EXPERMENTAL

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- **MATERIALS AND PROCEDURES:**

2.1. MATERIALS:

2.1.1. Monomers:

(a) Maleic anhydride:

Formula

$$O=C \underset{O}{\overset{CH=CH}{\diagdown \diagup}} C=O$$
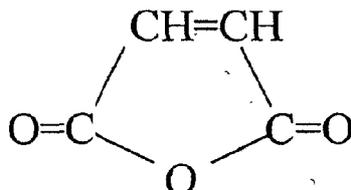
Mwt = 98.06
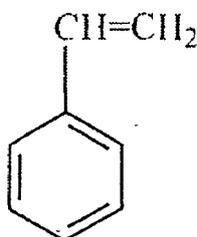mp   = 51 to 56°C
bp   = 200°C
purity = 99%

(b) Styrene:

Systematic name: Vinyl benzene
Formula

$CH=CH_2$

Mwt = 104.15
mp   = -31°C
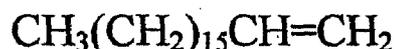bp   = 145-146°C
n^{20}_D = 1.546
density = 0.909 g/ml 25°C
purity = 99%

It is a colorless liquid, acid odor and polymerizes readily. It is immiscible with water but miscible with benzene. It was purified before use. The purification procedure is out lined in the following section.

(c) Octadecene:
Formula
$$CH_3(CH_2)_{15}CH=CH_2$$
Mwt   = 252.48
mp   = 14 to 16°C
bp   = 179°C
n^{20}_D = 1.444
density = 0.789 g/ml 25°C
purity = 99.8%

2.1.2. Alcohols:
(A) Dodecyl alcohol
Systematic name: 1-Dodecanol
Formula
$$CH_3(CH_2)_{11}OH$$
Mwt   = 186.33 ·
mp   = 22 to 26°C
bp   = 266-262°C
density = 0.833 g/ml 25°C
n^{20}_D = 1.442

It is a colorless liquid at room temperature (30°C). Soluble in xylene, acetone and toluene and insoluble in water.

(B) Hexadecyl alcohol
Systematic name: 1-Hexadecanol
Formula
$$CH_3(CH_2)_{15}OH$$
Mwt   = 242.44
mp   = 49 to 50°C
bp   = 190°C
purity = 99%

(C) Octadecyl alcohol

Systematic name: 1-Octadecanol

Formula

$$CH_3(CH_2)_{17}OH$$

Mwt   = 270.49

mp   = 56 to 59°C

density = 0.812 g/ml 25°C

(D) Behenyl alcohol

Systematic name: 1-Docosanol

Formula

$$CH_3(CH_2)_{21}OH$$

Mwt   = 326.60

mp   = 65 to 72°C

bp   = 180°C

2.1.3. Amines:

(A) Dodecyl amine

Formula

$$CH_3(CH_2)_{11}NH_2$$

Mwt   = 185.35

mp   = 27 to 29°C

bp   = 247-249°C

density = 0.806 g/ml 25°C

(B) Hexadecyl amine

Formula

$$CH_3(CH_2)_{15}NH_2$$
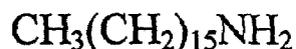
Mwt   = 241.46

mp   = 43 to 45°C

bp   = 330°C

(C) Octadecyl amine

Formula

$$CH_3(CH_2)_{17}NH_2$$
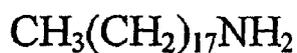
Mwt   = 269.51
mp   = 50 to 52°C
bp   = 232°C

2.1.4. Initiator:

(a) Benzoyl peroxide (BPO)

Formula

$$C_6H_5CO-O-O-CO-C_6H_5$$

Mwt   = 242.23
mp   = 103 to106°C

2.1.5. Catalyst:

p.Toluene sulphonic acid (PTSA) monohydrate
Formula

$$CH_3C_6H_5SO_3H.H_2O$$
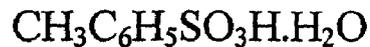
Mwt   = 190.22
mp   = 103 to106°C
purity   = 99%

2.1.6. The Solvent:

Solvent	bp	Source
Xylene	138-139°C	Aldrich Chemical Co. Ltd. (U.K)
Benzene	80°C	Aldrich Chemical Co. Ltd. (U.K)
Acetone	56°C	Aldrich Chemical Co. Ltd. (U.K)
Methanol	64.7°C	Aldrich Chemical Co. Ltd. (U.K)
Ethanol	78°C	Aldrich Chemical Co. Ltd. (U.K)
Butanon	80°C	Aldrich Chemical Co. Ltd. (U.K)
Petrolum ether (40-60°C)	40-60°C	Aldrich Chemical Co. Ltd. (U.K)

