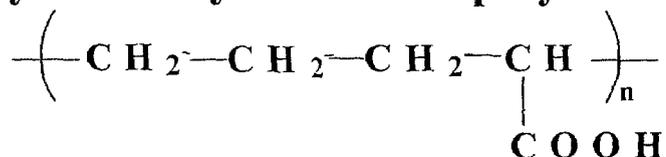EXPERIMENTAL

II- EXPERIMENTAL

2.1. RAW MATERIALS

2.1.1 Polyethylene/Acrylic Acid Copolymer Waste (PEAA)

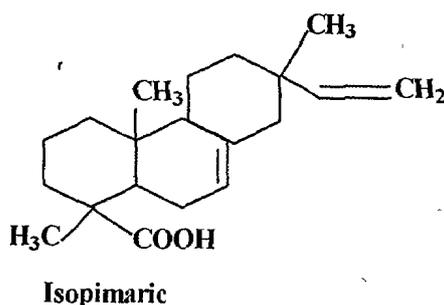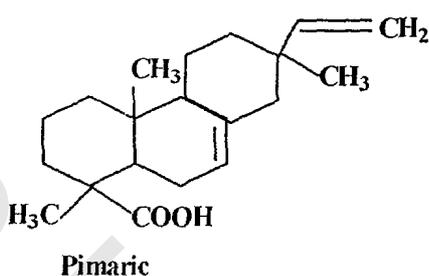$$-\left(CH_2-CH_2-CH_2-\underset{\underset{COOH}{|}}{CH}\right)_n-$$

Ethylene acrylic acid copolymer (PEAA) was obtained from Basell Polyolefine (Germany). It was used as adhesive for coating of petroleum pipelines with Polyolefine three-layer system under commercial name Lucalen A2910M. It was used for coating of petroleum pipelines that carried out by PETROJET coating plant (Egypt). There are a lot of wasted materials were obtained during the coating processes. Its specifications were listed in **Table (2.1)**.

2.1.2. Colophony (Rosin Acids)

Abietic Type

Abietic

Neoabietic

dehydroabietic

Palustric

Levopimaric

Pimaric type

Pimaric

Isopimaric
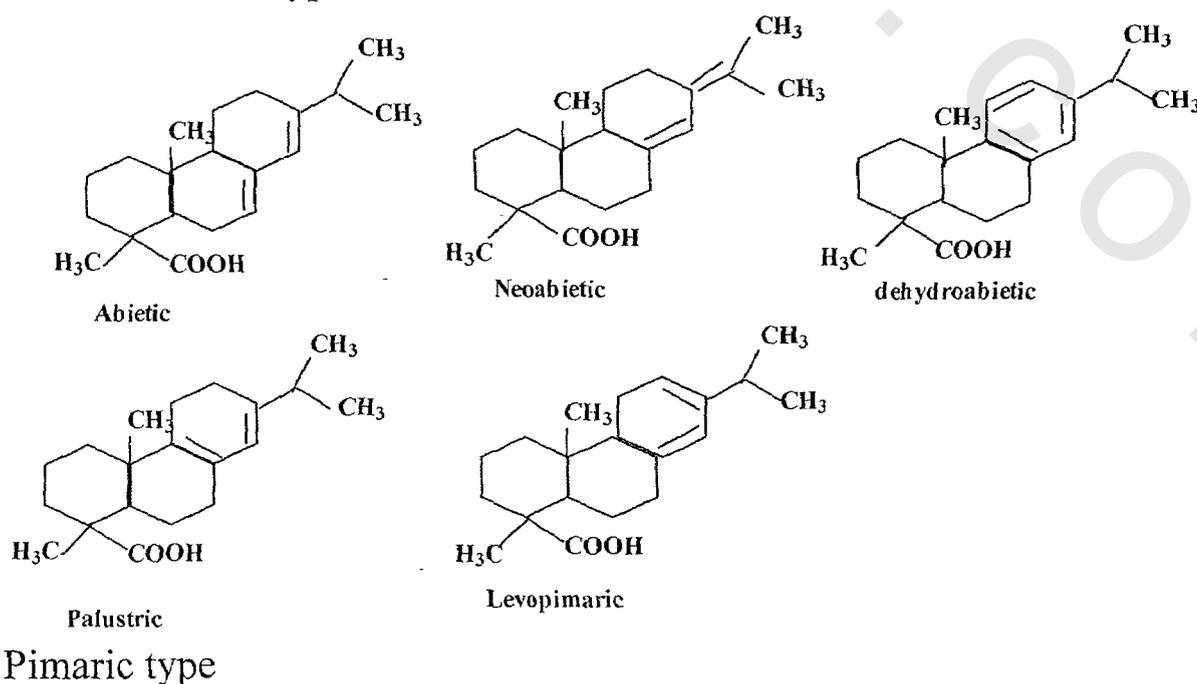
Colophony is natural product and contains more than 95% of rosin acid. The rosin acids were heated at 150 °C for 4h and at 200°C for 30 min in nitrogen atmosphere. Rosin acids were separated by crystallization from the cooled concentrated acetone solution of commercial rosin and purified by recrystallization from the same solvent [117]. The yield of the purified rosin was (92%). The product was characterized by the following specifications:-

