EXPERIMENTAL

EXPERIMENTAL

(A) Synthesis and Characterization

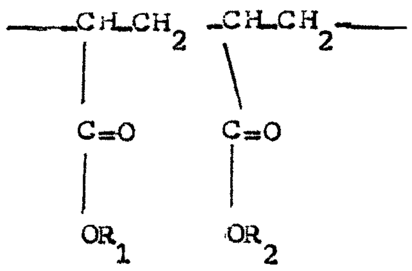
Experimental I

ESTERS OF POLY(n-ALKYL UNDECYLENATE-CO-MALEIC ANHYDRIDE)

General

A linear polymer or copolymer with pendant side chains of specific length and nature is one of the general structural characteristics of pour point depressants and flow improvers for fuel oils. In copolymers one of the comonomers may or may not contain a pendant side chain.

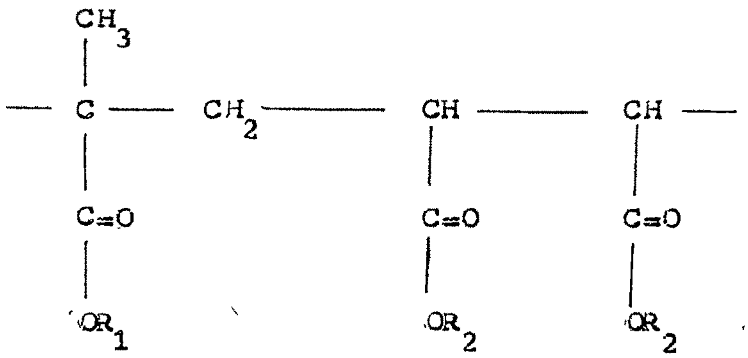
e.g. 1.



Poly alkyl acrylate

R_1 and R_2 = higher n-alkyl chains, either the same or different.

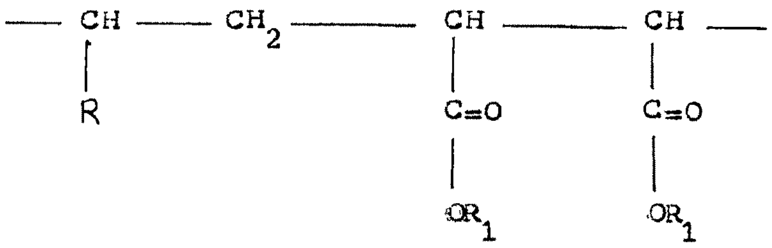
2.



Poly(alkyl methacrylate Co-dialkyl maleate)

R_1 and R_2 are either the same or different n-alkyl chains.

3.



Poly(propylene-Co-di-alkyl maleate)

$R = CH_3$; R_1 = higher n-alkyl chains

Depending upon the nature of R, R_1 and R_2 a lot of products are possible and are described in sufficient details in the introduction part of this dissertation. Some of these are alpha olefines of C_2

to C_{30} ; styrene, vinyl pyridine, vinyl acetate and vinyl esters, vinyl ethers, alkyl acrylates and methacrylates, allyl esters, etc. However very little work is reported regarding copolymers of esters of higher chain length terminal olefinic acids and dialkyl maleates. These may be taken as higher homologous members of alkyl acrylate di-alkyl maleate copolymers, and an increase in the molecular weight and degree of polymerization of these copolymers are synthesized under this investigation for studying their characteristics in keeping with the object as elaborated in an earlier section.

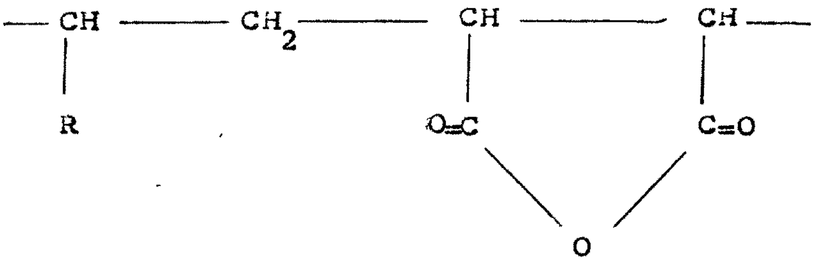
n-Alkyl Undecylenate Copolymers

Undecylenic acid is a C_{11} fatty acid with a double bond between C_{10} and C_{11} carbon atoms as shown :

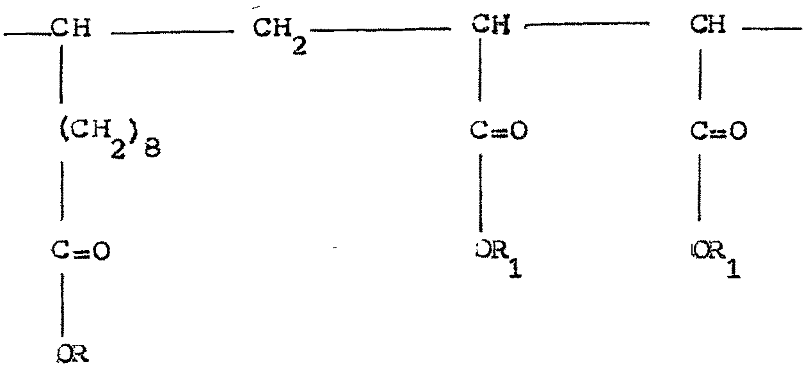
$$CH_2 = CH(CH_2)_nCOOH, \qquad n = 8$$

when the value of n = 0, it is acrylic acid. In all its reactions involving the double bond undecylenic acid behaves similar to acrylic acid, but with lesser degree of reactivity. Homopolymers and copolymers of undecylenic acid as well as its esters are known.

Maleic anhydride in normal conditions of free radical catalysed solution polymerization does not homopolymerize but readily copolymerizes with vinyl monomers generally to produce alternating 1:1 copolymers of the type :



This property of maleic anhydride is made use of in the synthesis of the products of this class under this investigation. Regarding the requirements of pendant chains, both comonomers of this class contribute towards this. A single basic unit of the final polymer will contain three pendant chain as shown below :



R varies from ethyl (C_2) to behenyl (C_{22}) and for every R R_1 varies from C_{10} to C_{22} except C_{20}. The synthesis part consists of preparation of n-alkyl ester of undecylenic acid (222) and its copolymerization with maleic anhydride. The polymerization can be done in bulk with sufficient amount of benzene to act as a solvent. The radical generating catalyst, benzoyl peroxide, may be used as initiator for polymerization. The conditions (eg. catalyst solvent and temperature) have to be so adjusted as to produce low or medium molecular weight copolymers avoiding formation of high molecular weight species.

EXPERIMENTAL

1. Undecylenic acid n-alkyl esters : Esterification

The most usual method for preparation of esters is the reaction of carboxylic acid and an alcohol with elimination of water. Excellent reviews are given by Goldsmith (439) Keyes (440) and Reid (441). Since esterification is a reversible process for conversions approaching 100%, a number of methods are used to boost the forward reaction. They are generally azofetroping (442), desiccation and other chemical means (443, 444).

Catalyst such as hydrogen chloride, sulfuric acid, phosphoric acid, silica gel, sulfonic acid and cation exchange resins (445) are also used for the purpose.

Method :

All the undecylenic esters were prepared by the conventional acid catalyzed esterification method under azeotropic conditions using Dean and Stark apparatus. Toluene to the extent of 60 to 80% of the total weight of the reactants was used as azeotroping agent. The lower members, viz. ethyl n-butyl and n-hexyl were directly esterified using excess of the alcohol. In n-butanol and n-hexanol esterification, the alcohol itself functioned as the azeotroping agent, In higher alkyl esters, 2% of undecylenic acid was used in excess than the required quantity. Sulfuric acid was used as the catalyst in all the cases ; one ml. of conc. sulfuric acid per mole of undecylenic acid was found to be alright. The progress of the esterification in all the cases except ethyl ester could be followed by the volume of water azeotroped and collected in the Dean and Stark apparatus. The amount of water azeotroped in all cases except ethyl, butyl and hexyl ester was quantitative. The time of the esterification varied from 6 hrs. to 18 hrs. depending upon the batch size. For higher alkyl esters time taken for completion was comparatively more.

The crude ester in all cases was neutralized in cold with 10% sodium bicarbonate solution to remove mineral acidity as well as traces of undecylenic acid. For higher esters (eg. C_{16} to C_{22}) further dilution of the crude product with fresh toluene was necessary to prevent crystallization as well as for ease of working. The neutral solution was washed free of all impurities and the product thus obtained was dried over anhydrous sodium sulfate and then the solvent was recovered by distillation. The crude esters except n-C_{18} and n-C_{22} were distilled under reduced pressure. C_{18} and C_{22} crude esters were crystallized out from acetone. Saponification value was checked and compared with calculated values to ascertain the purity of the esters. Quantities of the materials and analysis of the products are summarized in Table 6.

Table 6

n-Alkyl Undecylenate esters

Sr. No.	Code*	Raw materials				Yield in gm	Sap. value	% purity
		Undecylenic acid in g & (mole)	Alcohol in g and (mole)	Sulfuric acid in ml	Toluene in ml.			
1	2	3	4	5	6	7	8	9
1	2-Un	57.04 (0.31)	Ethanol 28.52 (0.62)	0.5	-	55	262.5	99.20
2	4-Un	36.8 (0.2)	n-Butanol (29.6) (0.4)	0.3	-	45	232	99.25
3	6-Un	55.2 (0.3)	n-Hexanol 61.2 (0.6)	0.3	-	50	208	99.36
4	8-Un	46.92 (0.25 + 2%)	n-Octanol 29.5 (0.25)	0.25	70	70	185	97.64
5	18-Un	46.92 (0.25 +2%)	i-Octanol (29.5) (0.25)	0.25	70	65	184	97.09

cont...

Table 6 cont..

6	10-Un	37.53 (0.2 + 2%)	n-Decanol 31.6 (0.20)	0.2	70	60	169.5	97.92
7	12-Un	37.53 (0.2 + 2%)	n-Dodecanol 37.2 (0.2)	0.2	90	65	156.5	98.20
8	14-Un	56.30 (0.3 + 2%)	n-Tetradecanol 64.2 (0.3)	0.3	100	110	144	97.54
9	16-Un	37.53 (0.2 + 2%)	n-Hexadecanol 48.4 (0.2)	0.2	80	65	136.12	99.00
10.	18-Un	37.53 (0.2 + 2%)	n-Octadecanol 59.0 (0.2)	0.2	60	88	127.5	99.10
11	22-Un	37.53 (0.2 + 2%)	n-Docosanol 63.0 (0.2)	0.2	125	90	116.1	99.15

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* 2-Un stands for ethyl undecylenate ; similarly for others

** mentioned in parenthesis

2. Copolymerization with maleic anhydride

The unique nature of maleic anhydride to produce 1:1 alternating copolymer (446, 447) is made use of in synthesizing this type of poly anhydride copolymers. Polymerization in bulk i.e. from undiluted low molecular weight starting materials is the simplest and the oldest method for the synthesis of macromolecules. The increase in molecular weight occurs by a rapid sequential addition of monomer molecules to the growing centre. The molecular weight of an alternating copolymer is a dependent upon the concentration of activated complex. The higher the temperature the lower the complex concentration and the lower the molecular weight of the copolymer chain (448). The effect of solvent on rate of polymerization has variously been attributed to complex formation (449). Usually a gel effect is observed in the radical polymerization. Due to this, there is a marked increase in the average molecular weight of the polymer formed. The control of the molecular weight in free radical polymerization beyond the gel effect can be achieved by many ways, viz.

(i) increase in the temperature of polymerization,

(ii) method of weak inhibition (450-452) and

(iii) use of transfer agent.

The imposition of a temperature sequence is not an universal method to control the molecular weight of the polymer formed, because it cannot be x applied. There are many polymeric systems which are heat sensitive and their properties change when exposed to high temperatures. In such cases the use of weak inhibition is useful. The method of weak inhibition is based upon the nature of the inhibition process in xxxx viscous media. Utilization of transfer agents in the polymerization mass could also lead to polymer molecules of low molecular weight. Molecules of low molecular weight lead to viscosity increase of the reaction mass at a much slower pace compared to molecules of higher molecular weight. The method of weak inhibition and chain transfer with benzene is supposed to be involved in the control of the molecular weight in these copolymers eventhough it is not specifically studied.

Experimental Assembly

The set up used for the synthesis of the copolymers is as follows :

It essentially consisted of a three necked flask kept in a thermostatically controlled oil bath. The flask carried a speed regulated mechanical stirrer through the central neck. The two side necks carried respectively a thermometer pocket with a sensitive thermometer and water condenser with a calcium chloride guard tube which also was the inlet for nitrogen. Extra stirring of the oil bath was done using another stirrer to keep the temperature of the oil bath uniform.

Method :

The following method is developed in the laboratory under this investigation. First introduced solvent benzene into the polymerization flask. Then alkyl undecylenate ester was charged along with maleic anhydride. Pure dry nitrogen was introduced into the system to replace air ; nitrogen passing was continued so that the reactants were always blanketted with nitrogen atmosphere. Benzoyl peroxide was dissolved in benzene and taken in a small dropping funnel which was previously purged with nitrogen and kept under nitrogen. The catalyst solution was introduced into the polymerization flask just before commencement of heating. Once catalyst addition was over, heating was gradually started in such a way that the temperature of the mass attained 70°C. Initially the polymerization proceeded quite smoothly but at about 70°C it became slightly exothermic. Proper conditions were maintained to control the exothermic range between 70° and 75°C. The stage lasted for 1/2 to 1 hr. and then continue the heating at 70°C for another 14 to 15 hr. Then the product was taken out of the flask while hot and by scrapping a gently if necessary. The polymers in all cases were transparent pale yellow solids. The lower alkyl ester copolymers were brittle ; brittleness changed to waxy hard nature as the alkyl chain length increased. Quantities of materials are summarized in Table 7 .

Purification of the polymer

Polymers made in solution can be purified by the solvent non-solvent method. Adding 5-10 volumes of non-solvent with agitation to the polymer, it precipitated. The precipitant must be miscible with the polymerization solvent, a non-solvent for the polymer and ideally a solvent for the initiator or catalyst additives and oligomers. After collection by filtration or centrifugation the polymer should be washed or extracted by various solvents to move traces of other reactants.

Poly(ethyl undecylenate-Co-maleic anhydride) ;
Poly(n-butyl undecylenate-Co-maleic anhydride) ;
Poly(n-hexyl undecylenate-Co-maleic anhydride) ;

these three copolymers was purified by dimethyl sulfoxide as solvent and toluene as non-solvent. The precipitate was filtered and washed with toluene and vacuum dried at 70°C/25" Hg for 24 hrs. These products was subsequently used for the preparation of dialkyl esters.

Poly(n-octyl undecylenate-Co-maleic anhydride) ;
Poly(iso-octyl undecylenate-Co-maleic anhydride) ;
Poly(n-decyl undecylenate-Co-maleic anhydride) ;
Poly(n-dodecyl undecylenate-Co-maleic anhydride) ;
Poly(n-tetradecyl undecylenate-Co-maleic anhydride)

these five copolymers was purified by benzene as solvent and cold methanol as non-solvent. The precipitated copolymer was evaporated free of methanol at room temperature and finally at 50°C/25" Hg vacuum for 24 hrs.

Poly(n-hexylundecylenate-Co-maleic anhydride) was purified by benzene as solvent and acetone as nonsolvent. The acetone was evaporated from the filtered precipitate and finally dried under vacuum at 50°C/25" Hg for 24 hrs.

Poly(n-octadecyl undecylenate-Co-maleic anhydride) ;

Poly(n-Docosyl undecylenate-Co-maleic anhydride),

these two copolymers was purified by benzene as solvent and mixture of equal volumes of acetone and methanol in cold. The acetone and methanol mixture was evaporated from the filtered precipitate and finally dried under vacuum at 50°C/25" Hg for 24 hrs.

Table 7

Poly(n-alkyl undecylenate-Co-maleic anhydride)

Sr. No.	Code	Raw materials			Benzene in ml.	Yield in g.	Appearance
		Alkyl undecylenate ** in g & (mole)	Maleic anhydride in g & (mole)**	Benzoyl peroxide in g (% on wt. of total monomers			
1	2	3	4	5	6	7	8
1	2-UnMA*	2-Un 42.52 (0.2)	19.6 (0.2)	0.621 (1)	75	58	Cream coloured powder
2	4-UnMA	4-Un 35.25 (0.155)	15.19 (0.155)	0.5244 (1)	50	45	Pale Yellow Powder
3=	6-UnMA	6-Un 48.2 (0.188)	18.42 (0.188)	0.666 (1)	85	55	Pale yellow powder
4	8-UnMA	8-Un 41.63 (0.135)	13.23 (0.135)	0.5486 (1)	65	52	Pale yellow powder
5	18-UnMA	18-Un 30.2 (0.1)	9.8 (0.1)	0.50 (1)	52	33	Pale yellow powder

cont...

Table 7 cont...

6.	10-UnMA	10-Un 38.52 (0.118)	11.564 (0.118)	0.5008 (1)	75	45	Pale yellow waxy
7.	12-UnMA	12-Un 36.28 (0.1)	9.802 (0.1)	0.470 (1)	75	40	Yellow waxy
8.	14-UnMA	14-Un 45.32 (0.119)	11.662 (0.119)	0.568 (1)	70	50	Pale yellow waxy
9.	16-UnMA	16-Un 52 (0.127)	12.48 (0.127)	0.6448 (1)	100	56	Pale yellow waxy
10.	18-UnMA	18-Un 52.5 (0.12)	11.76 (0.120)	0.642 (1)	105	57	Pale yellow waxy
11.	22-UnMA	22-Un 29.62 (0.0602)	5.899 (0.0602)	0.3551 (1)	45	31	Cream coloured powder

* 2-UnMA = Poly(ethyl undecylanate-Co-maleic anhydride) ; similarly for others

** mentioned in parenthesis

3. Analysis and Characterisation

The copolymers prepared were analyzed for their composition, sequence of monomer arrangement, chain structure by functional group analysis, molecular weight, etc. as per the following :

(i) C and H analysis of anhydride copolymers :

The actual C and H content determined were compared with calculated values for a copolymer composition of 1:1 monomer ratio. Their results are incorporated in Table 8.

(ii) Solution Viscosity :

Dilute solution viscosity studies of all anhydride copolymers were done at 30°C using Ubbelohde viscometer. Dimethyl sulfoxide was used as solvent for 2-UnMA, 4-UnMA and 6-UnMA. Toluene was used as the solvent in the remaining cases. The inherent viscosity in each case was calculated and the results are incorporated in Table 9.

(iii) Molecular weight :

Molecular weight from dilute solution viscosity could not be calculated for want of values of 'K' and 'a' in the Mark-Houwink equation. However, molecular weight of a few of them were determined by vapour pressure osmometry, Rast's Camphor Method (453). The results are incorporated in Table 9.

(iv) Spectroscopic Studies :

IR Spectra-

One typical copolymer (2-UnMA) was checked for its I.R. Spectra (Fig. 9) in chloroform solution. The analysis of the spectral data is given in Table 10.

