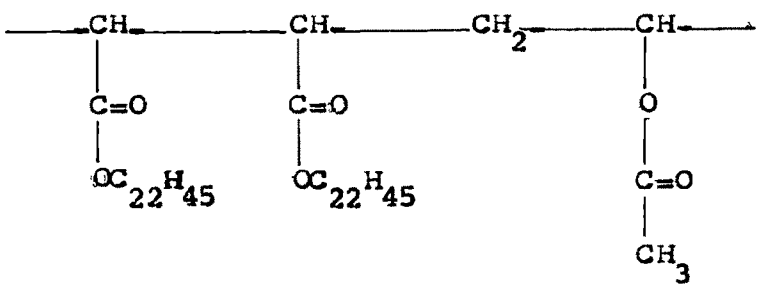


where R_1 = straight chain even alkyl group of C_{14} to C_{18} and C_{22}

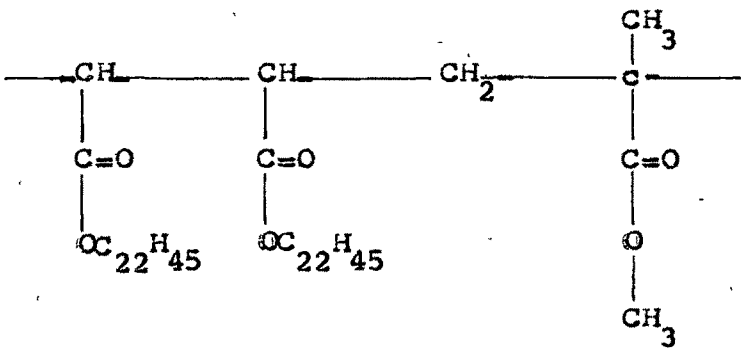
Class 4. Polymers of dibehenyl maleates :

Dibehenyl maleate prepared from maleic anhydride and behenyl alcohol and recrystallized from acetone. Then the dibehenyl maleate polymerized with various comonomers.

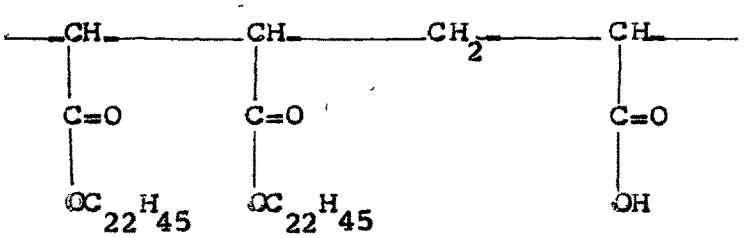
a. Poly(dibehenyl maleate-Co-vinyl acetate)



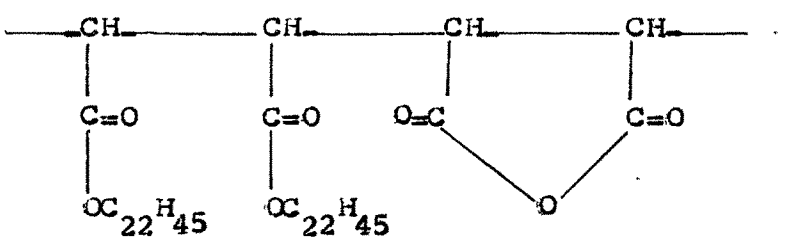
b. Poly(dibehenyl maleate-Co-methyl methacrylate)



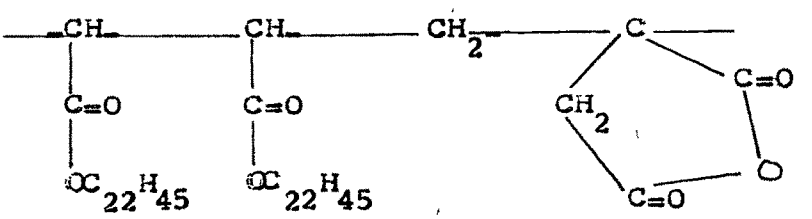
c. Poly(dibehenyl maleate-Co-acrylic acid) :



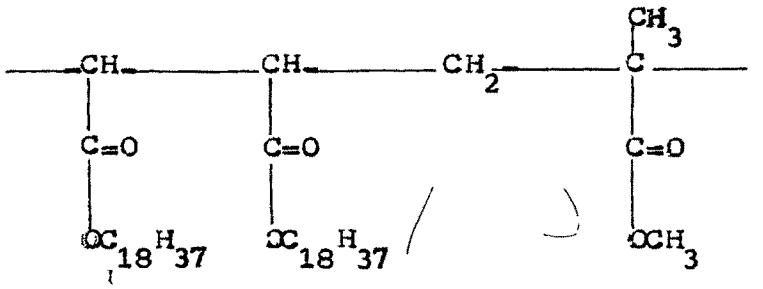
d. Poly(dibehenyl maleate-Co-maleic anhydride) :