mp   : 161-163°C

Acid value   : 186 mg KOH. g^{-1}

Mwt   : 289

2.1.3. Alcohols

a) Ethanol (EA)

It is obtained from Aldrich Chemical Co. Ltd. (UK) with specifications:

M.wt.   :   46.07

b.p, °C   :   78

Density (g/cm^3)   :   0.785

b) Methanol (ME)

It is obtained from Aldrich Chemical Co. Ltd. (UK) with specifications:

M.wt.   :   32.04

b.p, ^{o}C   :   64.6

Density (g/cm^3)   :   0.791

2.1.4 Polyethylene Glycols

General formula:

H (OCH$_2$ CH$_2$)$_n$OH

a) Polyethylene Glycol 400 (PEG$_{400}$), H (OCH$_2$ CH$_2$)$_9$OH

It is obtained from Aldrich Chemical Co. Ltd. (UK) with the following specifications:

<M.wt>   : 400

Viscosity (98°C)   : 7.3 centistoks

Softening temperature: -6 ^{o}C

It is a moist solid below its melting temperature, miscible with water.

b) Polyethylene Glycol 1000 (PEG$_{1000}$), H (OCH$_2$ CH$_2$)$_{23}$OH

PEG1000 is supplied from Aldrich Chemical Co. Ltd. (UK) with the following specifications:

<M.wt.>   : 1000

Viscosity (98°C)   : 17.4 centistokes

Melting range   : 33-40°C

It is hygroscopic waxy solid, soluble in water.

Table (2.1): Properties of PEAA Adhesive Copolymer:

Property	Value	Test Method
Mass Density, g/cm^3 (23°C)	0.924	DIN 53479
Melt Flow Index, g/10min (190°C/2.16 Kg)	6.8	DIN 53735
Melting temperature, $^{\circ}$C (DSC)	98	-
Tensile Stress at break, N/mm^2	22	DIN53453
Shore Hardness A	90	DIN 53505

c) Polyethylene Glycol 4000 (PEG$_{4000}$), H (OCH$_2$ CH$_2$)$_{91}$OH

PEG4000 is purchased from Aldrich Chemical Co. Ltd. (UK) with the following specifications:

<M.wt.>   : 4000

Melting range   : 49-52 °C

It is white water soluble chips.

d) Polyethylene Glycol 600 (PEG$_{600}$), H (OCH$_2$CH$_2$)$_{13}$OH

It is obtained from Fluka Chemical Co. with the following specifications:

Density (g/cm^3)   : 1.12

M.wt. (g/mol)   :   600

m.p, °C   :   17 - 22

2.1.5 1-Hexadecylamine (HDA), CH$_3$ (CH$_2$)$_{15}$NH$_2$

It is purchased from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

M.wt.   :   241.46

m.p, °C   :   43-45

2.1.6. P-Toluenesulfonic Acid Monohydrate (PTSA)
CH$_3$C$_6$H$_4$SO$_3$H.H$_2$O

It is purchased from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

M.wt.   :   190.22

m.p, °C   :   103-106

2.1. 7. Benzoyl Peroxide (BZ_2O_2)

$$(C_6H_5CO)_2O_2$$

It is purchased from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

M.wt.   :   242.23

m.p, ^{o}C   :   104-106

2.1.8. Vinyl Acetate (VA)

$$CH_2=CH\ OCOCH_3$$

It is purchased from Aldrich Chemical CO. Ltd.(U.K.) with the following specifications:

M.wt.   :   86.09

b.p, ^{o}C   :   72-73

density (g/cm^3)   :   0.934

2.1.9. Maleic Anhydride (MA)

It is produced from B.D.H. CO. Ltd.(U.K.) with the following specifications:

M.wt. (g/mol)   :   98.06

m.p, ^{o}C   :   54-56

b.p, ^{o}C   :   200

2.1.10. NAFOL

A saturated linear long chain alcohol blend, Nafol 20^{+}, was supplied by CONDEA Chemical Co., India. The typical analysis was listed in **Table (2.2).**

Table (2.2): Typical Analysis of Linear Long-Chain Alcohol Blends (Nafol 20$^+$).