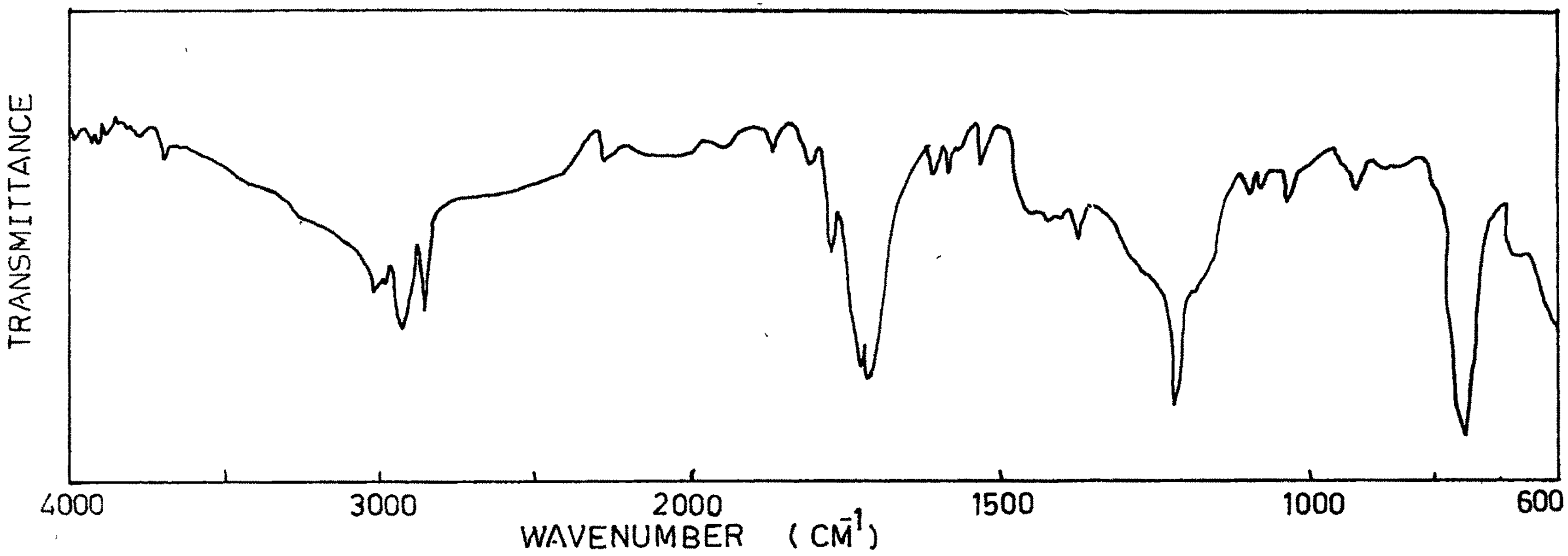


FIG. 9 IR SPECTRA OF 2-UnMA

Table 8

Elemental analysis of the copolymer (Poly(n-alkyl undecylenate-Co-maleic anhydride)

Sr. No.	Copolymer code (Molecular formula = mole. wt. of the repetition unit)	Percentage of C and H			
		Calculated for 1:1		Actual	
		C	H	C	H
1.	2-UnMA ($C_{17}H_{26}O_5$=310)	65.8	8.38	64.98	8.13
2.	4-UnMA ($C_{19}H_{30}O_5$=338)	67.47	8.87	67.12	8.34
3.	6-UnMA ($C_{21}H_{34}O_5$=366)	68.85	9.29	68.58	8.98
4.	8-UnMA ($C_{23}H_{38}O_5$=394)	70.04	9.64	69.54	9.25
5.	18-UnMA ($C_{23}H_{38}O_5$=394)	70.04	9.64	69.67	9.86
6.	10-UnMA ($c_{25}H_{42}O_5$=422)	71.09	9.951	70.86	9.67
7.	12-UnMA ($C_{27}H_{46}O_5$=450)	72.01	10.22	72.34	9.89
8.	14-UnMA ($C_{29}H_{50}O_5$=478)	72.8	10.46	71.92	10.12
9.	16-UnMA ($C_{31}H_{54}O_5$=506)	73.51	10.67	73.15	9.98
10.	18-UnMA ($C_{33}H_{58}O_5$=534)	74.16	10.86	73.56	9.86
11.	22-UnMA ($C_{36}H_{64}O_5$=576)	75.0	11.11	74.56	11.01

Table 9

Copolymers of undecylenic ester and maleic anhydride

Sr. No.	Copolymer code	Inherent viscosity dl/g of anhydride copolymer *	Molecular weight M_n of anhydride copolymer
1.	2-UnMA	0.162 (a)	2545 (b) 2410 (d) 2735 (c)
2.	4-UnMA	0.139 (a)	
3.	6-UnMA	0.115 (a)	
4.	8-UnMA	0.121	
5.	i8-UnMA	0.124	
6.	10-UnMA	0.134	
7.	12-UnMA	0.117	3865 (b)
8.	14-UnMA	0.126	
9.	16-UnMA	0.106	
10.	18-UnMA	0.154	
11.	22-UnMA	0.176	

* determined in toluene at 30°C

(a) determined in Dimethyl sulfoxide at 30°C

(b) by Vapour pressure osmometry against Dibenzyl as std. in DMF at 70°C (Hewlett Packard V.P.O. Model 302 B)

(c) by Rast's Camphor method

(d) determined in Tetrahydro furan solution against standard poly styrene by (Gel-Permeation chromatography, Varian vista 401 - Apple II)

Table 10

Analysis of the I.R. Spectral data :*

Poly(ethyl undecylenate-Co-maleic anhydride)

Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}	Reference
930	Cyclic anhydride Maleic anhydride Unit in copolymer	960-930	(454)
1050	Maleic anhydride unit	1230, 1070 and 930	(455)
1220	Cyclic anhydride	1210-1310	(456)
1780	Higher ester and C=O in cyclic anhydride in copolymer	1780	(455)
1730	Cyclic anhydride	1865	(455)
1780	and ester carbonyl	1785	
2950	Residual unsaturation due to terminal double bond in low D.P. polymers	3000	(455)

* Perkin-Elmer Part No. 5100 4367

Solvent = Chloroform

4. Esterification of Anhydride Copolymers : Poly(n-alkyl undecylenate-Co-dialkyl maleate) :

General :

Maleic anhydride, polymaleic anhydride and polymeric carboxylic acid upon treatment with alcohols under the suitable conditions of temperature and catalyst yield esters with varying degree of esterification. The general methods of esterification of such polymers are extensively dealt with the Cohen (457, 458) and Heller, et al., (459). Typical esterification methods under azeotropic conditions are mostly patented (213, 215).

All anhydride copolymers prepared as above were convereted into the corresponding diesters using sulfuric acid catalyst. The water formed was removed using xylene as the azeotroping agent as well as medium of the reaction.

Method :

The experimental set up used for the preparation of the diesters is as follows :

The apparatus consisted of a three necked flask fitted in a controlled heating mantle, a mercury seal stirrer and a Dean and Stark water separator.

For a better reflux and azeotroping, the proportion of xylene was kept (by experience with a 250 ml, 3 necked flask) between 20 - 25 ml per 0.01 mole of the copolymer basic unit. The fatty alcohol was used in two molar proportion to one mole of the copolymer. The molecular weight of the copolymer basic unit was calculated as the sum of the molecular weights of alkyl undecylenate and malecc anhydride since all of them are 1:1 copolymers. Sulfuric acid catalyst was used to the extent of 0.1 ml per 0.017 to 0.03 mole of the copolymer basic unit. The temperature of the reaction to start with was 145 - 150°C which towards the end of the reaction was raised to 160 - 165°C by removing part of xylene by distillation. The time of the esterification varied from product to product depending upon the progress of the esterification, which on an average was between 20 to 30 hrs.

After esterification the crude product was diluted with xylene (just to facilitate easy handling) and treated with solid sodium bicarbonate to remove any mineral acidity if present, filtered through a bed of Hyflow-supercel. The solvent was then recovered by distillation to get a concentrated form of the product. Purification of the crude product was done by precipitation of the product in excess of acetone. The unreacted fatty alcohol and the remaining xylene went into the acetone layer. The product from the first precipitation was made free of acetone, dissolved in just sufficient amount of xylene and reprecipitated in acetone. After evaporating the acetone, the product was dried under vacuum at 70°C/25" Hg.

Esters using n-fatty alcohols of chain length C_{14}, C_{16}, C_{18} and C_{22} were prepared thus. The amounts of materials etc ; are tabulated in Tables 11 to 14 for such of the products which later were found to possess pour point depressing and flow improving properties.

Table 11

n-Tetradecyl esters of Poly(n-alkyl undecylenate-Co-maleic anhydride)

Sr. No.	Copolymer in g and (mole)*	n-Tetradecand in g and (mole)*	Xylene in ml	H_2SO_4 in ml	Yield in g.
1.	2-UnMA 9.3 (0.03)	13.9 (0.06)	45	0.1	17
2.	4-UnMA 10.82 (0.032)	13.91 (0.064)	45	0.1	18
3.	6-UnMA 10.45 (0.028)	12.35 (0.056)	45	0.1	15
4.	8-UnMA 10.63 (0.027)	12.318 (0.054)	45	0.1	16
5.	18-UnMA 9.85 (0.025)	10.85 (0.05)	40	0.1	14
6.	10-UnMA 8.44 (0.02)	8.74 (0.04)	45	0.1	11
7.	12-UnMA 7.22 (0.016)	6.847 (0.032)	25	0.1	8
8.	14-UnMA 7.62 (0.0159)	6.809 (0.0318)	25	0.1	8
9.	16-UnMA 7.12 (0.014)	6.013 (0.028)	25	0.1	10
10.	18-UnMA 13.35 (0.025)	10.85 (0.05)	50	0.10	16
11.	22-unMa 6.65 (0.011)	4.793 (0.022)	25	0.03	6

* mentioned in parenthesis

Table 12

n-Hexadecyl esters of Poly(n-alkyl undecylenate-Co-maleic anhydride)

Sr. No.	Copolymer in g and (mole)*	n-Hexadecanol in g and (mole)*	Xylene in ml	H_2SO_4 in ml	Yield in g.
1.	2-UnMA 6.94 (0.0223)	10.79 (0.0446)	35	0.13	11
2.	4-UnMA 7.10 (0.02)	10.158 (0.04)	40	0.15	11
3.	6-UnMA 8.32 (0.0227)	10.98 (0.045)	45	0.13	13
4.	8-UnMA 10.638 (0.027)	13.18 (0.054)	35	0.14	17
5.	18-UnMA 9.85 (0.025)	12.2 (0.05)	30	0.12	16
6.	10-UnMA 10.55 (0.025)	12.2 (0.05)	45	0.1	18
7.	12-UnMA 6.94 (0.0154)	7.454 (0.030)	25	0.1	10
8.	14-UnMA 7.22 (0.015)	7.286 (0.030)	25	0.1	10
9.	16-UnMA 7.42 (0.0146)	7.091 (0.0293)	25	0.1	6
10.	18-UnMA 8.43 (0.0157)	7.598 (0.0314)	25	0.1	11
11.	22-UnMA 6.42 (0.0108)	4.985 (0.02)	25	0.03	7

* mentioned in parentheses

Table 13

n-Octadecyl esters of Poly(n-alkyl undecylenate-Co-maleic anhydride)

Sr. No.	Copolymer in g. and (mole)*	n-Octadecanol in g. and (mole)*	Xylene in ml	H_2SO_4 in ml	Yield in g.
1.	2-UnMA 6.71 (0.0216)	11.664 (0.043)	35	0.1	12
2.	4-UnMA 6.82 (0.02)	10.887 (0.04)	40	0.05	11
3.	6-UnMA 8.24 (0.0225)	12.15 (0.045)	45	0.13	12
4.	8-UnMA 10.638 (0.027)	14.58 (0.054)	45	0.15	16
5.	18-UnMA 9.85 (0.025)	13.5 (0.05)	40	0.1	15
6.	10-UnMA 6.12 (0.0145)	7.83 (0.029)	25	0.1	8
7.	12-UnMA 6.82 (0.0152)	8.181 (0.03)	25	0.1	7
8.	14-UnMA 7.42 (0.0752)	8.377 (0.031)	25	0.1	10
9.	16-UnMA 7.32 (0.0144)	7.695 (0.028)	25	0.1	6
10.	18-UnMA 8.24 (0.0154)	8.316 (0.0308)	25	0.1	9
11.	22-UnMA 4.32 (0.0073)	3.958 (0.0146)	20	0.02	5

* mentioned in parenthesis

Table 14

n-Docosyl esters of Poly(n-alkyl undecylenate-Co-maleic anhydride)

Sr. No.	Copolymer in g. and mole*	n-Docosanol ~~and~~ in g. and mole*	Xylene in ml	H_2SO_4 in ml	Yield in g.
1.	2-UnMA 6.82 (0.022)	14.34 (0.044)	35	0.12	12
2.	4-UnMA 6.52 (0.019)	12.388 (0.038)	40	0.05	11
3.	6-UnMA 8.12 (0.0221)	14.40 (0.044)	45	0.13	15
4.	8-UnMA 10.638 (0.027)	17.01 (0.054)	45	0.16	20
5.	18-UnMA 9.85 (0.025)	15.75 (0.05)	40	0.1	16
6.	10-UnMA 6.21 (0.0147)	9.584 (0.029)	25	0.1	10
7.	12-UnMA 6.74 (0.0149)	9.747 (0.029)	25	0.1	10
8.	14-UnMA 7.23 (0.0151)	9.845 (0.03)	25	0.1	7
9.	16-UnMA 7.22 (0.0142)	9.296 (0.028)	25	0.1	12
10.	18-UnMA 8.13 (0.015)	9.91 (0.030)	25	0.1	11
11.	22-UnMA 4.20 (0.0071)	4.646 (0.014)	20	0.02	6

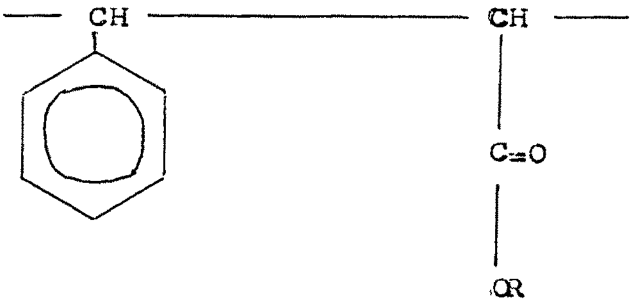
* mentioned in parenthesis

Experimental II

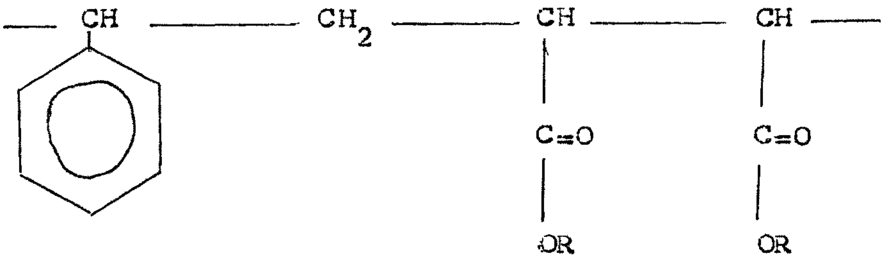
Esters of Poly(n-Alkyl Cinnamate-Co-maleic Anhydride)

General :

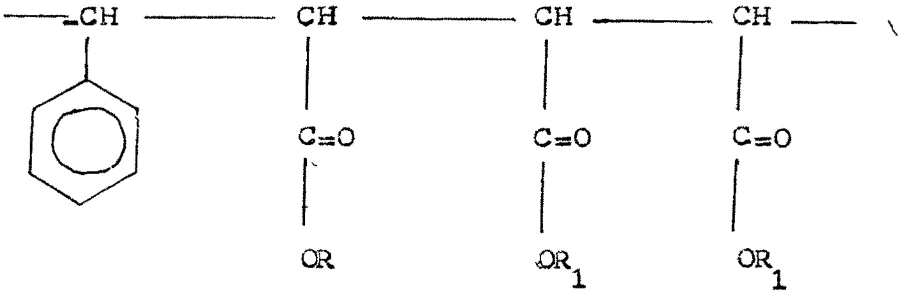
Homopolymers of higher alkyl cinnamates prepared in bulk or emulsion with peroxide catalyst are known to depress the pour point of lubricating oils (460). Copolymers of styrene and higher alkyl maleates are efficient pour point depressants for waxy crude oils (461).



I. Poly alkyl cinnamate

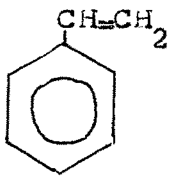


II. Poly(Styrene-Co-dialkyl maleate)

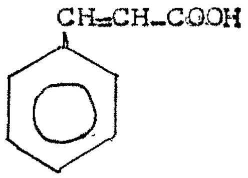


III. Poly(alkyl cinnamate-Co-dialkyl maleate)

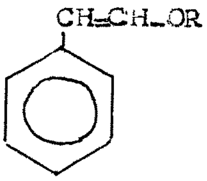
Cinnamic acid is a derivative of styrene-beta substituted styrene.



Styrene



Cinnamic acid



2-phenyl vinyl
alkyl ether

Copolymerization behaviour of cinnamic acid, cinnamates and 2-phenyl vinyl alkyl ethers are similar to styrene (462). But the reactivity is comparatively less due to the less electron density at the vinyl double bond. Cinnamic esters homopolymerize readily than cinnamic acid (463). Copolymerization reactions of cinnamic acid, its derivatives and related compounds are extensively dealt with by Marvel et al., (464). A number of patents and papers cover copolymerization of cinnamaldehyde (465), cinnamic acid (466, 467), cinnamic esters (460, 468-472), cinnamonitrile and derivatives (472-474). Terpolymerization of acrylonitrile, styrene and esters of alpha cyano cinnamic acid and the study of the nature of the products is described in a series of two papers by Ronel and Kohn (475).

Very little work is reported on the copolymerization behaviour of cinnamic esters with maleic anhydride and utilization of the copolymers for industrial purposes. On observing the structure II and III it may be seen that III with one more additional pendant chain may behave better than a styrene copolymer II. Products of this class are copolymers of cinnamic esters, both short chain alkyl and long chain alkyl with dialkyl maleates.

EXPERIMENTAL

1. n-Alkyl Cinnamates :

Method :

Cinnamic esters were prepared from cinnamic acid and the corresponding alcohols in the usual manner using sulfuric acid as the catalyst for esterification similar to the preparation of esters of undecylenic acid. Ethyl cinnamate was prepared using excess of absolute ethanol while higher alkyl cinnamates, viz., C_{10} to C_{18} and C_{22} by the azeotropic distillation method using sulfuric acid as catalyst and toluene as the azeotroping agent.

Equimolar quantities of the acid and the corresponding higher alcohol though sufficient, 5% excess of cinnamic acid was used in order that no fatty alcohol in the crude product was left unreacted. After esterification the crude product was diluted further with toluene, neutralized with dilute $NaHCO_3$ solution after drying over anhydrous Na_2SO_4 was distilled to get the crude product. The esters of C_2, C_{10} to C_{16} were vacuum distilled to purify where as C_1, C_{18} to C_{22} esters were crystallized out of acetone. The purity has been ascertained by saponifaction. The details of esterification experiment are summarized in Table 15.