2.1.7. Auxiliary Chemicals:

Name	Source
Sodium hydroxide	Aldrich Chemical Co. Ltd. (U.K)
Calcium chloride anhydrous	Aldrich Chemical Co. Ltd. (U.K)

2.2. PROCEDURES:
2.2.1. Preparation of Styrene-Maleic Anhydride
Copolymer:

The copolymerization of styrene and maleic anhydride was carried out in a three-necked round bottom flask equipped with a stirrer, an inlet tube for the introduction of nitrogen. In the flask was placed 250ml of the freshly distilled benzene and one mole of maleic anhydride. The temperature was raised to the boiling point of the benzene solvent while constant stirring to dissolve the maleic anhydride. The mixture was flushed with nitrogen for 10 minutes to attain an inert atmosphere and then the rate of bubbling of nitrogen was reduced to about 5 bubbles / minute. The desired weight of initiator (benzoyl peroxide) was 2%wt of maleic anhydride; added to the solution. After complete dissolution of the initiator one mole of styrene was added dropwise and the temperature was maintained at 80°C for one hour when the reaction was completed, the temperature was allowed to reduce to the room temperature. The copolymer was precipitated as a fine white powder, then added to cold butanone and put on petroleum ether (40°C-60°C), the product was filtered and dried in a vacuum oven at 60°C.

2.2.2. Esterification of Styrene-Maleic Anhydride Copolymer:

The esterification of the prepared styrene-maleic anhydride copolymer with a series of n-alkanols have increasing number of carbon atoms [dodecyl alcohol C_{12}, hexadecyl alcohol C_{16}, octadecyl alcohol C_{18} and docosanol C_{22}] . In a 4 necked round bottom flask fitted with a mechanical stirrer, an efficient condenser, a thermometer, and a nitrogen gas inlet, the desired weight from the dry copolymer was esterified with different alcohols in presence of p-toluene sulphonic acid as a catalyst, and xylene as a solvent. Reaction is readily carried out by heating at 130°C. The designations of the prepared compounds are listed in Table (2.1).

2.2.3. The reaction of Styrene-Maleic Anhydride Copolymer with Different Amines:

The prepared styrene-maleic anhydride copolymer was reacted with different amines [dodecyl C_{12}, hexadecyl C_{16} and octadecyl C_{18}]. The reactions were carried out in a 4-necked round bottom flask fitted with a mechanical stirrer, an efficient condenser, a thermometer, and a nitrogen gas inlet. The desired weight from the dry copolymer was reacted with different amines in presence of xylene as a

solvent at 120-140°C. The designations of the prepared compounds are listed in Table (2.1).

Table (2.1) The designation of the prepared compounds

Styrene-maleic anhydride copolymer with	
ALCOHOLS	**AMINES**
Dodecyl alcohol (A) Hexadecyl alcohol (B) Octadecyl alcohol (C) Docosanol (D)	Dodecyl amine (E) Hexadecyl amine (F) Octadecyl amine (G)

2.2.4. Preparation of Octadecene-Maleic Anhydride Copolymer:

The copolymerization of octadecene and maleic anhydride was carried out in a three-necked round bottom flask equipped with a stirrer, an inlet tube for the introduction of nitrogen. In the flask was placed one mole of octadecene with one mole of maleic anhydride in presence of benzoyl peroxide 0.5% as an initiator for the copolymerization and used xylene as a solvent. The reactants were mixed and heated gradually from room temperature to 130°C ±0.5°C using a well-controlled thermostat after the reaction occurred put the product in cold methanol then filtrate to obtain the copolymer.

2.2.5. Esterification of Octadecene-Maleic Anhydride Copolymer:

The esterification of the prepared octadecene-maleic anhydride copolymer with a series of n-alkanols have increasing number of carbon atoms [dodecyl alcohol C_{12}, hexadecyl alcohol C_{16}, octadecyl alcohol C_{18} and docosanol C_{22}]. In a 4 necked round bottom flask fitted with a mechanical stirrer, an efficient condenser, a thermometer, and a nitrogen gas inlet, the desired weight of the dry copolymer was esterified with different alcohols in presence of p-toluene sulphonic acid as a catalyst, and xylene as a solvent. Reaction is readily carried out by heating at 130°C. The designations of the prepared compounds are listed in Table (2.2).