Alcohol Composition (wt%)	Content
$C_{18}H_{37}OH$ (Wt %)	6
$C_{20}H_{41}OH$(Wt %)	50 ± 10
$C_{22}H_{45}OH$(Wt %)	29 ± 16
$C_{24}H_{49}OH$(Wt %)	14 ± 4
$C_{26}H_{53}OH$(Wt %)	5 ± 3
Alcohol content (wt%)	~80
Density (g cm^{-3})	~0.825
Hydroxyl number (mg KOH g^{-1})	130-150
Saponification number (mg KOH g^{-1})	10 max
Neutralization number (mg KOH g^{-1})	1.0 max
Iodine number (mg 1-100 mg)	20 max
Water content (wt%)	0.1 max

2.1.11. Solvents

The solvents used in this work were analytical reagents. They were dried overnight with anhydrous magnesium sulfate and distilled at atmospheric pressure. The following solvents were used: -

Solvent	Source	B.P. (^{o}C)
Toluene	EPRI(Egypt)	109-111
Acetone	EPRI(Egypt)	56
n-Heptane	EPRI(Egypt)	98
O-Xylene	EPRI(Egypt)	137-140
Chloroform	EPRI(Egypt)	60
Tetrahydrofuran (THF)	Aldrich Chemical Co. Ltd (Germany)	67

2.2. METHOD OF PREPARARTION

2.2. 1 Esterification of Alcohols onto (PEAA)

PEAA copolymer was first dissolved in refluxing toluene, and then PTSA catalyst, ME and EA were added to reaction medium. PEAA esters were prepared by reacting PEAA waste with EA and ME under N_2 gas at 90 ^{o}C using toluene as a solvent in the presence of 1% PTSA (wt % based on total weight of reactants). The reaction was carried out in a four-neck glass flask equipped with a stirrer, thermometer, nitrogen gas inlet and a reflux condenser as represented in **Scheme (2.1)**.

The water of the esterification reaction was removed throughout the course of the reaction using Dean and Stark separator. The prepared esters were purified by precipitating the reaction products into excess of acetone. The yield of PEAA esters with ethanol and methanol are 95 and 98 %, respectively.

2.2.2. Grafting of VA onto (PEAA) Grafts:

The esterified PEAA with methanol or ethanol were placed into reaction reactor with suitable amount of Diesel fuel with concentration 35 wt %. The esterified polymers were blended with 30 % of equivalent weight ratio of vinyl acetate monomer. The mixture was bubbled with nitrogen for 1 h and the reaction temperature was raised up to 65 ^{o}C. Then the initiator BZ_2O_2 (with 0.2 wt % based on total weight of both PEAA and VA monomer) dissolved in toluene with suitable concentration was added to the mixture. The temperature was maintained at the temperature of 65 ^{o}C for 6h until the reaction viscosity was increased. At the end of the reaction period, the reaction mixture was diluted with Diesel fuel up to 10 wt % to be used as flow improver and wax deposition additives [118]. The yields for grafting of VA with PEAA methyl and PEAA ethyl ester are 93 and 90%, respectively.

2.2.3. Preparation of Rosin Ester and Amide:

Polyethylene glycol (PEG) having different Mwt. 400, 600, 1000 and 4000 (which have ethylene oxide number 9, 13, 23

and 91, respectively) were used to prepare polyoxyethylene rosin esters. Nafol 20$^+$ and hexadecylamine were used to prepare long chain alkyl rosin ester and amide, respectively.

The rosin ester or amide was obtained by direct esterification of 1 mol rosin acid with (1.1 mol) of Nafol 20$^+$ or Polyethylene glycol or (1.1 mol) hexadecylamine in presence of 0.1% p-toluene sulphonic acid as catalyst. The ingredients were charged in the reaction vessel in presence o-xylene as solvent. The mixture was heated under nitrogen atmosphere. The reaction was carried out at reflux temperature (140°C) until the theoretical amount of water was collected azeotropically in Dean and Stark trap.