2. Copolymerization of cinnamic esters with maleic anhydride : Poly(n-alkyl cinnamate-Co-maleic anhydride) :

Synthesis of maleic anhydride copolymer with 2-phenyl vinyl alkyl ether is reported (476) where a 1:1 alternating copolymer is produced under the free radical catalytic conditions. All of the eleven copolymers of this class were synthesized using a single method.

EXPERIMENTAL ASSEMBLY

The polymerization was carried out in the absence of light by lagging the polymerization flask using thick black paper in order to avoid photochemical effect (477, 478).

Method :

The process is developed a new in this investigation. First introduced solvent benzene into

Table 15

n-Alkyl cinnamates

Sr. No.	Code	Raw materials				Yield in gm	Results			
		Cinnamic acid in g & (mole*)	Alcohol in g & (mole*)	H_2SO_4 in ml	Toluene in ml		Physical appearance	Acid value	Ester value	% Ester
1.	1-C	42.92 (0.29)	Methanol 19.2 (0.6)	0.4	-	45	Cream coloured solid	-	-	-
2.	2-C	59.2 (0.4)	Ethanol 46 (1)	1	-	65	Colourless liquid	0.5	316.25	99.2
3.	4-C	34.125 (0.21)	n-butanol 16.206 (0.21)	0.2	100	45	Dark brown liquid	-	-	-
4.	6-C	30 (0.202+5%)	n-Hexanol 20.67 (0.202)	0.2	80	47	Dark brown liquid	-	-	-
5.	8-C	30 (0.202+5%)	n-Octanol 23.92 (0.202)	0.2	80	50	Dark brown liquid	-	-	-
6.	10-C	18.9 (0.12+5%)	n-Decanol 19.118 (0.121)	0.13	50	35	Colourless viscous	0.12	195.1	100.15

cont....

Table 15 cont....

7.	12-C	38.85 (0.25+5%)	n-Dodecanol 46.6 (0.25)	0.25	110	75	Colourless viscous liquid	0.4	172.0	96.88
8.	14-C	31.71 (0.204+5%)	n-Tetradecanol 43.656 (0.204)	0.2	100	70	Colourless viscous liquid	0.36	160.64	98.5
9.	16-C	31.08 (0.20+5%)	n-Hexadecanol 48.4 (0.20)	0.2	100	73	Pale yeloow liquid	0.21	145.7	96.61
10.	18-C	38.85 (0.25 + 5%)	n-Octadecanol 67.5 (0.25)	0.25	120	97	Pale yellow needles	0.1	135.8	96.82
11.	22-C	38.85 (0.25 + 5%)	n-Docosanol 81.5 (0.25)	0.25	130	110	White needles	0.1	120.0	95.19

1-C and 2-C stands for methyl cinnamates and ethyl cinnamates ; similarly for others

* mentioned in parenthesis

the polymerization flask. Then n-alkyl cinnamate esters was charged along with maleic anhydride, in 1:1 mole ratio and purged with pure dry nitrogen to free it from oxygen. Nitrogen passing was continued so that the reactants were always blanketted with nitrogen atmosphere. The maleic anhydride dissolved in the solution of n-alkyl cinnamate ester and benzene on heating to 50°C under stirring. Then the solution was cooled to 30°C. Lauryl peroxide was dissolved in benzene and taken in a small droping funnel which was previously purged with nitrogen and kept under nitrogen. The catalyst solution was introduced into the flask just before commencement of heating. Once catalyst addition was over, heating was gradually started in such a way that the temperature of the mass attained at 70°C. Then the mass becomes viscous as indicated by the difficulty in stirring. Stirring rate at this stage was increased to facilitate thorough mixing. The exothermic nature of the polymerization raised the temperature to 80°C which lasted for 20 minutes. When the heat evolution ceased the mass was heated to 70°C and kept constant for 18 hrs.

The benzene solution was concentrated by distilling under reduced pressure and taken out in hot condition and evaporated as a thin layer under $60^{o}C/25"$ Hg vacuum for 7 to 8 hrs. Then the copolymers purified by solvent non-solvent method. In most of the cases solvent is benzene and nonsolvent cold methanol. Again dried the copolymers under $60^{o}C/25"$ Hg vacuum for 24 hrs. and then taken for the preparation of dialkyl esters. The details of the experiment are summarized in Table 16.

3. Analysis and characterization

(i) C and H analysis of anhydride copolymer :

The actual C and H content determined were compared with calculated values for a copolymer composition of 1:1 monomer ratio. Their results are incorporated in Table 17.

(ii) Solution Visocisity :

Inherent viscosity of the anhydride copolymer except 1-CMA and 2-CMA determined in toluene at $30^{o}C$ using Ubbelohde viscometere. The solution viscosity of 1-CMA and 2-CMA of anhydride copolymers are determined in Dimethyl sulfoxide. The results are given in Table 18.

(iii) Molecular weight :

The molecular weight of 2-CMA was determined by Rast's method, vapour pressure osmometer and Gel permeation chromatography. Results are tabulated in Table 18.

(iv) IR Spectra-

The I.R. Spectrum of 2-CMA is shown in Fig. 10. The analysis of spectral data is given in Table 19.

Table 16

Poly(n-alkyl cinnamate-Co-maleic anhydride)

Sr. No.	Code of copolymer	Raw materials				Yield in gm	Appearance
		n-alkyl cinnamates in g and mole*	Maleic anhydride in g and mole*	Lauryl peroxide in g (% on wt.)	Benzene in ml		
1.	1-CMA	1-C 59.32 (0.363)	35.67 (0.363)	0.949 (1%)	120	80	White powder
2.	2-CMA	2-C 45 (0.25)	24.5 (0.25)	0.695 (1)	65	60	White powder
3.	4-CMA	4-C 40.5 (0.198)	19.45 (0.198)	0.60 (1)	80	50	Cream coloured powder
4.	6-CMA	6-C 42 (0.181)	17.74 (0.181)	0.60 (1)	85	56	Cream coloured powder
5.	8-CMA	8-C 45 (0.173)	16.954 (0.173)	0.619 (1)	90	56	Cream coloured powder

cont....

Table 16 cont...

6.	10-CMA	10-C 45 (0.156)	15.31 (0.156)	0.603 (1)	90	55	Cream coloured & waxy
7.	12-CMA	12-C 51 (0.161)	15.796 (0.161)	0.668 (1)	100	60	Cream coloured & waxy
8.	14-CMA	14-C 55 (0.156)	15.37 (0.156)	0.7067 (1)	110	58	Cream coloured & waxy
9.	16-CMA	16-C 35 (0.094)	9.22 (0.094)	0.442 (1)	55	38	Cream coloured & waxy
10.	18-CMA	18-C 30 (0.092)	9.04 (0.092)	0.3904 (1)	45	35	Pale yellow & waxy
11.	22-CMA	22-C 36.22 (0.079)	7.766 (0.079)	0.439 (1)	40	40	Cream coloured powder

2-CMA stands for poly(ethyl cinnamate-Co-maleic anhydride) ; similarly for others

* mentioned in parenthesis

Table 17

Elemental analysis of the copolymer Poly(n-alkyl Cinnamate-Co-maleic anhydride)

Sr. No.	Copolymer code (Mole. formula - Mole. wt. of the repetition unit)	Percentage of C and H			
		Calculated for 1:1		Actual	
		C	H	C	H
1.	1-CMA ($C_{14}H_{12}O_5$=260)	64.61	4.61	64.12	4.02
2.	2-CMA ($C_{15}H_{14}O_5$=274)	65.69	5.10	64.96	4.98
3.	4-CMA ($C_{17}H_{18}O_5$=302)	67.54	5.9	67.23	5.41
4.	6-CMA ($C_{19}H_{22}O_5$=330)	69.09	6.66	68.86	6.21
5.	8-CMA ($C_{21}H_{26}O_5$=358)	70.39	7.26	69.98	7.13
6.	10-CMA ($C_{23}H_{30}O_5$=386)	71.50	7.77	71.19	7.52
7.	12-CMA ($C_{25}H_{34}O_5$=414)	72.46	8.21	72.33	7.91
8.	14-CMA ($C_{27}H_{38}O_5$=442)	73.30	8.59	73.04	8.21
9.	16-CMA ($C_{29}H_{42}O_5$=470)	74.04	8.93	73.56	8.79
10.	18-CMA ($C_{31}H_{46}O_5$=498)	74.69	9.23	74.32	8.94
11.	22-CMA ($C_{34}H_{52}O_5$=540)	75.55	9.62	75.16	9.54

Table 18

Copolymers of alkyl cinnamate and maleic anhydride

Sr. No.	Copolymer Code	Inherent viscosity dl/g of anhydride copolymer (a)	Molecular weight M_n
1.	1-CMA	0.1972 (b)	2896 (c), 2779 (d), 2798 (e)
2.	2-CMA	0.1867 (b)	
3.	4-CMA	0.1534 (b)	
4.	6-CMA	0.523	
6.	8-CMA	0.169	
6.	10-CMA	0.153	4194 (c)
7.	12-CMA	0.193	
8.	14-CMA	0.156	
9.	16-CMA	0.142	
10.	18-CMA	0.167	
11.	22-CMA	0.185	

(a) determined in toluene at 30°C

(b) determined in dimethyl sulfoxide at 30°C

(c) by vapour pressure osmometry against Dibenzyl as std. in DMF at 70°C (Hewlett Packard V.P.O. Model 302 B)

(d) by Rast's Camphor method

(e) determined in tetrahydrofuran solution against std. polys styrene by (Gel-Permeation Chromatography, Varian Vista 401-Apple II) .

Table 19

Analysis of the I.R. Spectral data* Poly(n-alkyl cinnamate-Co-maleic anhydride)

Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}	Reference
920, 960	Cyclic anhydride, Maleic anhydride unit in copolymer	960-930	(452)
1020	Maleic anhydride unit	1230,1070 and 930	(453)
1860	Cyclic anhydride	1860	(452)
1780, 1720	C=O stretching	1850-1770	(479)
3040, 1500, 1210	Mono substituted benzene, aromatic C-H stretching	3080 1610-1440	(479) (480)
	Enolic hydroxyl. Free ester carbonyl was not observed at about 1750 cm^{-1} (This can be explained due to the presence of endization of ester carbonyl which is stabilized by seven membered hydrogen bonding with the anhydride carbonyl)	3500-3100	(454)

* Perkin-Elmer Part No. 5100 4267

Solvent = Chloroform

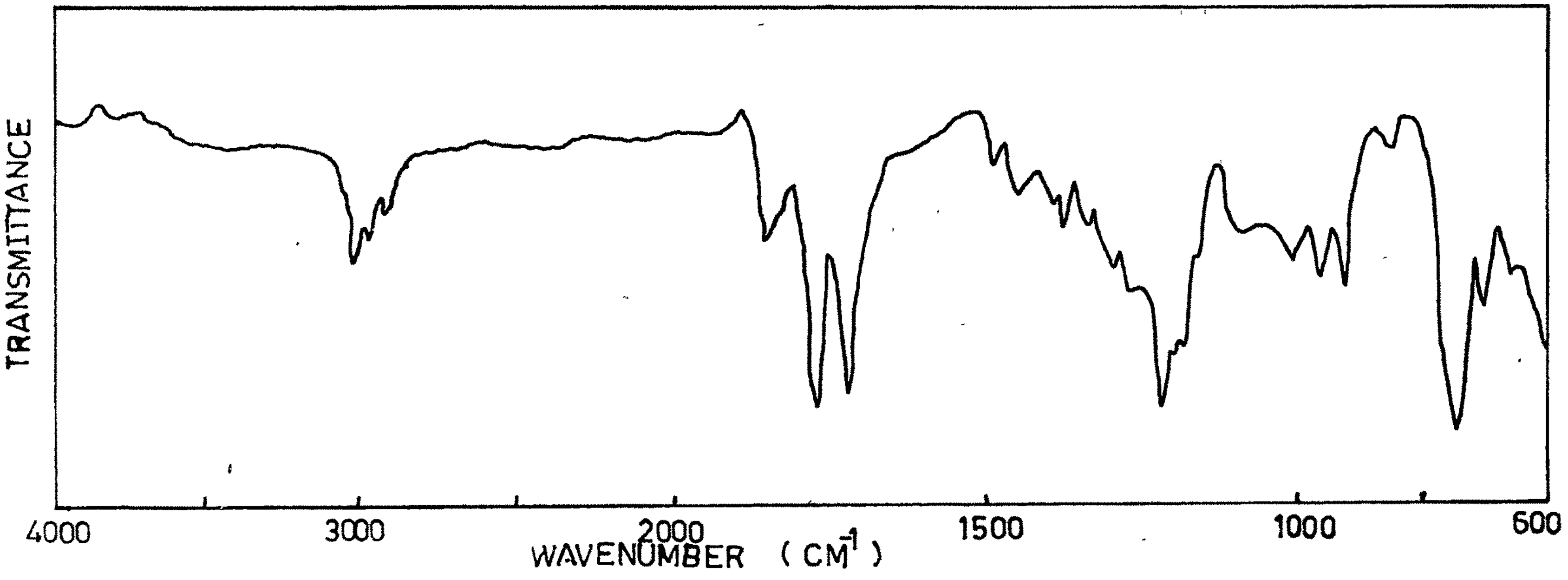


FIG 10 IR SPECTRA OF 2-CMA

4. Esterification of Anhydride Copolymers : Poly(n-alkyl cinnamate-Co-dialkyl maleate)

After characterizing the copolymers, all were esterified with fatty alcohols of chain length C_{14} to C_{18} and C_{22} to produce the respective maleates. Xylene was used as the medium of the reaction as well as the azeotroping agent and conc. H_2SO_4 and para-toluene sulfonic acid as catalysts of esterification.

EXPERIMENTAL ASSEMBLY

The set up for esterification used here also was the same as used for the preparation of undecyl ester maleate copolymers.

Method :

Proportion of the reagents used in the esterification.

Fatty alcohols

Two moles of the corresponding alcohol were used for every mole of the copolymer. Molecular weight of the copolymer was calculated as the sum of molecular weights of alkyl cinnamate and maleic anhydride.

Xylene

The proportion of xylene to the copolymer was maintained between 20 - 30 ml per 0.01 mole. This was fixed based on the ease of dissolution of the copolymer and the rate of the reaction.

H_2SO_4

3.5 to 4.5 ml of sulfuric acid per mole of the copolymer was used as catalyst.

PTSA

35 to 45 grams of p-toluene sulfonic acid per mole of copolymer was found to be necessary in addition to H_2SO_4 catalyst for a faster esterification.

Temperature Conditions

The major portion of the esterification was carried out between 140 - 150°C. This was the normal refluxing temperature of the reaction medium. To complete the esterification as far as possible, towards the last stage of the reaction, a part of xylene was withdrawn so that the temperature increased to 165-170°C. It was felt that increasing the temperature to more than 170°C could have increased the extent of esterification. But taking into consideration the possible polymer degradation at higher temperature (455), further increase in temperature was not resorted to. All of the ester preparation took 25 - 30 hrs for an optimum level of esterification.

Isolation and Purification

After the completion of the esterification all the products were diluted with fresh xylene. This was only with a veiw to increasing the rate of filtration at the later stage. After cooling to 30°C the crude ester solution was stirred with a pinch of $NaHCO_3$ powder for 2 hrs to complete the neutralization of the mineral and sulfonic acid (acidity) if present. After settling the precipitate the clear solution was filtered through a bed of Hyflow Supercel. The crude product was freedfrom the solvent to a ~~mx~~ maximum extent by distillation out xylene. The concentrated ester was then poured into excess of acetone under vigorous agitation to get a granular precipitate. After isolation from the acetone medium and evaporation of acetone, the product was once again dissolved in acetone. Filtration of the product, evaporation of residual acetone and finally drying under vacuum at 50°C/25" Hg for 18 to 20 hrs produced the ester in the final form.

The quantities of raw materials used in each esterification are tabulated in Table 20 to 23.

Table 20

n-Tetradecyl ester of Poly(n-alkyl cinnamate-Co-maleic anhydride)

Sr. No.	Copolymer in g and mole*	n-Tetradecanol in g and mole*	Xylene in ml	H_2SO_4 PTSA ml/g	Yield in g.
1.	1-CMA 7.23 (0.027)	11.556 (0.054)	50	$\frac{0.1}{0.892}$	14
2.	2-CMA 6.92 (0.025)	10.80 (0.05)	45	$\frac{0.1}{0.880}$	12
3.	4-CMA 7.42 (0.024)	10.5 (0.048)	50	$\frac{0.1}{0.944}$	13
4.	6-CMA 6.84 (0.02)	8.871 (0.04)	40	$\frac{0.1}{0.765}$	10
5.	8-CMA 8.12 (0.022)	9.672 (0.045)	50	$\frac{0.1}{0.791}$	12
6.	10-CMA 7.02 (0.018)	7.746 (0.036)	40	$\frac{0.1}{0.633}$	9
7.	12-CMA 8.32 (0.02)	8.56 (0.04)	45	$\frac{0.1}{0.70}$	11
8.	14-CMA 7.22 (0.016)	6.976 (0.032)	40	$\frac{0.1}{0.570}$	9
9.	16-CMA 7.05 (0.015)	6.51 (0.03)	40	$\frac{0.1}{0.75}$	8
10.	18-CMA 6.10 (0.0122)	5.22 (0.024)	35	$\frac{0.1}{0.427}$	7
11.	22-CMA 7.02 (0.012)	5.39 (0.024)	35	$\frac{0.1}{0.441}$	6

* mentioned in parenthesis

Table 21

n-Hexadecyl Ester of Poly(n-alkyl cinnamate-Co-maleic anhydride)

Sr. No.	Copolymer in g and mole*	n-Hexadecanol in g and mole*	Xylene in ml	H_2SO_4 PTSA in ml/g	Yield in g
1.	1-CMA 7.45 (0.028)	12.26 (0.056)	60	$\frac{0.12}{0.92}$	12
2.	2-CMA 7.22 (0.026)	12.753 (0.052)	60	$\frac{0.1}{0.94}$	12
3.	4-CMA 8.35 (0.027)	12.358 (0.055)	60	$\frac{0.1}{0.966}$	13
4.	6-CMA 9.32 (0.028)	13.64 (0.056)	50	$\frac{0.1}{0.987}$	15
5.	8-CMA 7.85 (0.021)	10.599 (0.042)	50	$\frac{0.1}{0.766}$	12
6.	10-CMA 7.32 (0.018)	9.147 (0.036)	45	$\frac{0.1}{0.64}$	11
7.	12-CMA 8.24 (0.019)	9.631 (0.039)	45	$\frac{0.1}{0.696}$	12
8.	14-CMA 8.82 (0.019)	9.63 (0.038)	40	$\frac{0.1}{0.70}$	12
9.	16-CMA 4.50 (0.009)	4.598 (0.018)	25	$\frac{0.08}{0.335}$	6
10.	18-CMA 6.28 (0.012)	6.001 (0.024)	25	$\frac{0.1}{0.43}$	6
11.	22-CMA 6.82 (0.012)	5.593 (0.024)	25	$\frac{0.1}{0.43}$	6

* mentioned in parenthesis

Table 22

n-Octadecyl ester of Poly(n-alkyl cinnamate-Co-maleic anhydride)