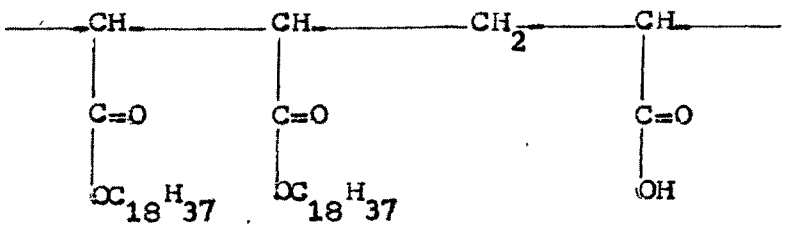
e. Poly(dibehenyl maleate-Co-itaconic anhydride) :



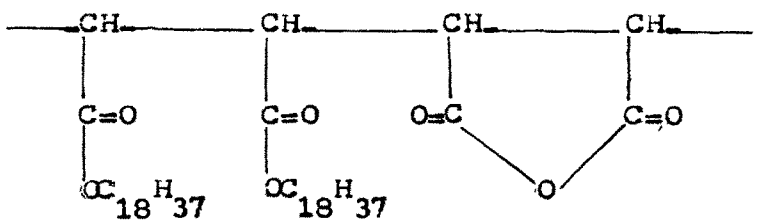
b. Poly(dioctadecyl-maleate-Co-methyl methacrylate) :



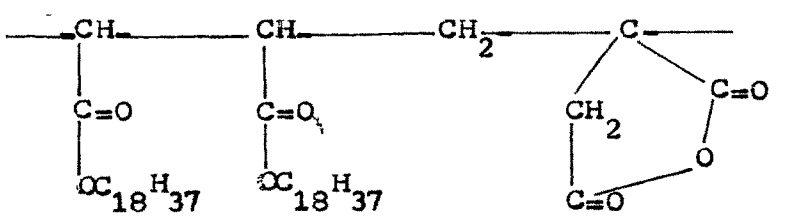
c. Poly(dioctadecyl-maleate-Co-acrylic acid) :



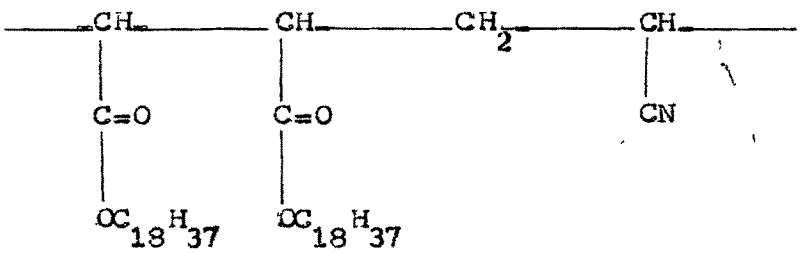
d. Poly(dioctadecyl-maleate-Co-maleic anhydride)



e. Poly(dioctadecyl maleate-Co-itaconic anhydride) :



f. Poly(dioctadecyl maleate-Co-acrylonitrile)



g. Poly(dioctadecyl maleate)

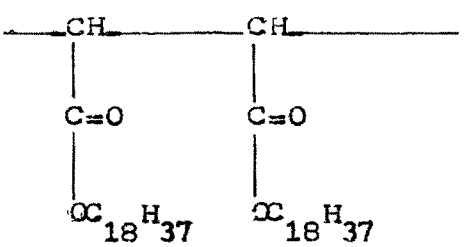


Table - 2

Abbreviated Nomenclature

Class	General Name	Abbreviation	Remarks
1.	Poly(alkyl undecylenate-Co-dialkyl maleate)	R_1-RUnMA	22-22 UnMA ↓ or 22-22 UnMA ↓
2.	Poly(alkyl cinnamate-Co-dialkyl maleate)	R_1-RCMA	22-22 CMA ↓ or 22-22 CMA ↓
3.	Poly(alpha olefin-Co-dialkyl maleate)	R_1-PA15(1),(2) R_1-PA21(1),(2)	C_{22}, C_{18}, C_{16} & C_{14} esters
4 & 5	Homopolymer and copolymers of dibehenyl maleate and dioctadecyl maleate	DBM_VAc DODM_VAc	Copolymer with vinyl acetate
		DBM_MMA DODM_MMA	Copolymer with methyl methacrylate
		DBM_AA DODM_AA	with acrylic acid
		DBM_MA DODM_MA	with maleic anhydride
		DBM_IA DODM_IA	with itaconic anhydride
		DBM_AN DODM_AN	with acrylo nitrile
		Poly DBM Poly DODM	Homopolymer

↓ indicates decrease in carbon chain length.