2.2.6. The reaction of Octadecene-Maleic Anhydride Copolymer with Different Amines:

The prepared octadecene-maleic anhydride copolymer was reacted with different amines [dodecyl C_{12}, hexadecyl C_{16} and octadecyl C_{18}]. The reactions were carried out in a 4-necked round bottom flask fitted with a mechanical stirrer, an efficient condenser, a thermometer, and a nitrogen gas inlet. The desired weight from the dry copolymer was reacted with different amines in presence of xylene as

a solvent at 120-140°C. The designations of the prepared compounds are listed in Table (2.2).

Table (2.2) The designation of the prepared compounds

Octadecene-maleic anhydride copolymer with	
ALCOHOLS	**AMINES**
Dodecyl alcohol (L)	Dodecyl amine (R)
Hexadecyl alcohol (M)	Hexadecyl amine (S)
Octadecyl alcohol (N)	Octadecyl amine (T)
Docosanol (O)	

2.2.7. The Solubility Test:

The solubility of the prepared copolymers was investigated by dissolving the polymer in free additive base oil (SAE 30). In a conical flask, 2 g of the copolymer was added to previously weight base oil (100g) and the mixture was allowed to stand overnight. This time was enough to procure the required swelling for the polymer. The conical flask was immersed in an oil bath placed on a thermostated hot plate fixed over a magnetic stirrer. The temperature of the oil bath was then raised to 60°C and at this point the mixture was agitated by a Teflon covered magnet for 20 minutes.

2.2.8. I.R. Spectroscopic Analysis:

I.R. spectra of the synthesized compounds were determined by using F.T.I.R. spectrometer Model Type Mattson Infinity Series Top 961.

2.2.9. Determination of the Molecular Weights:

The molecular weights of the prepared compounds were determined by using gel permeation chromatography (GPC), Water 600 E.

2.2.10. ^{1}HNMR Spectroscopic Analysis:

The ^{1}HNMR spectra of synthesized polymers were measured by using 300 MHS spectrometer W.P. 300, Bruker.

2.2.11. Evaluation of The Prepared Compounds as Lube Oil Additives:

A. As viscosity index improvers:

The prepared compounds were evaluated as viscosity index improvers using base oil (SAE 30) through the viscosity index test (VI) according to (American Society of Testing and Materials)ASTM D2270-87. The kinematic viscosity of the oil contains the tested compound was determined at 40°C and 100°C. Different concentrations between 0.25 wt% to 3.0 wt% were used to study the effect of concentration on VI of lube oil.

The VI was calculated from equations (2.1)-(2.2).

$$VI = [(L-U)/(L-H)] \times 100 \qquad (2.1)$$

Where

L= kinematic viscosity, in cSt (mm^2/s), at 40°C of an oil of 0 viscosity index having the same kinematic viscosity at 100 °C as the oil whose viscosity index is to be calculated,

H= kinematic viscosity, in cSt (mm^2/s), at 40°C of an oil of 100 viscosity index having the same kinematic viscosity at 100 °C as the oil whose viscosity index is to be calculated,

U= kinematic viscosity, in cSt (mm^2/s), at 40°C of the oil whose viscosity index is to be calculated.

Values of L and H were obtained from a special table from the ASTM D-2270-87 at which the basic kinematic viscosity values at 100°C are equal to or more than 2 cST (mm^2/s) and less than 70 cSt.

When the basic kinematic viscosity value at 100°C was above 70 cSt the values of L and H were calculated as follows:

$$L = 0.8353Y^2 + 14.67\,Y - 216 \qquad (2.2)$$

$$H = 0.1684Y^2 + 11.85\,Y - 97 \qquad (2.3)$$

Where Y= kinematic viscosity at 100°C.

If the measured kinematic viscosity values at 100°C were not listed in the table, but were within the range of 2-70 cSt

(the listed values), the corresponding values of L and H were obtained by linear interpolation.

When the obtained value of the viscosity index was above 100, it was recalculated, as recommended by the ASTM, on the basis that

$$Y^N = H/U$$

Where

Y= kinematic viscosity, in cSt (mm^2/s), of the unknown oil at 100°C.