Sr. No.	Copolymer in g and mole*	n-Octadecanol in g and mole*	Xylene in ml	H_2SO_4/ PTSA in ml/g	Yield in g
1.	1-CMA 5.40 (0.02)	11.178 (0.04)	35	$\frac{0.1}{0.759}$	11
2.	2-CMA 7.12 (0.025)	14.032 (0.05)	50	$\frac{0.1}{0.906}$	15
3.	4-CMA 8.42 (0.027)	15.012 (0.054)	50	$\frac{0.1}{0.973}$	12
4.	6-CMA 9.65 (0.029)	15.768 (0.058)	50	$\frac{0.1}{1.0}$	17
5.	8-CMA 7.75 (0.0216)	11.66 (0.043)	45	$\frac{0.1}{0.756}$	12
6.	10-CMA 7.22 (0.018)	10.098 (0.037)	45	$\frac{0.1}{0.64}$	11
7.	12-CMA 8.43 (0.02)	10.962 (0.04)	50	$\frac{0.1}{0.71}$	12
8.	14-CMA 8.72 (0.019)	10.63 (0.039)	50	$\frac{0.1}{0.689}$	12
9.	16-CMA 4.72 (0.010)	5.422 (0.02)	35	$\frac{0.07}{0.35}$	6
10.	18-CMA 6.10 (0.012)	6.588 (0.024)	40	$\frac{0.1}{0.427}$	8
11.	22-CMA 6.52 (0.011)	5.94 (0.022)	35	$\frac{0.1}{0.385}$	6

* mentioned in parenthesis

Table 23

n-Docosyl ester of Poly(n-alkyl cinnamate-Co-maleic anhydride)

Sr. No.	Copolymer in g and mole*	n-Docosanol in g. and mole*	Xylene in ml	H_2SO_4/ PTSA in ml/g	Yield in g.
1.	1-CMA 5.50 (0.021)	13.75 (0.042)	50	$\frac{0.1}{0.738}$	10
2.	2-CMA 7.52 (0.027)	18.84 (0.054)	60	$\frac{0.1}{0.959}$	16
3.	4-CMA 8.22 (0.02)	17.73 (0.04)	60	$\frac{0.1}{1.0}$	14
4.	6-CMA 9.42 (0.02)	18.58 (0.04)	60	$\frac{0.1}{1.0}$	15
5.	8-CMA 7.54 (0.021)	13.692 (0.042)	50	$\frac{0.1}{0.735}$	12
6.	10-CMA 7.12 (0.018)	11.996 (0.036)	50	$\frac{0.1}{0.644}$	11
7.	12-CMA 8.22 (0.019)	12.909 (0.039)	50	$\frac{0.1}{1.0}$	13
8.	14-CMA 8.42 (0.019)	12.388 (0.038)	50	$\frac{0.1}{1.0}$	13
9.	16-CMA 4.50 (0.0095)	6.242 (0.018)	40	$\frac{0.07}{0.435}$	6
10.	18-CMA 5.80 (0.0116)	7.593 (0.022)	40	$\frac{0.1}{0.385}$	6
11.	22-CMA 6.22 (0.011)	7.33 (0.022)	40	$\frac{0.1}{0.385}$	6

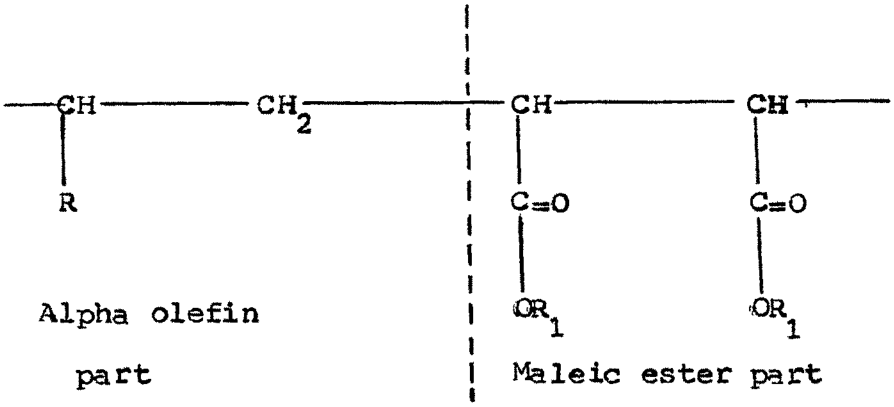
* mentioned in parenthesis

Experimental III

ESTERS OF POLY (n-ALPHA MONO OLEFIN-CO-MALEIC ANHYDRIDE)

General :

Both pendant chains - those as a part of the polymer backbone and the additional ones introduced into the backbone through ester linkages, at definite intervals, are a speciality of the products of this class. A typical example is given below :



R = alkyl chain of alpha mono olefin

R_1 = alkyl chain of the fatty alcohol

These are copolymers of higher alpha mono olefins and dialkyl maleates. Generally higher alpha mono olefins may be copolymerized with maleic anhydride to 1:1 alternating (447) copolymers. Products of this class are well known and many of them are commercially exploited as flow improvers (206, 207) and to a lesser extent as viscosity index improvers for lube oils.

Alpha mono olefins in common use range from C_2 to C_{30}. The fatty alcohols usually range from nC_{12} to nC_{24}. Exceptional cases like iso-octyl ester also are reported (216). A lot many products are patented and are reported in the literature as flow improvers and pour point depressants for waxy crude oils (203, 205, 211-213, 215, 216, 223, 224). Products of this class synthesized newly in this investigation are different not only with respect to the type of alpha olefin present in them but also with respect to the molecular weight. The present work deals with the synthesis of different types of alpha olefin maleic anhydride copolymers under free-radical catalyzed polymerization conditions, conversion to the dialkyl esters and their effect on pour point and rheological properties for different Indian Crude Oils.

EXPERIMENTAL

1. Alpha Olefin maleic anhydride copolymers :

Copolymerization of alpha olefin with maleic anhydride is an extensively studied area (447, 481).

For a lower alpha olefins such as ethylene, propylene, etc., the reaction is carried out under pressure (447). For higher alpha olefins atmospheric pressure polymerization is generally reported (212).

Material of alpha mono, olefin : (Specification) :

Alpha mono olefin (Ethyl Corporation, USA)

(i) C_{14-16} mono olefin (C_{12} = 1.4%, C_{14} = 65.5%, C_{16} = 31.0% and C_{18} = 2.1%). Total mono olefin = 99.5%.

Average molecular weight calculated on the given composition } 205.38

(ii) C_{18-24} mono olefin (C_{16} = 1.0%, C_{18} = 12.8%, C_{20} = 43.6% C_{22} = 27.9%, C_{24} = 10.8%, C_{26} = 2.8% and C_{28} = 1.1%).

Average molecular weight calculated on the given composition } 293.32

Method :

(i) Poly (C_{14-16} olefin -Co-maleic anhydride)

(PA-15(1) and PA-15(2) : Code name which will be used in this investigation hereafter).

Two different copolymers were prepared under different concentrations of catalyst, viz. 1% and 0.5% polymerization conditions in all the two cases were identical.

After purging the polymerization set up first introduced solvent benzene into the polymerization flask. Then C_{14-16} mono olefin was charged along with maleic anhydride, in 1:1 mole ratio. Under a slow stream of nitrogen the mixture was heated to 50°C with stirring. The solution was cooled to 30°C and the benzene solution of benzoyl peroxide (1% on the total weight of monomers) was charged into the reaction flask and thoroughly mixed under stirring. Then the contents were gradually heated up 70°C and kept constant. Heating was cut off at this stage. The slight exothermic nature of the reaction was sufficient to keep the temperature. After sometime the exothermic nature lasted for about 30 minutes and thereafter maintain the temperature at 70°C const. for about 16 hrs.

The benzene solution was concentrated by distilling under reduced pressure and taken out in hot condition. Then purified by solvent non solvent method.

The product was then evaporated in thin layer at 60°C/25" Hg vacuum for 20 hrs. and crushed to a cream coloured solid.

(ii) Poly (C_{18-24} olefin-Co-maleic anhydride) (PA-21(1) and PA-21(2) : Code names which will be used in this investigation hereafter).

Method is same as in the case of PA-15 copolymerization. All the four copolymers were used for the preparation of the alkyl esters.

The details regarding quantities of monomers, catalyst, etc ; are tabulated in Table 24.

2. Analysis and Characterization :

(i) C and H analysis of anhydride copolymer Table 25.

(ii) Solution viscosity of anhydride copolymers Table 25.

(iii) Molecular weight. Table 25.

Table 24

Copolymers of alpha olefins and maleic anhydride

Sr. No.	Copolymer Code	Raw material			Benzene in ml	Yield in g.	Appearance
		Alpha olefin in g & mole*	Maleic anhydride in g. and mole*	Benzoyl peroxide in g(% wt) (c)			
1.	PA-15(1)	51.345 (a) (0.25)	24.5 (0.25)	0.758 (1%)	110	65	Cream coloured powder
2.	PA-15(2)	51.345 (a) (0.25)	24.5 (0.25)	0.378 (0.5%)	110	68	Cream coloured powder
3.	PA-21(1)	35.198 (b) (0.12)	11.76 (0.12)	0.469 (1%)	80	40	Pale yellow waxy
4.	PA-21(2)	35.198 (b) (0.12)	11.76 (0.12)	0.234 (0.5%)	80	41	Pale yellow waxy

* mentioned in parenthesis

(a) C_{14-16} alpha olefin

(b) C_{18-24} alpha olefin

(c) % weight on the total weight of monomer

Table 25

Copolymers of alpha olefin and maleic anhydride

Sr. No.	Copolymer code (Mol. formula = Mole. wt.* of the repetition unit)	Percentage of C and H of anhydride copolymer				Inherent viscosity of anhydride copolymer dl/g	Molecular weight $\bar{M}_n$
		Calculated for 1:1		Actual			
		C	H	C	H		
1.	PA-15(1) (C18.0 H31.0 O3 = 303.0)	73.84	10.33	72.94	9.96	0.0851	2234(b), 2094(c) 3082(d)
2.	PA-15(2) (C18.0 H31.0 O3 = 303.0)	73.84	10.33	71.78	9.67	0.0912	
3.	PA-21(1) (C24.0 H43.0 O3 = 391.0)	76.52	11.22	74.58	10.87	0.0671	2470(b), 3241(c)
4.	PA-21(2) (C24.0 H43.0 O3 = 391.0)	76.52	11.22	76.13	10.94	0.0653	

* given in parenthesis

(a) determined in toluene at 30°C

(b) by Vapour pressure osmometry against Dibenzyl as std. in DMF at 70°C.

(c) by Rast's Camphor method

(d) determined in tetrahydrofuran solution against std. polystyrene by (Gel Permeation chromatography)

Table 26

Analysis of the I.R. spectral data* : PA-15(1)

Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}	Reference
750	Skeletal vibration of $-(CH_2)_n-$ chain	750	(480)
930-925	Maleic anhydride unit in copolymers	930(s) 730(w)	(453)
960	Cyclic anhydride	960	(452,482,479)
1700	Carboxylic acid ; due to race absorption of moisture and hydrolysis of the anhydride	1705 1725 1740-1660	(482,479)
1775	Cyclic anhydride in copolymers	1765	(452,482)
1840	Cyclic anhydride group in copolymers	1840	(452,482)
3200-3150(sh)	Carboxylic acid impurity due to the partial hydrolysis of the cyclic anhydride ring	3200-3150	(482)
2900-2840	$-CH_2-$ absorption due to vinyl polymer backbone	2930-2860	(482)

* Perkin-Elmer part No. 5100 4367

Solvent = Chloroform

Table 27

Analysis of the I.R. Spectral data* : PA-21(1)

Absorption at cm^{-1}	Assignment	Characteristic absorption cm^{-1}	Reference
725	Skeletal vibration of $-(CH_2)_n-$ chain	750	(480)
910	Maleic anhydride unit in copolymer	930(s) 730(w)	(453)
960	Cyclic anhydride	960	(452,482,486)
1700	Carboxylic acid ; due to race absorption of moisture and hydrolysis of the anhydride	1705 1725 1740– 1660	(482,486)
1760	Cyclic anhydride in copolymers	1765	(452,482)
3200– 3150(sh)	Carboxyl acid impurity due to the partial hydrolysis of the cyclic anhydride ring	3200– 3150	(482)
1830	Cyclic anhydride group in copolymers	1840	(452,482)
2900 2820	$-CH_2-$absorption due to vinyl polymer backbone	2930– 2860	(482)

* Perkin-Elmer part No. 5100 4367

Solvent = Chloroform

(iv) Spectroscopic studies :

IR Spectra of PA-15(1) and PA-21(1) were taken in chloroform. Spectral data is given in Tables 26 and 27 (Fig. 11).

3. Esterification of Anhydride Copolymers :

Poly(n-alpha olefin-Co-dialkyl maleate) :

All the four polyanhydride copolymers of this class were esterified into the corresponding diesters. Conc. H_2SO_4 was used as the esterification catalyst and solvent xylene as the medium of the reaction as well as the azeotroping agent.

Method :

The experimental set up used for the preparation of the esters is same as

For a constant reflux and azeotroping after a few pilot experiments the following properties were fixed :

Xylene	:	15 to 30 ml for 0.01 mole of anhydride copolymer.
H_2SO_4	:	3 ml to 5.8 ml per mole of anhydride copolymer.

Fatty alcohol : two moles per mole of the copolymer.

The esterification method is same as used in the case of undecylenic ester copolymer.

Types of fatty esters :

Esters of fatty alcohols ranging from n-tetradecyl to n-octadecyl and n-docosyl were prepared. The details of the esterification experiment are tabulated in Tables 28 to 31.

Table 28

n-Tetradecyl ester of Poly(n-alpha mono olefin-Co-maleic anhydride)

Sr. No.	Copolymer in g and mole*	n-Tetra-decanol in gm & mole*	Xylene in ml	H_2SO_4 in ml	Yield in gm
1.	PA-15 (1) 9.32 (0.024)	5.203 (0.048)	50	0.1	10
2.	PA-15 (2) 6.158 (0.020)	8.688 (0.04)	50	0.1	10
3.	PA-21 (1) 8 (0.02)	8.68 (0.04)	55	0.1	10
4.	PA-21 (2) 5.22 (0.013)	5.709 (0.026)	30	0.1	7

* mentioned in parenthesis

Table 29

n-Hexadecyl ester of poly(n-alpha olefin -Co-maleic anhydride)

Sr. No.	Copolymer in g. and mole*	n-Hexadecanol in g. and mole*	Xylene in ml	H_2SO_4 in ml	Yield in gm
1.	PA-15(1) 6.525 (0.022)	10.40 (0.044)	50	0.1	10
2.	PA-15(2) 9.60 (0.03)	14.64 (0.06)	55	0.1	15
3.	PA-21(1) 8 (0.02)	9.76 (0.04)	50	0.1	11
4.	PA-21(2) 5.42 (0.014)	6.703 (0.028)	40	0.1	6

* mentioned in parenthesis

Table 30

n-Octadecyl ester of poly(n-alpha olefin-Co-maleic anhydride)

Sr. No.	Copolymer in g. and mole*	n-Octadecanol in g. and mole*	Xylene in ml	H_2SO_4 in ml	Yield in g.
1.	PA-15(1) 9.552 (0.0315)	17.01	60	0.1	20
2.	PA-15(2) 6.826 (0.022)	12.15 (0.044)	50	0.1	14
3.	PA-21(1) 6.0 (0.015)	8.1 (0.03)	45	0.1	9
4.	PA-21(2) 5.32 (0.013)	7.341 (0.027)	35	0.1	8

* mentioned in parenthesis

Table 31

n-Docosyl ester of poly(n-alpha olefin-Co-maleic anhydride)

Sr. No.	Copolymer in g. and mole*	n-Docosanol in g. and mole*	Xylene in ml	H_2SO_4 in ml	Yield in g.
1.	PA-15 (1) 9.25 (0.03)	19.88 (0.061)	50	0.1	22
2.	PA-15 (2) 5.00 (0.016)	10.16 (0.033)	40	0.1	11
3.	PA-21 (1) 5.12 (0.013)	8.58 (0.026)	35	0.1	9
4.	PA-21 (2) 5.12 (0.013)	8.58 (0.026)	35	0.1	8

* mentioned in parenthesis

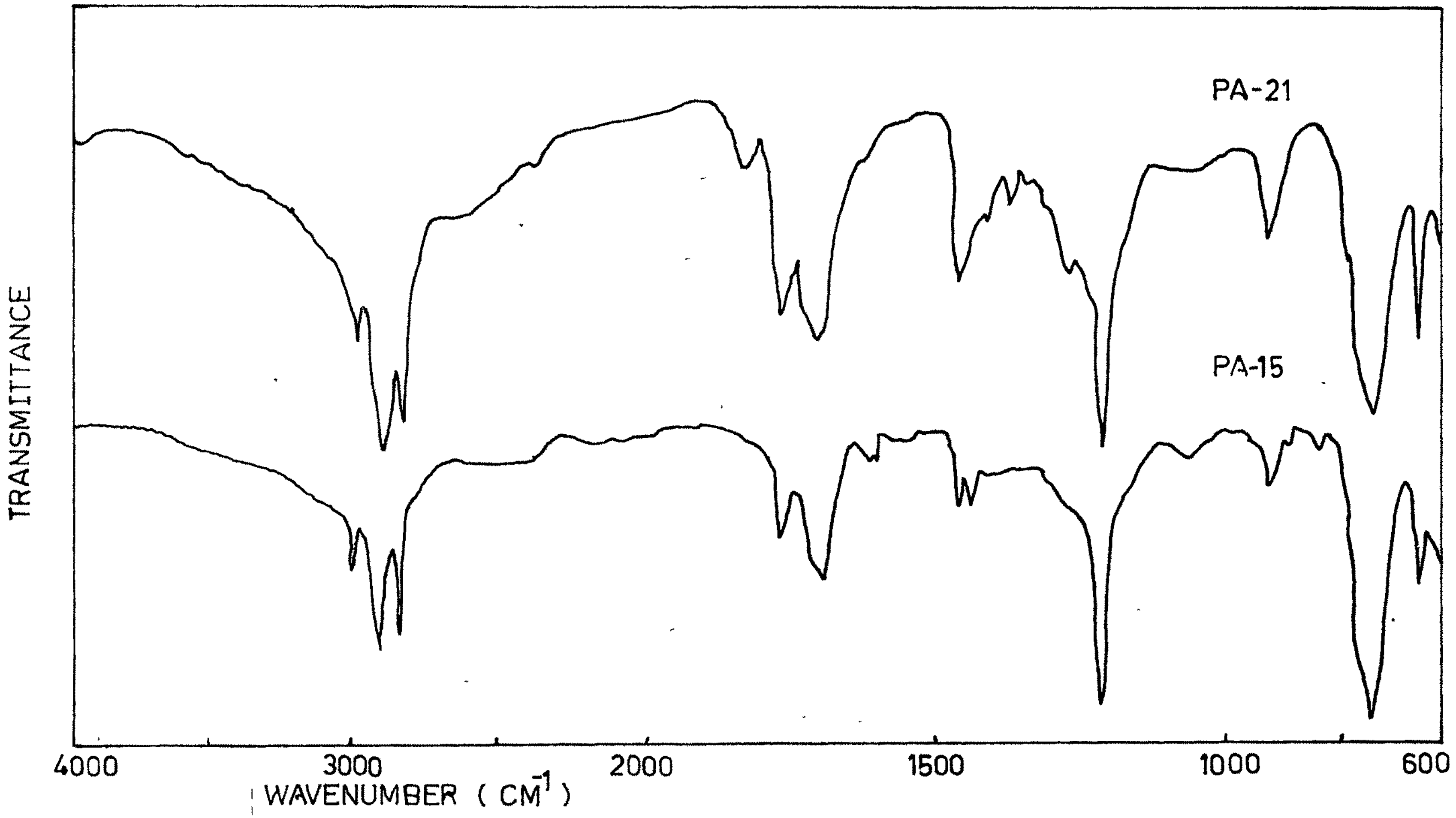


FIG **11** IR SPECTRA OF PA

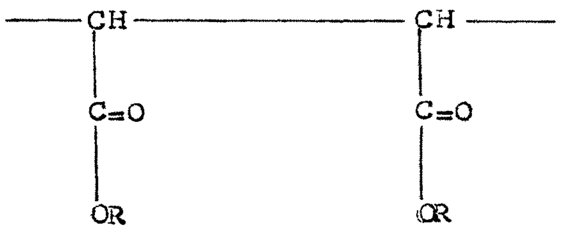
Experimental IV

POLYMERS OF DIBENENYL MALEATE

General :

Maleic anhydride does not undergo homopolymerization under normal conditions of free radical catalysed polymerization (483-494) though it can be polymerized to low degree polymers by special method (495-496). Maleic anhydride readily undergoes copolymerization with a number of vinyl monomers (497-499). A majority of them are 1:1 alternating copolymers. The readiness with which it does so increase with the increased electron density at the vinyl function of the comonomer and with decreasing sterric hindrance. Though for a long time it has been believed that disubstituted maleic anhydride would not undergo copolymerization a recent report is quite contradictory (500). Maleate and fumarate esters are known to homopolymerize to low degree polymers (286, 501, 502) and copolymerize with vinyl monomers (347, 285-304, 503).