The prepared Nafol 20$^+$-rosin ester was purified by extraction with n-hexane, distilling off the solvent under reduced pressure, washing with water to remove catalyst until the product become neutral, and finally recrystallizing twice from acetone. The polyoxyethylene rosin esters were purified after the o-xylene distilled off. The Rosin ester or amide were dissolved in chloroform and precipitated from cold diethyl ether.The product was dissolved in isopropanol and salted out with hot saturated sodium carbonate solution.

This procedure was repeated three times and isopropanol was removed by distillation. The purified products were dried in vacuum oven.

Experimental

1. Nitrogen gas cylinder
2. Paraffin oil
3. Mantle
4. Reaction vessel
5. Heat Control
6. Thermometer
7. Mechanical stirrer
8. Dean and Stark trap
9. Condenser
10. Cold water in
11. Water out
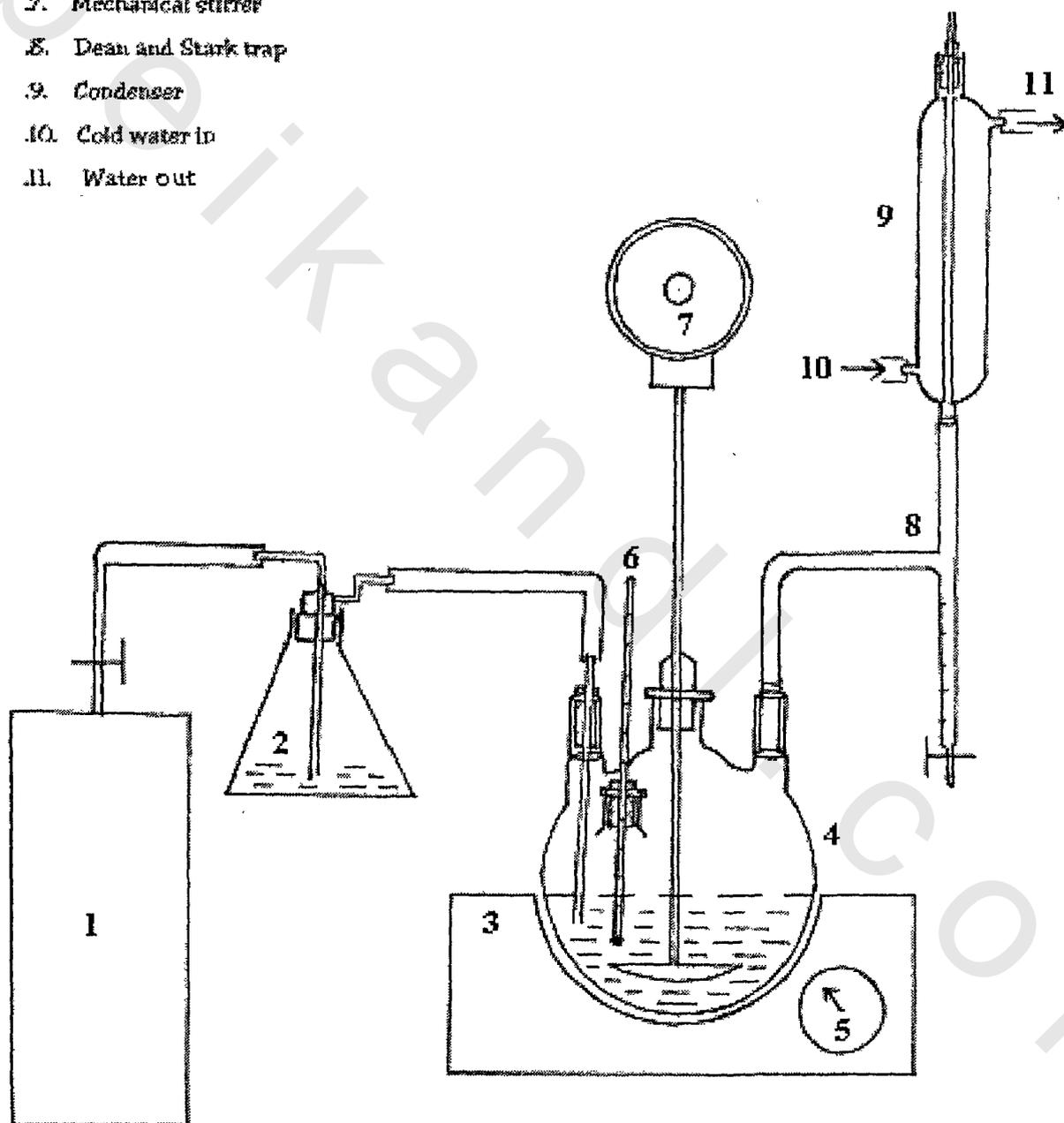
Scheme (2.1): Schematic Representation of Esterification Reaction Kettle.