N= (log H- log U) /log Y

H= kinematic viscosity, in cSt (mm^2/s), at 40°C of an oil of 100 viscosity index using the above mentioned procedure and having the same kinematic viscosity at 100°C.

$$VI = \{[(antilog\ N)-1]/\ 0.00715\} +100 \quad (2.5)$$

B. As pour point depressants:

The prepared compounds were evaluated as pour point depressants using base oil (SAE 30) through the pour point test according to the ASTM-97-87. The effect of additive concentration was investigated by using different concentration. The instrument used for measuring the pour point was the Cold Filter Plugging Point Automatic Tester (CFPPA-T), model 1st CPP97-2.
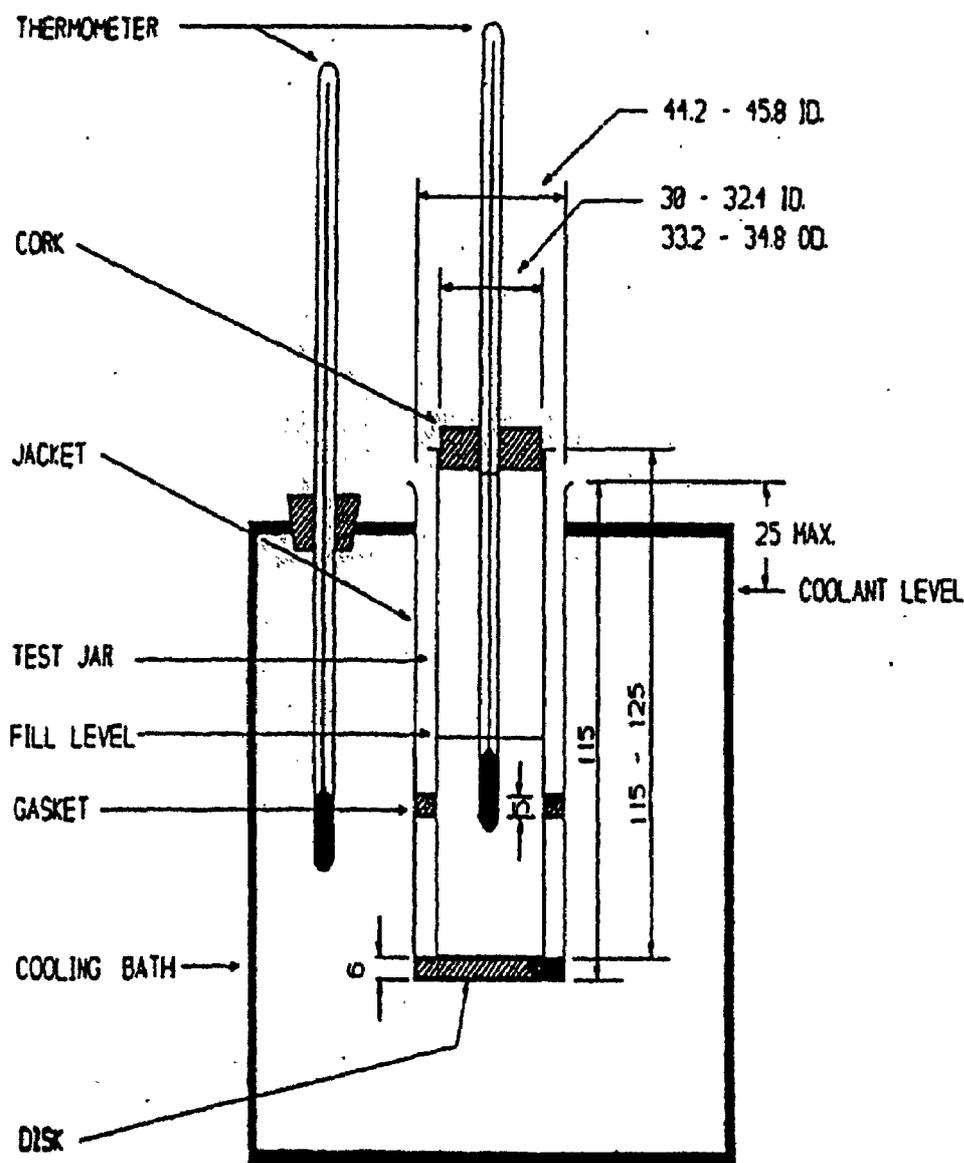
C. As dispersants:

By using spot method [Gatis et. al., 1955], the lube oil sample as well as its blends with 2 % by weight of each of the prepared additives were subjected to severe oxidation condition in the presence of copper and iron strips at 165.5°C for 72 hours using the Indiana test method of oxidation [Lamb et. al., 1941]. Drops were taken from the samples being oxidized in the Indiana test after 24 hours intervals of oxidation and up to 72 hours to make spots on special filter paper (Durieux 122) and the dispersancy of the sample were measured as follows:

$$\% \text{ Dispersancy} = \frac{\text{Diameter of black spot}}{\text{Diameter of the total spot}} \times 100$$

The efficiency of dispersants has been classified as follows:-

Up to 30% no dispersancy

30-50% medium dispersancy

50-60% good dispersancy

60-70% very good dispersancy

Above 70% excellent Dispersancy.