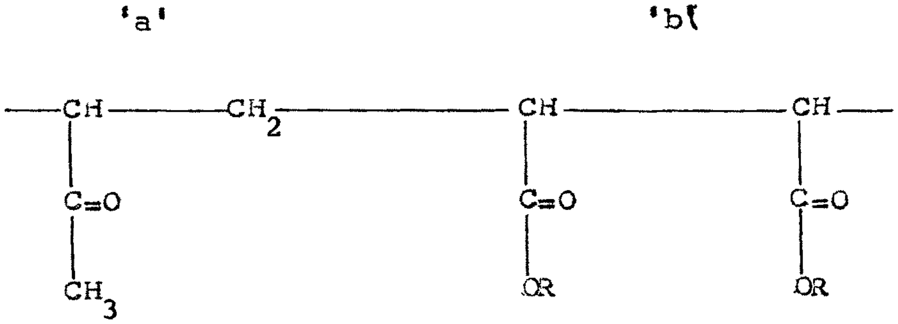
Here the desired products are synthesised to obtain maximum possible pendent chains which in other cases could not be achieved because of the limitation of direct esterification of poly anhydride copolymers with higher alcohols. Also an attempt to homopolymerize alkyl maleate (nC_{22} ester of maleic acid) to a poly alkyl succinate of the type shown below is made



$$-CH(COOR)-CH(COOR)-$$

I

Theoretically such a product (I) should have a better efficiency compared to a copolymer whose one comonomer only contributes towards a lengthy paraffinic pendant chain (II).



$$-CH(COCH_3)-CH_2-CH(COOR)-CH(COOR)-$$

II

The absence of segment 'a' from the basic repetition unit of I itself is a clear indication of higher efficiency irrespective of the influence of molecular weight on pour point depression and flow improving characteristic.

EXPERIMENTAL

Experimental Assembly :

The set up is same as in case of undecylenic ester maleic anhydride copolymers was used here too in all the experiments.

Dibehenyl maleate : (DBM)

Prepared from maleic anhydride and behenyl alcohol (1:2 mole ratio) and recrystallized from acetone.

1. Co-polymerization :

1. Poly(dibehenyl maleate-Co-vinyl acetate) :
   (Code : DBM-VAc)

Method :

First solvent benzene was taken in the polymerization flask. Then DBM along with vinyl acetate was introduced into the flask. The mixture was dissolved in benzene under stirring at 50°C. Cooled the mixture upto 30°C and then the catalyst solution in benzene was introduced drop by drop. Theh the heating was gradually increased upto 60°C and kept constant. At this time the heating was off, the exothermic nature ended between 20-25 minutes. Then maintained the temperature at 60°C for 16 hrs.

The crude product was purified by solvent nonsolvent method using acetone as nonsolvent. Then the granular precipitate upto filtration and dried at 50°C/25" Hg vacuum for 15 hrs gave the cream yellow waxy solids. Details regarding quantities of reactants etc ; are given in Table 32.

(ii) Poly(dibehenyl maleate-Co-methyl methacrylate) :
(Code : DBM-MMA)

Method :

The method is same as in (i) only the one comonomer is methyl methacrylate. Details regarding quantities of reactants, etc., are given in Table 32.

(iii) Poly(dibehenyl maleate-Co-acrylic acid) :
(Code : DBM-AA)

Method is same as in copolymerization of (i) the only change in comonomer as acrylic acid Table 32.

(iv) Poly(dibehenyl maleate-Co-maleic anhydride) :
(Code : DBM-MA)

Method is same as in the case of (i) only one comonomer is maleic anhydride Table 32.

(v) Poly(dibehenyl maleate-Co-acrylonitrile) :
(Code : DBM-AN)

Method is same as in copolymerization of (i) only one comonomer is acrylonitrile Table 32.

(vi) Poly(dibehenyl maleate-Co-itaconic anhydride) :
(Code : DBM-IA)

The copolymerization method is the same as in (i) only one comonomer is itaconic anhydride Table 32.

(vii) Poly(dibehenyl maleate) :
(Code : Poly DBM) :

Introduce solvent benzene into the polymerization flask along with DBM. Then heat the solution upto 50°C and dissolved under stirring.

Cooled to 30°C and then add the catalyst benzene solution into the flask. And maintain the temperature at 60°C for 16 hrs.

Purification of polymer by solvent nonsolvent method by using acetone-methanol (1:1) as nonsolvent. Then dried the product at 50°C/25" Hg vacuum for 15 hrs. Table 32.

2. <u>Analysis and characterization</u> :

(i)	C and H analysis	: Table 33
(ii)	Solution viscosity	: Table 33
(iii)	Molecular weight	: Table 33

The molecular weight was determined by V.P.O. ; Gel Permeation Chromatography and Rast's Camphor method.

((iv) I.R. Spectra-:

The I.R. spectrum taken in the solvent chloroform. Table 34 Fig. 12.

Table 32

Polymers of Dibehenyl maleate

Sr. No.	Dibehenyl maleate in g & mole	Comonomer in g and mole	Molar ratio of comonomers	Azobis iso-butyro nitrile in g & (% wt)	Benzene in ml.	Yield in g.	Appearance
1.	10 (0.0136)	Vinyl acetate 3 (0.0335)	1:2	0.016	40	11	White amorphous powder
2.	10 (0.0136)	Methyl meth-acrylate 3.48 (0.039)	1:2	0.016 (0.1)	40	9.4	White amorphous powder
3.	11.13	Acrylic acid 2.16 (0.0204)	1:2	0.016 (0.1)	50	11	White amorphous powder
4.	8 (0.01)	Maleic anhydride 0.98 (0.01)	1:1	0.009 (0.1)	30	7	White amorphous powder
5.	12 (0.016)	Acrylonitrile 1.74 (0.03228)	1:2	0.013 (0.1)	45	11	Pale yellow solids
6.	10 (0.0161)	Itaconic anhydride 1.8193 (0.0161)	1:1	0.0118 (0.1)	40	8	Cream coloured powder
7.	15 (0.02)	-	-	0.015 (0.1)	30	14.5	White powder

Table 33

Polymers of dibehenyl maleate

Sr. No.	Copolymer code (Mole. formula = Mole wt. of repetition unit)	% of C and H Calculated for 1:1 ratio		Actual		Inherent viscosity dt/g (a)	Molecular weight Mn
		C	H	C	H		
1.	DBM-VAc ($C_{52}H_{98}O_6$ = 818)	76.28	11.9	75.72	11.52	0.1023	5845 (b)
2.	DBM-MMA ($C_{53}H_{100}O_6$ = 832)	76.44	12.01	76.86	11.77	0.0941	
3.	DBM-AA ($C_{51}H_{96}O_6$ = 804)	76.11	11.9	76.34	11.58	0.0875	
4.	DBM-MA ($C_{52}H_{94}O_7$ = 830)	75.18	11.3	74.23	10.82	0.1268	
5.	DBM-AN ($C_{50}H_{94}O_4$ = 758)	79.15	12.40	78.85	11.89	0.0921	
6.	DBM-IA ($C_{53}H_{97}O_7$ = 845)	75.26	11.47	74.69	12.52	0.1429	
7.	Poly DBM ($C_{48}H_{92}O_4$ = 732)	78.68	12.56	77.96	12.22	0.0864	

(a) determined in toluene at 30°C

(b) determined in tetrahydrofuran solution against std. poly styrene by (Gel-Permeation chromatography, Varian Vista 401 - Apple II)

Table 34

Analysis of the I.R. Spectral data ; Polymers of dibehenyl maleates :

Absorption at cm^{-1}	Assignment	Characteristic absorption at cm^{-1}	References
i) DBM-VAc	(Perkin Elmer Part No. 5100 in chloroform soln) Fig. 12	4367	
1720	C=O stretching vibration of ester carbonyl	1900-1600	(454)
1210	-C-O stretching vibration of acetate ester	1275-1200	(451)
3000	Residual unsaturation in low degree polymer	3000	(482)
ii) DBM-MMA	in chloroform solution		
1700	C=O stretching vibration of ester carbonyl Fig. 12	1900-1600	(454)
1230 1210	-C-O stretching vibration	1300-900	(504)
1200	Characteristic absorption of acrylates		(454)
3000	Presence of double bond due to low degree polymeric nature	3000	(482)

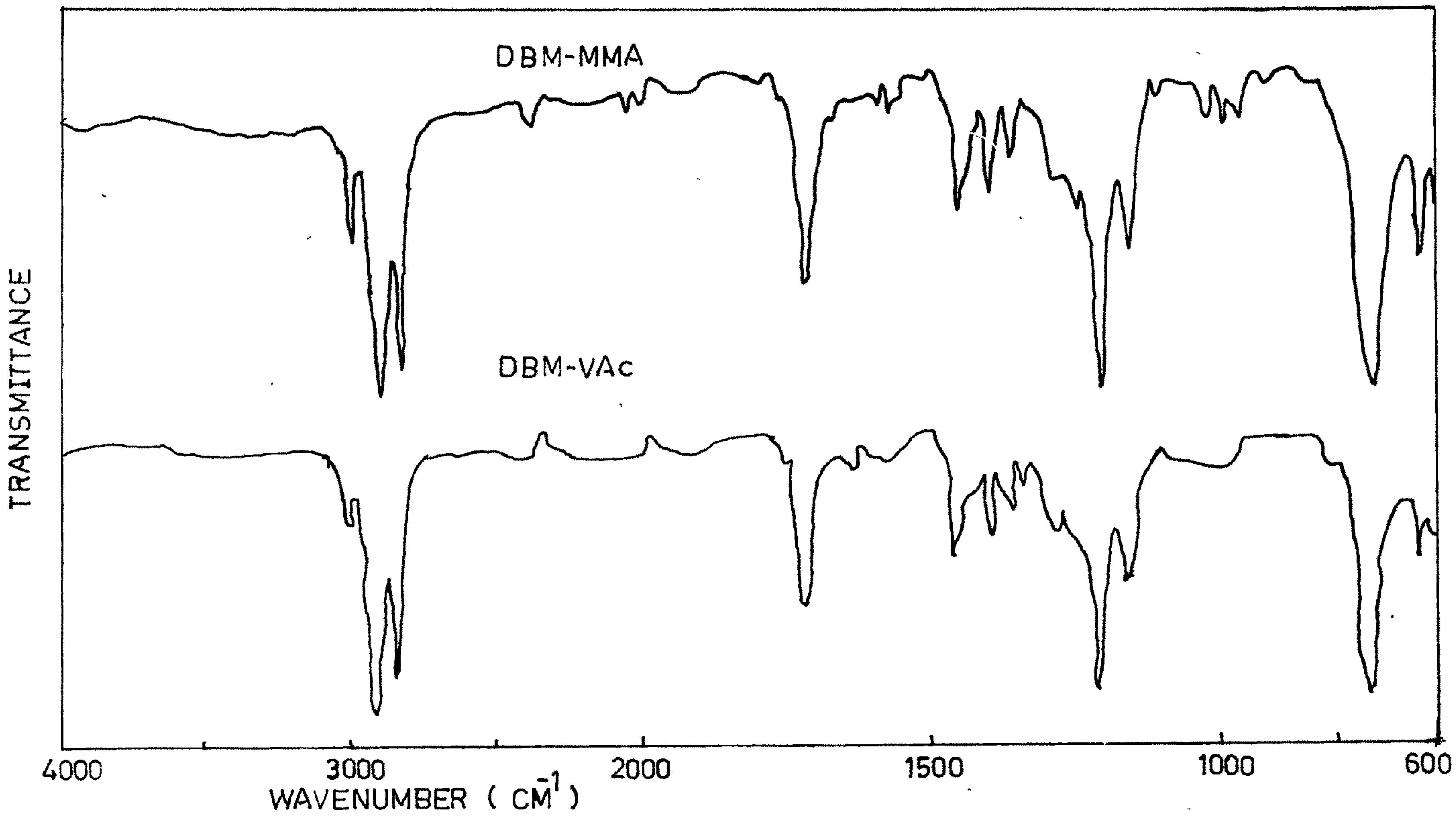


FIG **12** IR SPECTRA OF DBM-VAc AND DBM-MMA

EXPERIMENTAL V :

POLYMERS OF DIOCTADECYL MALEATE :

Experimental :

Experimental Assembly :

The set up used for this class of copolymerization is the same as of undecylenic ester maleic anhydride copolymer and was used here in all the experiments.

Dioctadecyl maleate : (DODM)

Prepared from n-octadecyl alcohol and maleic anhydride (2:1 mole ratio) and was recrystallized from acetone. This DODM copolymerized separately with

(i)	vinyl acetate,	(ii)	methyl methacrylate
(iii)	acrylic acid,	(iv)	maleic anhydride
(v)	acrylonitrile	(vi)	itaconic anhydride &

(vii) homopolymerized as poly DODM.

1. Copolymerization :

1) Poly(dioctadecyl maleate-Co-vinyl acetate)
(Code : DODM-VAc)

Method :

First solvent benzene was introduced into the polymerization flask. Then DODM along with vinyl acetate was introduced into the flask. The mixture was dissolved in benzene under stirring at 50°C. Cooled the mixture upto 30°C and then the benzene solution of azo-bis-isobutyro-nitrile was introduced drop by drop with stirring. Then increase the heat up to 60°C and maintained constant for 16 to 17 hrs.

Then the product was purified by solvent nonsolvent method using acetone as non-solvent. Then the precipitate upon filtration dried at 50°C/25" Hg vacuum for 15 hrs. Details of quantities of comonomers are tabulated in Table .

Similarly the following copolymers synthesised by using the above method.

(ii) Poly(dioctadecyl maleate-Co-methyl methacrylate)
(Code : DODM-MMA)

(iii) Poly(dioctadecyl maleate-Co-acrylic acid)
(Code : DODM-AA).

(iv) Poly(dioctadecyl maleate-Co-maleic anhydride)
(Code : DODM-MA).

(v) Poly(dioctadecyl maleate-Co-acrylonitrile)
(Code : DODM_AN).

(vi) Poly(dioctadecyl maleate-Co-itaconic anhydride)
(Code : DODM_IA).

(vii) Poly(dioctadecyl maleate)
(Code : Poly DODM)

Method :

Introduced monomer DODM along with benzene into polymerization flask ; dissolved under stirring at 50°C. Theh at 30°C added catalyst solution of benzene. Maintained the temperature at 60°C under stirring upto 16 to 17 hrs. Then purified the polymer as given in case (i). Details of quantity are given in Table 35.

2. Analysis and Characterization :

(i) C and H analysis : Table 36
(ii) Solution viscosity : Table 36
(iii) I.R. spectra : Table 37, Fig. 13.