The compound 22-22 UnMA work very efficiently as an additive for pour depression in the case of Bombay High crude. With just 30 ppm of the additive, the pour depression experienced is to the extent of 24°C ; with increasing concentration of the 22-22 UnMA ester polymer, the pour depression activity is also enhanced and the pour point of the BH crude becomes 3°C at 300 ppm of the additive. The homologues of this series of copolymers may be varied in their pendant alkyl chain lengths as $\underset{\downarrow}{22}$-22 UnMA or 22-$\underset{\downarrow}{22}$ UnMA or both $\underset{\downarrow}{22}$-$\underset{\downarrow}{22}$ UnMA while maintaining the general structure of the basic polymer unit the same and studied as additives for the BH crude. In Table 3 and 4 are recorded the data concerning pour depressions for BH Na and Mo oil.

It is clear observed that the best pour depression action is shown by the 22-22 UnMA copolymer. The basic copolymer unit has three pendent alkyl chains of 22 carbon length each. The pendant chain length seems to be playing significant role in the pour depression phenomenon as is evident from the data of Table 3 ; when two pendant alkyl chains, as in the case of 18-22 UnMA, are shortened by 4 carbon atoms each, maintaining the alkyl chain of the undecylenate sector of the copolymer as it is i.e. of 22 carbon

Table 3

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 3 - 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 3 - 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 3. 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 4

Extent of pour depression : Mo oil -℃.

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. 22-10 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 4 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

Table 5.3

% 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 5 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 5 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 6.3

% 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 6 : 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

atoms, the pour depression activity is sufficiently decreased as compared to that of 22-22 UnMA additive, though as the concentration of the 18-22 UnMA is increased, the pour depression activity also increases relatively. As the 22-22 UnMA series gets varied next by two carbon atoms each at each stage, the pour depression activity also gets reduced and becomes zero with 14-22 UnMA copolymer.

Nahorkatia and Moran crude is also very favourable reacted by the R_1-R UnMA series of ester polymers. Table 3 and 4 records the data. The data of BH and Na indicating thereby parallel effect of the additives of the undecylenate maleate series of copolymers, though in an overall manner, the series is more effective in the case of BH crude than the Na crude.

It can be seen that the UnMA series of copolymers are only fairly or poorly effective as pour depressing additives in the case of North Kadi and Amta crude oil.

Taking an overall view of the efficiency of pour depression activity by the various series of ester polymers, the first thing that strikes the mind is that

the general efficiency may be sought for the five classes of copolymers. The order is as follows for BH and Na crudes.

Efficiency order
(Pour depression)

UnMA > PA > CMA > DBM > DODM

In Table 5 and 6 the % pour depression at various ppm dosages for BH, Na and Mo crude oils are given. The studies refer to apparent viscosity, plastic viscosity and yield value. Some copolymers reduce the yield value of the BH crude to the extent of 90% or more.

Certain salient features that emerge from the discussion are as under :

(1) The interlinking group, if any, between the pendant alkyl chain and the carbon of the backbone chain of the copolymer has both positive and negative impact on the pour point depression function depending upon the overall disposition of the moiety vis-a-vis the length of the chains.

(2) Copolymers with pendant alkyl chains of sufficient length is responsible for bringing down the pour point. Copolymers with a segment where a simultaneous decrease in the length of both pendant alkyl chains occurs, the effectivity of pour depression becomes almost zero with the chains shortening to 14 carbons.

(3) The pour depression activity is well maintained even with a pendant alkyl chain length worth 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 ether two chain lengths, the copolymer regains its pour depression efficiency.

(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 depression activity is quite superior.

(8) The crude oil contents asphaltene and resin, it play a definite role in affecting the impact of the additives on pour depression ; it can be said that the pendant alkyl chains probe deeper into their counter parts of the two dimensional jelly like waxy portion of the crude oils and initiate a process of co-crystallization forming three dimensional crystals of microfine size leaving no scope for a jelly formation which essentially would result into breaking off the original jelly like structure of the crude oil ; 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 relatively their impact on pour depression is a little bit superior to that on the rheological property.

(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.