2.2.4. Synthesis of the Diels-Alder Rosin Adducts:

a)-Synthesis of acrylorosin acid (ARA)

A 0.5 L reaction flask provided with stirrer, thermometer, condenser and nitrogen inlet was charged with rosin (155g, 0.5 mol and RA 37 g, 0.5 mol) containing 0.5% hydroquinone, drained with a slow N_2 stream and heated up to 140 °C for 2 h. The reaction temperature was raised up to 160 °C for 2 h and, finally, at 190 °C for 1h. Finally, the reaction mixture was cooled and precipitated with cyclohexane and purified by reprecipitation which consisted of redissolution in trichloroethylene and precipitation into petroleum ether [119]. A final purification was carried out by extraction with diethyl ether. The purified product was characterized by (yield value 42%, acid value 295mg KOH g^{-1}).

b)-Synthesis of maleorosin acid (MRA)

In a first phase the above mentioned procedure was repeated in the simillar reaction flask. Rosin (155g, 0.5 mol) and MA (50 g, 0.5 mol) were heated at 150 °C under N_2 for 0.5h and at 170 °C for another 0.5 h [120]. Finally the reaction temperature was raised up to 190 °C for 3 h.the final product was specified as yield value 98%, mp 229-233 °C and acid value 414 mg KOH g^{-1}.

Physical characteristics of rosin amide and monoester

Sample	m.p	B.p	Yield%
Rosin- hexadecylamine	56	-	85
Rosin- PEG400	-	65	90
Rosin- PEG600	-	73	85
Rosin- PEG1000	45	-	80
Rosin- PEG4000	53	-	75
Rosin- Nafol 20^+	63	-	90

2.2.5. Preparation of Maleorosin Diester

To prepare rosin maleic- anhydride diester, the direct esterification was completed through two methods.

The first method is based on the reaction between (2.2 mol) Nafol 20^+ and (1 mol) rosin maleic- anhydride adduct. The **second method** was completed by two steps with complete reaction between (1 mol) rosin maleic- anhydride adduct and 1.1 mol Nafol 20^+ followed by reaction with (1.1 mol) polyethylene glycol (1000). The reactions were completed in xylene as a solvent and 0.1% of anhydrous p-toluene sulphonic acids catalyst. The reaction mixtures were heated under nitrogen atmosphere. The reaction was completed until the theoretical amount of water was collected. The prepared diester was precipitated in the methanol and discarding the products until they gave no trace of turbidity with water [121]. The reaction scheme of the modified products derived from rosin was

illustrated in **Scheme (2.2)**. The products purified was characterized by PEG1000, Nafol 20$^+$ (yield 73%, m.p 58 $^\circ$C) and Nafol 20$^+$, Nafol 20$^+$ (yield 90%, m.p 73 $^\circ$C).