Table 35

Polymers of Dioctadecyl maleate

Sr. No.	Raw materials						
	Dioctadecyl maleate in g & mole	Comonomer in g and (mole)	Molar ratio of comonomers	Azabis iso-butyro nitrile in gm & (% wt)	Benzene in ml	Yield in g.	Appearance
1.	10 (0.01)	Vinyl acetate 3.01 (0.0397)	1:2	0.013 (0.1)	50	11	Cream yellow waxy
2.	10 (0.0161)	Methyl methacrylate (0.0462)	1:2	0.0146 (0.1)	50	12	Cream yellow powder
3.	12 (0.0193)	Acrylic acid 1.83 (0.0286)	1:2	0.0138 (0.1)	50	10	Cream coloured powder
4.	14 (0.0225)	Maleic anhydride 2.2 (0.0321)	1:2	0.0162 (0.1)	50	14	Pale yellow solid
5.	10 (0.0161)	Acrylonitrile 1.74 (0.024)	1:2	0.011 (0.1)	50	9	Pale yellow solids
6.	15	Itaconic anhydride 2.712 (0.024)	1:1	0.017 (0.1)	50	11	Cream coloured waxy
7.	15 (0.024)	-	-	0.015 (0.1)	50	14	White powder

Table 36

Polymer of Dioctadecyl maleate

Sr. No.	Copolymer code (Mole formula = Mol. wt.) of repetition unit)	Percentage of C and H: Calculated for 1:1 ratio		Percentage of C and H: Actual		Inherent viscosity dl/g (a)
		C	H	C	H	
1.	DODM-VAc $(C_{44}H_{82}O_6 = 706)$	74.78	11.6	73.85	10.56	0.0732
2.	DODM-MMA $(C_{45}H_{84}O_6 = 720)$	75.00	11.6	74.53	11.85	0.0785
3.	DODM-AA $(C_{43}H_{80}O_6 = 692)$	74.56	11.5	74.32	10.91	0.0864
4.	DODM-MA $(C_{44}H_{78}O_7 = 718)$	73.53	10.8	73.32	11.02	0.0758
5.	DODM-AN $(C_{43}H_{77}O_4N = 671)$	76.90	11.47	75.85	11.21	0.0583
6.	DODM-IA $(C_{45}H_{78}O_7 = 730)$	73.97	10.68	73.24	9.13	0.0854
7.	Poly DODM $(C_{40}H_{76}O_4 = 620)$	77.41	12.1	76.89	11.91	0.0685

(a) determined in toluene at 30°C

Table 37

Analysis of the I.R. Spectral data :

Polymers of Dioctadecyl maleates :

Absorption at cm^{-1}	Assignment	Characteristic absorption at cm^{-1}	References
i) DODM-VAc	(Perkin Elmer Part No. 5100 4367 in chloroform solution) Fig. 13		
1745	C=O stretching vibration of ester carbonyl	1900-1600	(454)
1240	-C-O stretching vibration of acetate ester	1275-1200	(451)
2990	Residual unsaturation		
3060	in low degree polymer	3000	(482)
ii) DODM-MMA	in chloroform solution	Fig. 13	
1710	C=O stretching vibration of ester carbonyl	1900-1600	(454)
1280	-C-O stretching vibration	1300-900	(504)
1200	Characteristic absorption of acrylates		(454)
3000	presence of unsaturation due to low degree polymeric nature	3000	(482)

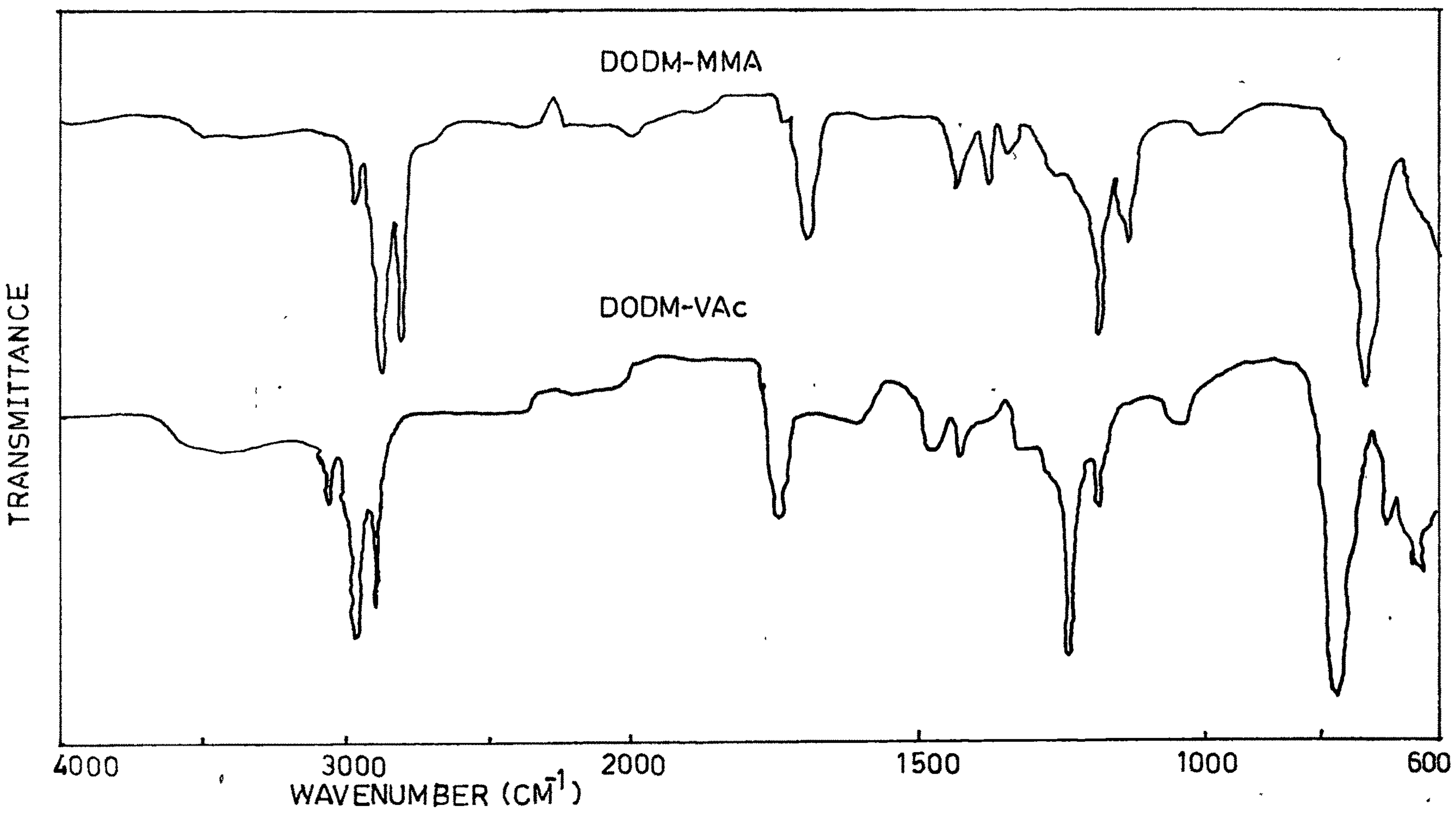


FIG **13** IR SPECTRA OF DODM-VAc AND DODM-MMA

B. METHODS OF STUDY

I. Composition of crude oils

All the five crude oils have been analysed for determining their composition by the following procedure. The modified method of French Institute of Petroleum, which is currently followed by ONGC, Baroda, was adopted for determining the compositions in this investigation.

(a) Asphaltene

About one g (accurate weight) of the sample residue obtained after distilling the crude upto 250°C was taken in a 250 ml flask. To this 60 ml of ethyl acetate was added and refluxed for 5-6 hrs. Filtration of the hot precipitated asphaltenes through whatmann No. 42 filter paper was carried out giving washings with hot ethyl acetate. The filtrate collected was used later for estimation of resins. Asphaltenes from the filter paper were extracted with hot benzene.

The major portion of benzene was removed by distillation. The concentrated extract containing asphaltenes was transferred into a weighed beaker. The remaining benzene was removed by evaporation and the beaker was kept in the oven at 105-110°C for half an hr. This mass was cooled and weighed.

(b) Resins :

Ethyl acetate was removed from the above filtrate of Ia. The residue so obtained was dissolved in petroleum ether (40° - 60°C). To this solution small quantities of activated silica gel were added, shaken well, and observed the colour of petroleum ether. If dark brown colour persisted, more silica gel was added and shaken well. This process was repeated until straw yellow colour was obtained.

The petroleum ether portion was decanted which contained only portion as well as wax and was used later on. The silica gel portion which contained resins and a little oily portion was dried up in a porcelein dish and then transferred into a timble for soxhlation with previously decanted petroleum ether for 6 hrs in order to make silica gel free of all oily portion.

After complete removal of adsorbed oily component from the silica gel the resins were extracted by soxhleting with carbon tetrachloride and their percentage was determined as usual.

(c) Wax :

About 2-3 g of the residue was weighed accurately and transferred into a separating funnel and diluted with 250 ml of petrolaum ether (40° - 60°C). The mass was treated successively thrice with conc. H_2SO_4 at half hr interval in between. Resins and asphaltenes were precipitated by H_2SO_4 and separated. The oily portion covering wax was left behind. It was washed with distilled water till the washings were neutral to litmus. Anhydrous $CaCl_2$ was added and the flask was kept over night to bring about absorption of water. The extract was transferred into another beaker quantitatively. The funnel was washed with hot petroleum ether and washings were transferred to the beaker. Activated charcoal was added, the mass was boiled and filtered. The filtrate was distilled and the residue was transferred to a weighed beaker and evaporated on a water bath. When all the petroleum ether had been evaporated it was weighed and the oily component was thus determined.

A small portion of the oily component (less than one gram) was taken in a conical flask and 40 ml of methyl ethyl ketone alongwith an equal volume of a mixture of 10 ml of methyl ethyl ketone and absolute alcohol were added to it. The conical flask was kept in an ice bath and maintained at -20°C for 45 minutes for wax precipitation. The precipitated wax was filtered by maintaining the temperature at -20°C. The wax from the filter paper was transferred to a weighed beaker and dried. It was weighed again to get the weight of wax.

II. Pour Point

The pour point determination was done by the standard procedure ASTM D-97 IP-15. Pour point appratus of M/s EMIL was used for the purpose. The pour points for the crude oils and additive treated crude oils have been recorded in tabular form.

III. Rheological properties :

The rheological properties of all virgin crude oils and additive treated crude oils were studied using rotational viscometer. Fann Viscometer Model 35 5A with an additional SR-12 gear box was used for the purpose.

Procedure for crude oil viscosity measurement, though reported in certain publications (105,106) was developed to suit the laboratory conditions and is narrated below :

The virgin crude oil was heated to 50-70°C depending on the crude, under stirring for half hr. and cooled over night without disturbing (12 hrs). Viscosity measurements at 3°C intervals and 6°C above and below the observed pour point were done at different speeds starting from 600 rpm to 3 rpm depending on the viscosity of the oil. Value of each shear rate was read when the dial pointer was steady. The shear rate was read when the dial pointer was steady. The shear stress was then plotted against each shear rate for obtaining rheograms at the temperature of the experiment. Yield value and plastic viscosity were calculated at desired temperature using the standard formula for the Fann Viscometer.

$$\text{Apparent viscosity} = \left(\frac{\text{Dial reading at 600 rpm}}{2} \right) \text{cps}$$

Plastic viscosity = (Dial reading at 600 rpm - Dial reading at 300 rpm) cps.

Yield value = Dial reading at 300 rpm - plastic viscosity) lb/100 ft^2

Additives were blended into the crude oil for half hr at a temperature between 50° - 70°C range depending on the crude. The samples were then naturally cooled statically for 12 hrs. The viscometer cup was filled to the indicated mark and cooled to the desired temperature under constant stirring. Readings were taken at 600 rpm and 300 rpm when the viscometer had registered a steady reading.

Apparent viscosity, plastic viscosity and yield value were calculated as mentioned above from these data and reported in tabular form.

Table 38

Characteristics of crude oils selected for study .

CrudeOil Field	API Gravity	Distillation characteristics				Base of oil	Asphaltene %	Resin %	Wax %	Pour Point of oil ^{o}C
		IBP- 150°C % vol.	150- 250°C % vol.	250- 300°C % vol.	Residue % vol.					
Bombay High	35.9	14	24	14	48	Paraffinic intermediate	0.5	NA	15	30
Nahorkatia	32.7	14	19	17	50	Naphthenic Paraffinic	2-4	NA	10-13	30
Moran	34.3	12	23	18	47	Paraffinic	0.9	NA	11.5	27
North Kadi	36.78	9	15	16	60	Asphaltene intermediate	10.5	3.5	9.5	18
Amta	39.86	13	12	20	55	Asphaltene	8	3.9	13	6

Source : ONGC and Oil India Ltd.

Table 39

Effect of temperature on shear stress

Crude oil : Bombay High (BH)

Shear rate sec^{-1}	Shear stress at ( )°C dy/sq. cm.				
	24	27	30	33	36
1022.04	105	68.5	33.5	10	9
511.02	65	42	20.5	5.25	4.5
340.68	42	27.5	15	3.75	3
170.34	24	16	9	2	1.5
102.204	12.5	8.75	5.75	-	-
51.102	7.5	5.25	3.75	-	-

Table 40

Effect of temperature on shear stress

Crude Oil : Nahorkatia (Na)

Shear rate sec^{-1}	Shear stress at ( )°C dy/sq. cm.				
	26	29	32	35	38
1022.04	429	293	85	54	49
511.02	207	170	44	29	24.6
340.68	140	118	32	19.7	17
170.34	67	61	17	12	8.6
102.204	39	34	9.8	7.4	-
51.102	22	20	7.4	4.9	-

Table 41

Effect of temperature on shear stress

Crude oil : Moran (Mo)

Shear rate sec^{-1}	Shear stress at ( )°C dy./sq.cm.						
	15	18	21	24	27	30	33
1022.04	55	28	18.5	13.0	12	11	10
511.02	31.5	15.5	9.5	6.5	6	5.5	5
340.68	22	9.5	7.0	5	5	4.5	4.5
170.34	13	5	3.5	2.5	2.5	2.5	2.5
102.240	5	1.5	0.5	0.5	0.5	-	-
51.102	4	1	-	-	-	-	-

Table 42

Effect of temperature on shear stress Crude Oil :
North Kadi (NK)

Shear rate sec^{-1}	Shear stress at ( )^{o}C dy./sq. cm.								
	30	33	36	39	42	45	48	51	54
1022.04	-	-	-	-	-	--	275	234	203
511.02	-	-	276	240	200	160	141.5	120.5	104
340.68	-	248	181	156	134	108	97	80	70
170.34	155	125	91	78.5	67.5	55	49.5	41	35
102.240	10	8	7	6	5	4	4	3	2.5
51.102	5	4	3.5	3	2.5	2	2	1.5	1

Table 43

Effect of temperature on shear stress

Crude Oil : Amta (Am)

Shear rate sec^{-1}	Shear stress at ( )°C dy./sq. cm.								
	30	33	36	39	42	45	48	51	54
1022.04	-	-	-	-	-	-	266	225	194
511.02	-	-	-	-	201	176	137	115.5	99
340.68	259	233	198	178	134	117	91	76	68
170.34	132	118	100	91	69.5	59.5	46	39	34
102.240	8	7.5	6.5	6.0	4.5	4.0	3	2.5	2
51.102	5	4	3.5	3	2.5	2	1.5	1.5	1

Table 44

Plastic viscosity of different crude oil Vs. Temperature

Oil	Plastic viscosity in cps at ( )°C												
	24	26	27	29	30	32	33	35	36	38	48	51	54
BH	41	-	26.5	-	13	-	4.75	-	4.5	-	-	-	-
Na	48	46	-	25	-	8.25	-	5	-	5	-	-	-
Mo	6.5	-	6	-	5.5	-	5	-	-	-	-	-	-
NK	-	-	-	-	-	-	-	-	-	-	133.5	113.5	99
Am	-	-	-	-	-	-	-	-	-	-	129	109.5	94.5

Table 45

Yield value of different crude oils Vs. Temperature

Oil	Yield value lb/100 ft^2 at ( )°C												
	24	26	27	29	30	32	33	35	36	38	48	51	54
BH	25	-	15.5	-	7.5	-	0.5	-	0	-	-	-	-
Na	123	93	-	47	-	3.7	-	4.9	-	0	-	-	-
Mo	0	-	0	-	0	-	0	-	-	-	-	-	-
NK	-	-	-	-	-	-	-	-	-	-	8	7	5
Am	-	-	-	-	-	-	-	-	-	-	8	6	5

Table 46

Pour point (^{o}C) of polymer treated crude oil (BH)

Sr. No.	Copolymer esters →	n-C_{22} ester						n-C_{18} ester		n-C_{16} ester		n-C_{14} ester	
	Concentration in ppm →	100	200	300	400	500	1000	500	1000	500	1000	500	1000
	Copolymer Code ↓												
1.	2 -U$_n$MA	9	6	6	3	0	-	27	21	30	27	30	30
2.	4 -U$_n$MA	9	6	3	3	0	-	27	24	30	30	30	30
3.	6 -U$_n$Ma	21	15	15	9	6	6	27	27	30	30	30	30
4.	8 -U$_n$MA	21	21	15	9	6	6	27	27	30	30	30	30
5.	18 -U$_n$MA	12	9	3	3	0	-	27	24	30	30	30	30
6.	10 -U$_n$MA	12	9	6	3	0	-	27	24	30	30	30	30
7.	12 -U$_n$MA	12	9	6	3	3	0	27	24	30	30	30	30
8.	14 -U$_n$MA	12	12	9	6	3	0	27	27	30	30	30	30
9.	16 -U$_n$MA	9	6	3	0	0	-	27	24	30	30	30	30

cont...

Table 46 cont..

10.	18-UnMA	9	6	3	0	0	-	21	18	30	30	30	30
11.	22-UnMA	6	3	3	0	0	-	15	12	18	12	27	24
12.	1-CMA	21	18	18	15	12	9	27	24	30	30	30	30
13.	2-CMA	15	12	12	9	9	6	27	24	30	27	30	30
14.	4-CMA	18	15	15	12	12	9	30	27	30	30	30	30
15.	6-CMA	18	18	15	15	12	-	30	27	30	30	30	30
16.	8-CMA	15	15	15	12	9	6	27	27	30	30	30	30
17.	10-CMA	18	18	15	15	12	9	30	27	30	30	30	30
18.	12-CMA	18	18	12	9	6	6	27	27	30	30	30	30
19.	14-CMA	18	15	12	9	6	3	27	27	30	30	30	30
20.	16-CMA	18	15	12	12	9	6	27	24	30	30	30	30
21.	18-CMA	18	15	12	6	3	0	27	24	30	27	30	30
22.	22-CMA	9	9	6	3	0	-	6	3	12	12	24	21
23.	PA-15(1)	9	6	3	0	0	-	27	24	27	27	30	27
24.	PA-15(2)	12	9	6	3	0	-	27	27	30	27	30	30
25.	PA-21(1)	15	12	12	9	6	3	27	27	30	27	30	30
26.	PA-21(2)	12	9	6	6	3	0	27	24	30	27	30	30

Table 47

Pour point (^{o}C) of polymer treated crude oil (BH)

Sr. No.	Comonomer 1 → Concentration in ppm → Comonomer 2 ↓	Dibehenyl maleate						Dioctadecyl maleate					
		100	200	300	400	500	1000	100	200	300	400	500	1000
1.	VAc	12	12	9	6	6	3	18	15	15	12	9	6
2.	MMA	18	18	15	12	9	6	21	18	18	15	12	12
3.	AA	12	12	9	9	6	3	18	18	15	12	12	9
4.	MA	15	12	9	6	6	3	15	15	12	12	9	6
5.	IA	9	9	6	3	3	0	12	12	9	6	6	3
6.	AN	15	15	12	12	9	6	21	21	18	15	12	9
7.	Poly	15	12	12	9	6	0	12	12	9	6	6	3

Table 48

Pour point (°C) of polymer treated crude oil (Na)

Sr. No.	Copolymer esters →	n-C_{22} ester						n-C_{18} ester		n-C_{16} ester		n-C_{14} ester	
	Concentration in ppm →	100	200	300	400	500	1000	500	1000	500	1000	500	1000
	Copolymer Code ↓												
1.	2-UnMA	15	9	6	6	0	-	27	24	30	30	30	30
2.	4-UnMA	18	18	12	9	6	3	30	27	30	30	30	30
3.	6-UnMA	24	24	21	12	6	0	30	27	30	30	30	30
4.	8-UnMA	24	21	15	12	12	9	30	30	30	30	30	30
5.	18-UnMA	24	12	6	3	3	0	30	27	30	30	30	30
6.	10-UnMA	21	15	12	9	6	3	27	27	30	30	30	30
7.	12-UnMA	21	15	12	12	9	6	27	27	30	30	30	30
8.	14-UnMA	15	15	12	12	9	6	27	27	30	30	30	30
9.	16-UnMA	15	12	12	9	6	3	30	27	30	27	30	30
10.	18-UnMA	12	12	9	6	6	3	30	27	30	30	30	30

cont...

Table 48 cont...

11.	22-UnMA	12	9	9	6	0	-	12	15	21	18	27	24
12.	1-CMA	27	24	21	18	18	15	30	30	30	30	30	30
13.	2-CMA	21	18	18	12	12	9	27	27	30	30	30	30
14.	4-CMA	24	24	18	15	12	9	30	27	30	30	30	30
15.	6-CMA	24	18	18	15	12	9	30	30	30	30	30	30
16.	8-CMA	18	15	15	12	12	9	30	27	30	30	30	30
17.	10-CMA	18	15	12	12	12	9	30	27	30	30	30	30
18.	12-CMA	12	12	9	6	3	0	27	24	30	30	30	30
19.	14-CMA	15	12	9	6	3	0	27	27	30	30	30	30
20.	16-CMA	12	12	9	6	3	0	27	24	30	30	30	30
21.	18-CMA	18	15	12	9	6	3	27	27	30	30	30	30
22.	22-CMA	15	12	12	6	6	3	18	15	15	12	27	24
23.	PA-15(1)	18	15	12	9	6	6	30	27	30	30	30	30
24.	PA-15(2)	15	12	12	9	6	3	27	27	30	30	30	30
25.	PA-21(1)	15	12	12	12	9	6	30	27	30	30	30	30
26.	PA-21(2)	18	15	15	12	6	3	30	27	30	30	30	30

Table 49

Pour point (^{o}C) of polymer treated crude oil (Na)

Sr. No.	Comonomer-1 →	Dibehenyl maleate						Dioctadecyl maleate					
	Concentration in ppm →	100	200	300	400	500	1000	100	200	300	400	500	1000
	Comonomer-2 ↓												
1.	VAc	18	15	12	12	9	6	21	18	15	15	12	9
2.	MMA	18	18	15	12	12	9	21	18	18	15	12	9
3.	AA	15	12	12	9	6	3	21	18	18	15	12	9
4.	MA	15	12	9	9	6	3	15	12	12	9	9	9
5.	IA	12	9	6	6	3	0	15	15	12	9	6	6
6.	AN	18	15	15	12	9	9	21	18	18	15	12	9
7.	Poly	15	15	9	6	3	0	15	12	12	9	9	6

Table 50

Pour point (°C) of polymer treated crude oil (Mo)

Sr. No.	Copolymer esters →	n-C_{22} ester						n-C_{18} ester		n-C_{16} ester		n-C_{14} ester	
	Concentration in ppm →	100	200	300	400	500	1000	500	1000	500	1000	500	1000
	Copolymer Code ↓												
1.	2-UnMA	6	3	0	-3	-6	-	9	0	24	21	27	27
2.	4-UnMA	9	6	6	0	-3	-	12	9	24	21	27	27
3.	6-UnMA	18	12	12	6	3	-3	15	12	24	24	27	27
4.	8-UnMA	18	15	15	9	6	3	12	12	24	21	27	27
5.	18-UnMA	21	12	6	3	0	-	12	12	24	21	27	27
6.	10-UnMA	18	15	12	6	6	3	15	15	24	24	27	27
7.	12-UnMA	18	18	12	9	9	6	15	15	24	21	27	27
8.	14-UnMA	18	15	15	9	9	6	15	12	24	24	27	27
9.	16-UnMA	12	12	9	6	3	0	15	12	24	21	27	27
10.	18-UnMA	9	9	6	3	0	-3	12	12	24	24	27	27
11.	22-UnMA	9	6	0	0	-6	-	9	9	18	15	21	21

cont...

Table 50 cont..

12.	1-CMA	18	12	12	9	6	3	18	15	24	24	27	27
13.	2-CMA	15	12	6	6	0	-	12	12	24	21	27	27
14.	4-CMA	15	15	12	9	6	3	15	12	24	24	27	27
15.	6-CMA	18	15	12	12	9	6	18	15	24	24	27	27
16.	8-CMA	15	12	12	9	6	3	15	15	24	21	27	27
17.	10-CMA	12	12	9	9	6	3	15	15	24	24	27	27
18.	12-CMA	12	9	9	6	3	0	12	12	24	21	27	27
19.	14-CMA	9	6	6	3	0	-3	15	12	24	21	27	27
20.	16-CMA	12	9	9	6	3	0	18	15	24	21	27	27
21.	18-CMA	6	6	3	0	-3	-	12	9	21	18	27	27
22.	22-CMA	6	6	3	0	-3	-	6	3	12	9	18	15
23.	PA-15(1)	9	6	6	0	-3	-	15	12	24	21	27	27
24.	PA-15(2)	6	3	0	0	-3	-	15	12	27	24	27	27
25.	PA-21(1)	6	6	3	0	-3	-	15	15	24	21	27	27
26.	PA-21(2)	6	6	0	0	-3	-	18	15	24	21	27	27

Table 51

Pour point (°C) of polymer treated crude oil (Mo)

Sr. No.	Comonomer-1 →	Dibehenyl maleate						Dioctadecyl maleate					
	Concentration in ppm →	100	200	300	400	500	1000	100	200	300	400	500	1000
	Comonomer-2 ↓												
1.	VAc	9	6	6	3	0	-	15	15	12	9	6	3
2.	MMA	12	9	6	3	3	0	18	15	12	12	9	6
3.	AA	9	9	6	6	3	0	12	9	6	6	6	3
4.	MA	12	6	6	3	0	-	12	12	9	9	6	3
5.	IA	9	6	6	3	0	-	12	9	6	6	6	3
6.	AN	9	9	6	3	0	-	12	12	9	6	6	3
7.	Poly	9	6	6	3	0	-	9	6	3	3	0	-

Table 52

Pour point (°C) of polymer treated crude oil

Sr. No.	Oil →	NK		Am	
	Concentration in ppm →	500	1000	500	1000
	Copolymer Code ↓				
1.	22-2 UnMA	18	18	6	6
2.	22-4 UnMA	18	18	6	6
3.	22-6 UnMA	18	18	6	6
4.	22-8 UnMA	18	18	6	6
5.	22-10 UnMA	18	18	6	6
6.	22-12 UnMA	18	18	6	6
7.	22-18 UnMA	18	18	6	6
8.	22-22 UnMA	18	18	6	6
9.	22-2 CMA	18	18	6	6
10.	22-10 CMA	18	18	6	6
11.	22-18 CMA	18	18	6	6
12.	22-22 CMA	18	18	6	6
13.	22-PA15(1)	18	18	6	6
14.	22-PA15(2)	18	18	6	6
15.	DBM-VAc	18	18	6	6
16.	DBM-IA	18	18	6	6
17.	DODM-VAc	18	18	6	6
18.	DODM-IA	18	18	6	6

Table 53

Fann viscometric data, Product : n-C_{22} ester of 2-U_nMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M_o Properties		
		1	2	3	1	2	3	1	2	3
200	18	59.5	45.5	28	42.5	32	21	10.5	10	1
	21	42	33	18	31.5	24	15	7.5	7	1
	24	30.25	24	12.5	25	21	8	4.25	4	o.5
300	18	50	38	24	36.5	29	15	-	-	-
	21	36.5	30	13	25.5	20	11	-	-	-
	24	23	19	8	16	14	4	-	-	-
500	18	33	26.5	13	24	19	10	-	-	-
	21	14	13	2	15	13	4	-	-	-
	24	6.5	6	1	7.5	7	0.5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 54

Fann viscometric data, Product : n-C_{22} ester of 4-$^{U}_{n}$MA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M$_o$ Properties		
		1	2	3	1	2	3	1	2	3
200	18	54	41	26	57.5	42	31	12	11	2
	21	38.5	31	15	40.5	30	21	9.5	9	1
	24	28.5	22	13	28	22	12	6.25	6	0.5
300	18	40.5	30	21	48.5	36	25	-	-	-
	21	30.5	25	11	33	27	12	-	-	-
	24	18.5	15.5.	7	20	17	6	-	-	-
500	18	21.5	13.5	5.5	36.5	30	13	-	-	-
	21	18	12	5	19.5	17	5	-	-	-
	24	7	3	1	11.5	11	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 55

Fann viscometric data, Product : n-C_{22} ester of $6\text{-}{}^{u}_{n}\mathrm{MA}$

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
	18	57.5	45	25	55	43	24	12.5	11	3
200	21	41.5	32	19	38.5	31	15	8.5	8	1
	24	29.5	23	12	27	22	10	5.5	5	1
	18	49.5	39	20	44.5	36	17	-	-	-
300	21	33	25	16	30.5	25	11	-	-	-
	24	22.5	18	9	18.5	16	5	-	-	-
	18	27.5	24	7	34	28	12	-	-	-
500	21	14	12	4	19	17	4	-	-	-
	24	8.5	8	1	10.5	10	1	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 56

Fann viscometric data, Product = n-C_{22} ester of $8\text{-}U_{n}MA$

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M● Properties		
		1	2	3	1	2	3	1	2	3
200	18	51.5	40	23	56.5	44	25	11.5	10	3
	21	34.5	27	15	38	30	16	8	7	2
	24	26	21	10	28.5	23	11	6	5	2
300	18	38.5	31	15	45.5	36	19	-	-	-
	21	26	21	10	29	24	10	-	-	-
	24	17	15	4	18	16	4	-	-	-
500	18	17	15	4	35	29	12	-	-	-
	21	9	8	2	20.5	18	5	-	-	-
	24	3.5	3	1	11.5	11	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 57

Fann viscometric data, Product : n-C_{22} ester of $\overset{\circ}{1}8\text{-}{}^{\cup}{}_{n}\text{MA}$

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M$_\bullet$ Properties		
		1	2	3	1	2	3	1	2	3
200	18	56.5	45	23	49	36	26	12.5	11	3
	21	39.5	32	15	36.5	28	17	10	9	2
	24	30	24	12	21	15	12	6.5	6	1
300	18	46.5	38	17	34.5	24	21	-	-	-
	21	29.5	25	9	36	27	18	-	-	-
	24	18	15	6	23	16	14	-	-	-
500	18	32	28	8	24	17	14	-	-	-
	21	16.5	15	3	12.5	10	5	-	-	-
	24	7.5	7	1	6	6.5	0.5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 58

Fann viscometric data, Product : n-C_{22} ester of 10-U_nMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
	18	53	44	18	54.5	37	35	9.5	9	1
200	21	34	27	14	47	32	30	7.25	7	0.5
	24	26.5	22	9	41	28	26	6	6	0.5
	18	42.5	36	13	46.5	33	27	-	-	-
300	21	24.5	20	9	29.5	27	25	-	-	-
	24	17	15	4	33.5	23	21	-	-	-
	18	27	25	4	33.5	25	17	-	-	-
500	21	9.5	9	1	27	21	12	-	-	-
	24	4.5	4	1	13.5	11	5	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 59

Fann viscometric data, Product : n-C_{22} ester of 12-${}^{U}_{n}$MA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M_e Properties		
		1	2	3	1	2	3	1	2	3
200	18	53	44	18	39.5	30	19	11	10	2
	21	33	26	14	31	24	14	9.5	9	2
	24	26	22	8	22	18	8	7.5	7	1
300	18	40.5	35	11	29	24	10	-	-	-
	21	23	19	8	19.5	17	5	-	-	-
	24	15	14	2	12.5	12	1	-	-	-
500	18	27	25	4	12.5	10	5	-	-	-
	21	10	9	2	9	8	2	-	-	-
	24	4.5	4	1	5	4.5	0.5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 60

Fann viscometric data, Product : n-C_{22} ester of 14-ψnMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
200	18	55.5	44	23	61.5	45	33	12	11	2
	21	39	30	18	49.5	37	25	9.5	9	1
	24	30.5	24	18	34	25	18	7.25	7	0.5
300	18	42.5	34	17	51	37	28	-	-	-
	21	31	24	14	36.5	28	17	-	-	-
	24	21	17	8	21	16	10	-	-	-
500	18	28	24	8	37.5	29	17	-	-	-
	21	19	16	6	28.5	23	11	-	-	-
	24	9	8	2	11	10	2	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 61

Fann viscometric data, Product : n-C_{22} ester of 16-$^{u}_{n}$MA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M. Properties		
		1	2	3	1	2	3	1	2	3
	18	52	43	18	45.5	33	25	9	8	2
200	21	34.5	28	13	30.5	22	17	6.52	6	1.5
	24	22	18	8	20	14	12	6.5	5	1
	18	39	33	12	35	26	18	-	-	-
300	21	24	22	6	22	16	12	-	-	-
	24	8.5	8	1	15	11	8	-	-	-
	18	19	17	4	27	21	12	-	-	-
500	21	8.5	8	1	13.5	11	5	-	-	-
	24	2.5	2	0.5	7.5	7	1	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 62

Fann viscometric data, Product : n-C_{22} ester of 18-$^{U}{}_{n}$MA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
200	18	59	48	22	41	31	20	7.5	7	1
	21	38.5	30	17	30	23	14	6.25	6	0.5
	24	30	24	12	18	14	8	4.25	4	0.5
300	18	52	44	16	31.5	24	15	-	-	-
	21	33.5	27	13	21.5	18	7	-	-	-
	24	22.5	18	9	12	10	4	-	-	-
500	18	33	30	6	20	16	8	-	-	-
	21	18	16	4	12.5	11	3	-	-	-
	24	8.5	8	1	7	6.5	0.5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = AYield value lb/100 ft^2

* Properties at °C

Table 63

Fann viscometric data, Product : n-C_{22} ester of 22-$^{\omega}$nMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M_o Properties		
		1	2	3	1	2	3	1	2	3
200	18	54	44	20	29.5	25	9	8.5	8	1
	21	33	27	12	19	16	6	6.25	6	0.5
	24	19	16	6	13	11	4	5.25	5	0.5
300	18	36	30	12	29.5	22	5	-	-	-
	21	21	18	6	14	13	2	-	-	-
	24	7.5	7	0.5	9.5	9	1	-	-	-
500	18	17.5	17	1	16.5	15	3	-	-	-
	21	8.5	8	1	8.5	8	1	-	-	-
	24	2.5	2	0.5	6.5	6	0.5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 64

Fann viscometric data, Product : n-C_{18} ester of 22-^{4}nMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
	18	-	-	-	-	-	-	16.5	14	5
200	21	-	-	-	-	-	-	14	12	4
	24	-	-	-	-	-	-	12.25	10	4.5
	18	45.5	39	13	32	27	10	-	-	-
300	21	28.5	23	11	21.5	18	7	-	-	-
	24	19	17	4	17	14	6	-	-	-
	18	31.5	29	5	32.5	28	9	-	-	-
500	21	13.2	12	2.5	20.5	17	7	-	-	-
	24	6.5	6	1	17.5	15	5	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 65

Fann viscometric data, Product : n-C_{22} ester of 2-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
200	18	59.5	46	27	51	38	26	11.5	10	3
	21	43.5	34	19	42.5	32	21	9	8	2
	24	33	27	12	32.5	24	17	7.25	7	0.5
300	18	52	40	24	44.5	33	23	-	-	-
	21	35	28	14	33.5	25	17	-	-	-
	24	25	21	8	27	21	13	-	-	-
500	18	39	30	18	35.5	26	19	-	-	-
	21	27	23	8	28.5	21	15	-	-	-
	24	15.5	14	3	20.5	15	11	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3= Yield value lb/100 ft^2

* Properties at °C

Table 66

Fann viscometric data, Product : n-C_{22} ester of 4-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
200	18	72.5	56	33	61.5	44	35	12	11	3
	21	55	43	24	45	31	28	11.25	10	2.5
	24	42.5	34	17	37	27	20	9	8	2
300	18	66	51	30	55.5	40	31	-	-	-
	21	48.5	38	21	32.5	20	25	-	-	-
	24	38	31	14	27	19	16	-	-	-
500	18	58	45	26	29	28	22	-	-	-
	21	42	34	16	24	15	18	-	-	-
	24	30.5	26	9	14	9	10	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3=Yield value lb/100 ft^2

* Properties at °C

Table 67

Fann viscometric data, Product : n-C_{22} ester of 6-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-M_g Properties		
		1	2	3	1	2	3	1	2	3
	18	72	55	34	-	-	-	12.25	11	2.5
200	21	55.5	44	23	-	-	-	9.8	9	2
	24	44	35	18	-	-	-	9	8	2
	18	64	50	28	70	50	41	-	-	-
300	21	47	37	20	47	33	28	-	-	-
	24	36	30	12	40.5	30	21	-	-	-
	18	56	44	24	52	36	32	-	-	-
500	21	42.5	35	15	41.5	30	23	-	-	-
	24	29	25	8	31	23	16	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 68

Fann viscometric data, Product : n-C_{22} ester of 8-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	74.5	55	39	-	-	-	13.5	12	3
	21	66	40	26	-	-	-	11.25	10	2.5
	24	40	30	20	-	-	-	9.5	9	1
300	18	71	52	38	68	48	40	-	-	-
	21	57	43	28	43.5	30	27	-	-	-
	24	43	33	20	37.5	28	19	-	-	-
500	18	65.5	48	35	48.5	33	31	-	-	-
	21	52	39	26	38.5	28	21	-	-	-
	24	39	30	18	27.5	21	13	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at oC

Table 69

Fann viscometric data, Product : n-C_{22} ester of 10-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	70	52	36	68	48	40	9.5	9	2
	21	48.5	38	21	48	34	28	7.5	7	1
	24	35.5	28	15	41	30	22	6.25	6	0.5
300	18	67.5	50	35	58.5	42	33	-	-	-
	21	46	35	22	39	28	22	-	-	-
	24	36	29	14	36.5	27	19	-	-	-
500	18	58	43	30	40	28	24	-	-	-
	21	40	31	18	30	22	16	-	-	-
	24	29	24	10	21	16	10	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic Viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 70

Fann viscometric data, Product : n-C_{22} ester of 12-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
2000	18	73.5	55	37	35	25	20	11	10	2
	21	57	42	30	26.5	19	15	9.5	9	1
	24	45.5	34	23	19	14	10	7.25	7	0.5
300	18	66	49	34	25.5	20	11	-	-	-
	21	54	39	30	17.5	14	7	-	-	-
	24	40.5	30	21	10	8	4	-	-	-
500	18	58	43	30	21.5	18	7	-	-	-
	21	42.5	31	23	14	12	4	-	-	-
	24	31.5	24	15	7.5	7	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 71

Fann viscometric data, Product : n-C_{22} ester of 14-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	73	55	36	65	46	38	10.5	10	1
	21	55.5	42	27	49.5	35	29	8.5	8	0.5
	24	44	33	22	40.5	30	21	7.25	7	0.5
300	18	62.5	48	29	55.5	40	31	-	-	-
	21	49	38	22	37	27	20	-	-	-
	24	33	25	16	33.5	25	17	-	-	-
500	18	56.5	44	25	37.5	26	23	-	-	-
	21	38	29	18	28.5	21	15	-	-	-
	24	29.5	22	15	19	14	10	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 72

Fann viscometric data, Product : n-C_{22} ester of 16-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
200	18	67	52	30	30.5	22	17	8.5	8	1
	21	50.5	38	25	23	17	12	7.25	7	0.5
	24	36.5	29	15	16	12	8	5.25	5	0.5
300	18	57	45	24	23	18	10	-	-	-
	21	41	33	16	18	15	6	-	-	-
	24	31	26	10	12	10	4	-	-	-
500	18	49	39	20	18.5	15	7	-	-	-
	21	32.5	27	11	12.5	11	3	-	-	-
	24	20.5	18	5	8.5	8	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 73

Fann viscometric data, Product : n-C_{22} ester of 18-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
	18	72	55	34	37	27	20	9	8	2
200	21	54.5	42	25	27.5	20	15	7	6.5	1
	24	45.5	34	23	19.5	14	11	6.25	6	0.5
	18	51	39	24	26	21	10	-	-	-
300	21	46	36	20	19.5	16	7	-	-	-
	24	33.5	26	15	13.5	11	5	-	-	-
	18	46.5	36	21	21.5	17	9	-	-	-
500	21	35	29	12	15	13	4	-	-	-
	24	29.5	20	9	10.5	10	1	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	--	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 74

Fann viscometric data, Product : n-C_{22} ester of 22-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Me Properties		
		1	2	3	1	2	3	1	2	3
	18	57	44	26	37	26	22	11.5	11	1
200	21	42	32	20	30	22	16	8.25	8	0.5
	24	28.5	23	11	25	18	14	5.25	5	0.5
	18	48	38	20	31	22	18	-	-	-
300	21	33.5	26	15	24	17	14	-	-	-
	24	21	17	8	19	14	10	-	-	-
	18	35	29	12	24.5	18	13	-	-	-
500	21	25.5	21	9	16	12	8	-	-	-
	24	12.75	11	3.5	12.5	10	5	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 75

Fann viscometric data, Product : n-C_{18} ester of 22-CMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	-	-	-	17.5	15	5
	21	-	-	-	-	-	-	13.5	12	3
	24	-	-	-	-	-	-	11.5	10	2.5
300	18	62	47	30	30	21	18	-	-	-
	21	45.5	34	23	22	16	12	-	-	-
	24	39	29	20	18	13	10	-	-	-
500	18	56.5	43	27	23	17	12	-	-	-
	21	43	32	22	19	14	10	-	-	-
	24	33	25	16	13.6	10	7	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 76

Fann viscometric data, Product : n-C_{22} ester of PA-15 (1)

Additive * ppm		Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
	18	43.5	35	17	37	27	20	11	10	2
200	21	31.5	26	11	31.5	23	17	8.5	8	1
	24	19.5	17	5	28.5	21	15	8.25	7.5	1.5
	18	31	25	12	28.5	21	15	-	-	-
300	21	19.5	17	5	22.5	17	11	-	-	-
	24	9	8.5	1	18.5	14	9	-	-	-
	18	12	10	4	20	15	10	-	-	-
500	21	6.5	5.5	2	15.5	12	7	-	-	-
	24	3.5	3	0.5	12	10	4	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 77

Fann viscometric data, Product : n-C_{22} ester of PA-15(2)

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
	18	35	28	14	34	25	18	9.5	9	1.5
200	21	21.5	19	5	27.5	20	15	8.52	8	1.5
	24	11.5	11	1	24	18	12	6.5	6	1
	18	31	25	12	23	17	12	-	-	-
300	21	23	20	6	19	14	10	-	-	-
	24	10.5	10	1	13.5	10	7	-	-	-
	18	10.5	8	5	17.5	14	7	-	-	-
500	21	4.5	4	1	12.5	10	5	-	-	-
	24	4	3.5	0.5	9	8	2	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at ^{o}C

Table 78

Fann viscometric data, Product : n-C_{22} ester of PA-21 (1)

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	50.5	42	17	35	25	20	8.5	8	1
	21	41	34	14	29.5	22	15	6.5	6	1
	24	26	21	10	23	17	12	5.52	5.5	0.5
300	18	41	35	12	29.5	22	15	-	-	-
	21	29	24	10	22.5	17	11	-	-	-
	24	18	15	6	17.5	13	9	-	-	-
500	18	28	24	8	20	15	10	-	-	-
	21	15	13	4	13.5	11	5	-	-	-
	24	5	4.5	0.5	11.5	10	3	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 79

Fann viscometric data Product : n-C_{22} ester of PA-21(2)

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	50.5	41	19	30.5	22	17	8.5	8	1
	21	43	35	16	26.5	20	13	6.25	6	0.5
	24	26	20	12	20	15	10	5.25	5	0.5
300	18	39.5	33	13	26.5	20	13	-	-	-
	21	27.5	25	5	19	14	10	-	-	-
	24	22.25	20	4.5	14.5	11	7	-	-	-
500	18	25	22	6	16	12	8	-	-	-
	21	15.5	14	3	9.5	8	3	-	-	-
	24	4.5	4	0.5	6.5	6	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at ^{o}C .

Table 80

Fann viscometric data Product : Poly (Dibehenyl maleate-co-vinyl acetate):DBM_VAc.

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
	18	59	46	27	27.5	21	13	11	10	2
200	21	39	30	18	21	17	8	9.5	9	1
	24	31.5	25	13	18	15	6	7.25	7	0.5
	18	49	38	22	20	16	8	-	-	-
300	21	29	23	13	15.5	13	5	-	-	-
	24	24.5	20	9	11.5	10	3	-	-	-
	18	36	28	16	14.5	12	5	-	-	-
500	21	26	22	8	11.5	10	3	-	-	-
	24	14.5	13	3	8.5	8	1	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C.

Table 81

Fann viscometric data Product : Poly(Dibehenyl maleate-co-methylmethacrylate): DBM_MMA

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	59.5	46	27	30	22	16	12.25	11	2.5
	21	45	34	22	25	19	12	11	10	2
	24	32.5	25	15	21	16	10	8.5	8	1
300	18	55	43	24	24	18	12	-	-	-
	21	37	29	16	19	15	8	-	-	-
	24	25.5	21	9	16	13	6	-	-	-
500	18	45	35	20	20	16	8	-	-	-
	21	27	21	12	15	13	4	-	-	-
	24	18.5	16	5	10.5	10	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C

Table 82

Fann viscometric data, Product : Poly (Dibehenyl maleate-co-acrylic acid): DBM-AA.

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	66	52	28	27	21	12	10.5	10	1
	21	44.5	34	21	19	16	6	10	9.5	1
	24	31.5	25	13	15.5	13	5	9.25	9	0.5
300	18	57	45	24	18.5	15	7	-	-	-
	21	37.5	30	15	13.5	11	5	-	-	-
	24	24	19	10	11.5	10	3	-	-	-
500	18	47.5	39	17	12.5	10	5	-	-	-
	21	29.5	24	11	9	8	2	-	-	-
	24	16.5	14	5	6.5	6	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C.

Table 83

Fann viscometric data, Product : Poly(Dibehenyl maleate-Co-Maleic anhydride): DBM-MA.

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
	18	59.5	47	25	25	20	10	10.0	9	2
200	21	43	35	16	18	15	6	8.25	8	0.5
	24	28	24	8	14.5	12	5	6.25	6	0.5
	18	52	41	22	18.5	16	5	-	-	-
300	21	34	28	12	13.5	12	3	-	-	-
	24	21.5	18	7	11	10	2	-	-	-
	18	41.5	34	15	12	10	4	-	-	-
500	21	28	25	6	8	7	2	-	-	-
	24	12.5	12	1	6.5	6	1	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C .

Table 84

Fann viscometric data Product : Poly (Dibehenyl maleate-Co-Itaconic anhydride) : DBM-IA ·

Additive ppm	*	Oil-BH Properties 1	Oil-BH Properties 2	Oil-BH Properties 3	Oil-Na Properties 1	Oil-Na Properties 2	Oil-Na Properties 3	Oil-Mo properties 1	Oil-Mo properties 2	Oil-Mo properties 3
	18	51.5	40	23	42.5	32	21	9.5	9	1
200	21	40	30	20	35	27	16	7.25	7	0.5
	24	30.5	24	13	26.5	20	13	5.25	5	0.5
	18	38	30	16	35	26	18	-	-	-
300	21	30	23	14	26.5	20	13	-	-	-
	24	23	19	8	20.5	16	9	-	-	-
	18	16	15	2	25.2	19	12.5	-	-	-
500	21	13.5	12.5	2	18.7	15	7.5	-	-	-
	24	10.7	10	1.5	14	12	4	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	--	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at $^{\circ}$C .

Table 85

Fann viscometric data, Product : Poly(Dibehenyl maleate-Co-Acrylonitrile): DBM-AN .

Addative ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	57.25	45.5	23.5	-	-	-	14.5	13	3
	21	40	33	14	-	-	-	12.25	11	2.5
	24	26	22	8	-	-	-	11	10	2
300	18	52.5	42	21	19.5	15	9	-	-	-
	21	33.25	27.5	11.5	14	12	4	-	-	-
	24	19.75	16	7.5	11.5	10	3	-	-	-
500	18	41	32.5	17	12.5	11	3	-	-	-
	21	25	23	4	9.5	8.5	2	-	-	-
	24	13	12.5	1	7	6.5	1	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C .

Table 86

Fann viscometric data, Product : Poly (Dibehenyl maleate) : Poly (DBM).

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	56.5	44	25	28	22	12	7.5	7	1
	21	40	32	16	22.5	18	9	6.52	6.5	0.5
	24	28	23	10	18.5	15		5.25	5	0.5
300	18	42.5	33	19	18	15	6	-	-	-
	21	31	25	12	14	12	4	-	-	-
	24	20	17	6	11	10	2	-	-	-
500	18	28.5	23	11	11.5	10	3	-	-	-
	21	18.5	16	5	7.5	7	1	-	-	-
	24	9.5	9	1	5.0	4.5	0.5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C.

Table 87

Fann viscometric data, Product : Poly (Dioctadecyl maleate-Co-vinyl acetate) : DODM_VAc .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	37	27	20	13	12	2
	21	-	-	-	29	22	14	10.5	10	1
	24	-	-	-	25.5	20	11	9.5	9	1
300	18	57.5	44	27	29.5	22	15	-	-	-
	21	35	27	16	23.5	18	11	-	-	-
	24	29.5	24	11	18.5	14	9	-	-	-
500	18	43.5	33	21	21.5	17	9	-	-	-
	21	32	26	12	16.5	13	7	-	-	-
	24	21.5	17	9	13.5	11	5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at ^{o}C .

Table 88

Fann viscometric data, Product : Poly(Dioctadecyl maleate-Co-methylmethacrylate): DODM-MMA .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	37	27	20	14	13	2
	21	-	-	-	31.5	23	17	11.5	11	1
	24	-	-	-	27	20	14	10.5	10	1
300	18	59	45	28	30	22	16	-	-	-
	21	42	32	20	24.5	19	11	-	-	-
	24	32	25	14	20.5	16	9	-	-	-
500	18	50.5	39	23	26.5	21	11	-	-	-
	21	33.5	25	17	21.5	17	9	-	-	-
	24	24	19	10	16.5	13	7	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C .

Table 89

Fann viscometric data, Product : Poly(Dioctadecyl maleate-Co-Acrylic acid): DODM-AA .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
	18	-	-	-	35	27	16	10.5	10	1
200	21	-	-	-	27	21	12	8.25	8	0.5
	24	-	-	-	22	17	10	6.25	6	0.5
	18	60	47	26	32	21	12	-	-	-
300	21	41.5	32	19	21	16	10	-	-	-
	24	31	25	12	17.5	14	7	-	-	-
	18	53	43	20	22.5	17	11	-	-	-
500	21	36.5	29	15	17.5	14	7	-	-	-
	24	26	21	10	12.5	10	5	-	-	-
	18	-	-	-	-	-	-	-	-	-
1000	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties of °C .

Table 90

Fann viscometric data, Product : Poly(Dioctadecyl maleate-Co-Maleic anhydride): DODM_MA .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	37	29	16	8	7	2
	21	-	-	-	29	22	14	6.5	6	1
	24	-	-	-	25.5	20	11	4.25	4	0.5
300	18	57.5	45	25	32	25	14	-	-	-
	21	39	32	14	24.5	19	11	-	-	-
	24	42.5	37	11	21	16	10	-	-	-
500	18	47	37	20	21.5	17	9	-	-	-
	21	33	28	10	15	12	6	-	-	-
	24	19	15	8	12.5	10	5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at °C .

Table 91

Fann viscometric data, Product : Poly(Dioctadecyl maleate-Co-Itaconic anhydride) : DODM-IA .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	34.25	25	18.5	10.5	10	1
	21	-	-	-	28	21.5	13	8.5	8	1
	24	-	-	-	24.25	18.5	11.5	6.25	6	0.5
300	18	52.5	41	23	27	20	14	-	-	-
	21	31	24	14	22	17.5	9	-	-	-
	24	26	21	10	17	13	8	-	-	-
500	18	38.5	30	17	18.5	15	7	-	-	-
	21	27.5	23	9	14.5	12	5	-	-	-
	24	17.5	14	7	13	11.5	3	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at ^{o}C .

Table 92

Fann viscometric data, Product : Poly(Dioctadecyl maleate-Co-Acrylonitrile): DODM-AN .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	-	-	-	7	6.5	1
	21	-	-	-	-	-	-	4.25	4	0.5
	24	-	-	-	-	-	-	3.75	3.5	0.5
300	18	55	42	26	27.25	20.5	14	-	-	-
	21	49.5	30.5	18	22.75	17	11.5	-	-	-
	24	29	23	12	18	14	8	-	-	-
500	18	44	34	20	22.5	18	9	-	-	-
	21	29.5	22	15	18.5	15	7	-	-	-
	24	19.5	16	7	13.5	11	5	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at ^{o}C .

Table 93

Fann viscometric data, Product : Poly(Dioctadecyl maleate) : Poly(DODM) .

Additive ppm	*	Oil-BH Properties			Oil-Na Properties			Oil-Mo Properties		
		1	2	3	1	2	3	1	2	3
200	18	-	-	-	36	28	16	14	13	2
	21	-	-	-	28.5	22	13	11.75	11	1.5
	24	-	-	-	24.5	19	11	10.52	10	1.5
300	18	48	39	22	26	21	10	-	-	-
	21	38	30	16	21	17	8	-	-	-
	24	26.5	21	11	17	14	6	-	-	-
500	18	33.5	26	15	19	15	8	-	-	-
	21	29.5	20	9	13.5	11	5	-	-	-
	24	15.5	12	7	10.5	9	3	-	-	-
1000	18	-	-	-	-	-	-	-	-	-
	21	-	-	-	-	-	-	-	-	-
	24	-	-	-	-	-	-	-	-	-

1 = Apparent viscosity cps, 2 = Plastic viscosity cps, 3 = Yield value lb/100 ft^2

* Properties at ^{o}C .

Table 94

Fann Viscometric data :

Additive ppm	*	Oil North Kadi Properties Product n-C_{22} ester of 2-UnMA			n-C_{22} ester of 22-UnMA			n-C_{22} ester of 2-CMA			n-C_{22} ester of 22-CMA		
		1	2	3	1	2	3	1	2	3	1	2	3
	45	136.5	133	7	133	130	6	137	133	8	134	132	6
500	48	124	121	6	121.5	119	5	126.5	123	7	123.5	121	5
	51	109	107	4	109.5	108	3	116.5	114	5	113	111	4
	45	127.5	125	5	125	123	4	135	127	6	127.5	125	5
1000	48	117	115.5	3	115.5	114	3	122.5	120	5	118	116	4
	51	100	99	2	103	102	2	108	106	4	106	105	2

1 = Apparent viscosity cps ; 2 = plastic viscosity cps, 3 = yield value lb/100 ft^2

* Properties at °C .

Table 95

Fann Viscometric data :

Additive ppm	*	Oil North Kadi Properties Product											
		$n-C_{22}$ ester of PA-15(1)			$n-C_{22}$ ester of PA-21(1)			Poly(DBM-VAc)			Poly(DODM-VAc)		
		1	2	3	1	2	3	1	2	3	1	2	3
500	45	134.5	132	7	137.5	134	7	141	137	9	144	140	8
	48	122.5	120	5	121	118	6	124.5	121	7	128.5	125	7
	51	107.5	106	3	109.5	108	3	114	111	6	117	114	6
1000	45	123.5	121	5	125.5	123	5	130	127	6	132	129	6
	48	114	112	4	117	115	4	120.5	118	5	124.5	122	5
	51	99.25	98	2.5	101.5	100	3	107	105	4	110	108	4

1 = Apparent viscosity cps ; 2 = plastic viscosity cps ; 3 = Yield value lb/100 ft^2

* Preperties at °C .

Table 96

Fann viscometric data :

Additive ppm	*	Oil Amta Product Properties											
		n-C_{22} ester of 2-UnMA			n-C_{22} ester of 4-UnMA			n-C_{22} ester of 6-UnMA			n-C_{22} ester of 8-UnMA		
		1	2	3	1	2	3	1	2	3	1	2	3
500	45	138	136	4	139.75	137.5	4.5	140	138	4	136.25	134	4.5
	48	116.5	115	3	119	117	4	117	116	3.5	118	116.5	3
	51	96.5	96	1	100	99	2	100.7	99.5	2.5	99.25	98.5	1.5
1000	45	132.5	131	3	133.75	132	3.5	135	133	4	135.5	134	3
	48	111	110	2	113	112	2	112.5	111	3	113.75	112.5	2.5
	51	91.5	91	1	93.75	93	1.5	95.5	94.5	2	93.5	93	1

1 = Apparent viscosity, 2 = Plastic viscosity, 3 = Yield value

* Properties at °C.

Table 97

Fann viscometric data :

Additive ppm	*	Oil Amta Properties Product											
		n-C_{22} ester of 18-UnMA			n-C_{22} ester of 10-UnMA			n-C_{22} ester of 12-UnMA			n-C_{22} ester of 14-UnMA		
		1	2	3	1	2	3	1	2	3	1	2	5
	45	137	135	4	139	136.5	5	136.5	134.5	4	136.75	135	3.5
500	48	115.75	114	3.5	114	112	4	116.5	115	3	114.75	113.5	2.5
	51	96.5	96	1	95.75	94.5	2.5	97.75	97	1.5	96	95	2
	45	134.5	133	3	136.25	134.5	3.5	133.5	132	3	134.75	133.5	2.5
1000	48	112	111	2	110.25	109	2.5	112.5	111.5	2	110	109	2
	51	95	94.5	1	91.5	91	1	99	93.5	1	90.5	90	1

1 = Apparent viscosity, 2 = Plastic viscosity, 3 = Yield value

* Properties at °C .

Table 98

Fann Viscometric data :

Additive ppm	*	Oil Amta Properties											
		Product											
		n-C_{22} ester of 22-U$_n$MA			n-C_{22} ester of 2-CMA			n-C_{22} ester of 22-CMA			n-C_{22} ester of PA-15(1)		
		1	2	3	1	2	3	1	2	3	1	2	3
	45	135.7	134	3.5	144	142	4	134	132	4	132	130	4
500	48	114.5	113.5	2	120.5	119	3	116.5	115	3	115.5	114.5	2
	51	98	97	2	104	103	2	95	94	2	93.5	92.5	2
	45	130	129	2	132.5	131	3	128.5	127	3	126.5	125	3
1000	48	107	106	2	105.5	104	3	109	108	2	110	109	2
	51	92.5	92	1	96	95	2	94.5	94	1	92.5	92	1

1 = Apparent viscosity, 2 = Plastic viscosity, 3 = Yield value

* Properties at °C .

Table 99

Fann viscometric data :

Additive ppm	*	Oil Amta Properties Product					
		n-C_{22} ester of PA-21(1)			Poly (DBM-VAc)		
		1	2	3	1	2	3
	45	133.5	132	3	141	139	4
500	48	117	116	2	120	119	2
	51	95	94	2	98	97	2
	45	128.5	127	3	136	134	4
1000	48	107	106	2	110	111	3
	51	90.5	90	1	95.5	95	1

1 = Apparent viscosity, 2 = Plastic viscosity,

3 = Yield value * Properties at °C .