2.3. CHARACTERIZATION OF GRAFTS

2.3.1. Acid value

The acid value was determined by titrating the solution of the weighted quantity of resin in acetone with a standard alcoholic KOH solution (0.5N) using phenolphthalein as an indicator. (ASTM, D1639-90).
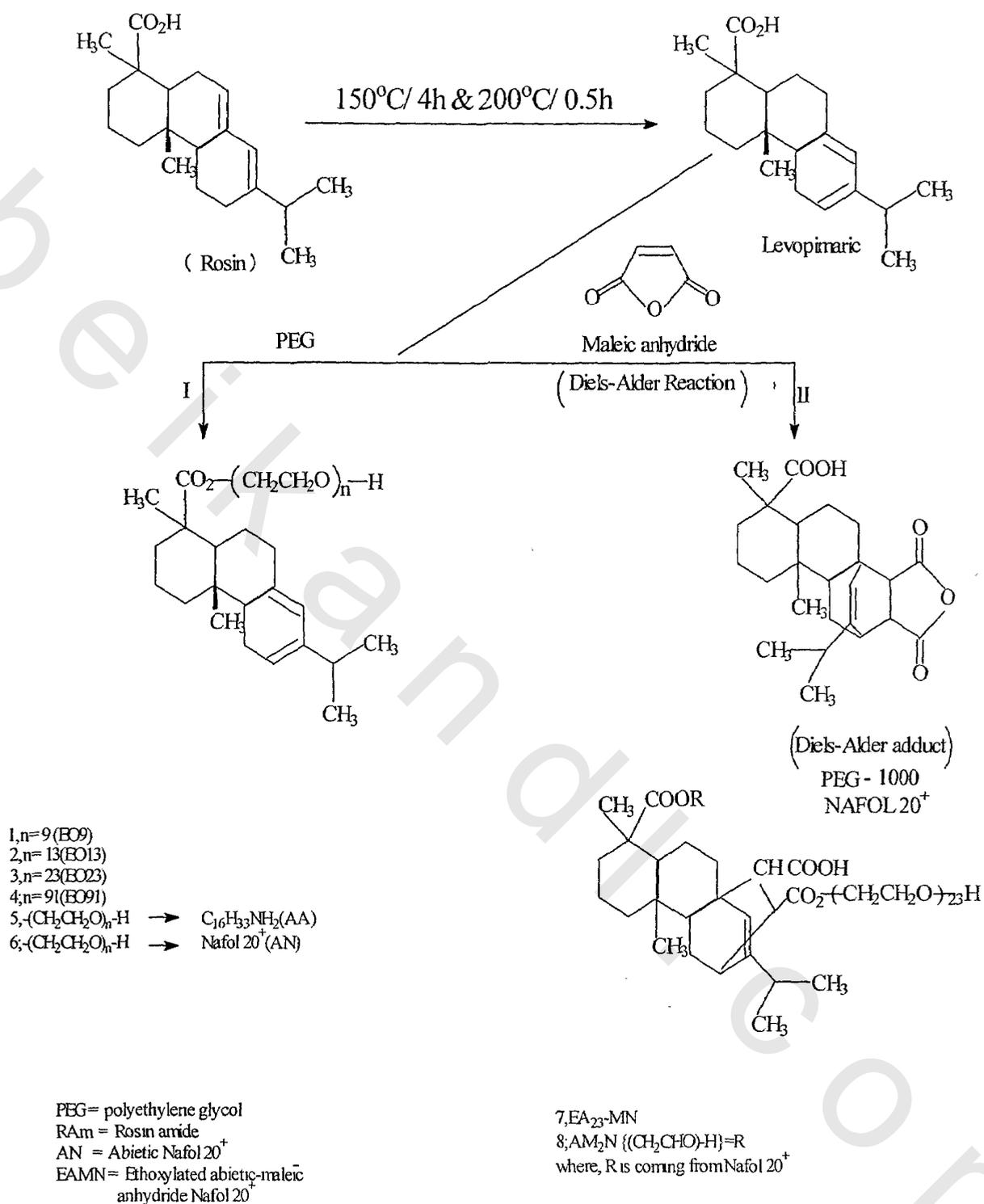
2.3.2. Infrared Spectrometry (IR)

FT-IR spectra were obtained by using a Bruker IFs 66 FT-IR Spectrometer. Films for IR analysis were solvent cast onto KBr discs from O-xylene or THF.

The solvent was evaporated at 100 $^\circ$C for 5 min, and the residue was analyzed. Films of PEAA grafts were formed by blending the solid samples with KBr to obtain transparent discs.

2.3.3. Nuclear Magnetic Resonance (^{1}HNMR)

^{1}HNMR Spectra were recorded on a Varian EM 360 spectrometer in deutrated chloroform (CDCl$_3$) with 1% tetramethylsilane (TMS) as internal solvent.

$150^{o}C/4h \& 200^{o}C/0.5h$

(Rosin)

Levopimaric

PEG

Maleic anhydride

(Diels-Alder Reaction)

I

II

$CO_2-(CH_2CH_2O)_n-H$

(Diels-Alder adduct)
PEG - 1000
NAFOL 20$^+$

1,n= 9 (EO9)
2,n= 13(EO13)
3,n= 23(EO23)
4;n= 91(EO91)
5,-(CH$_2$CH$_2$O)$_n$-H $\rightarrow$ C$_{16}$H$_{33}$NH$_2$(AA)
6;-(CH$_2$CH$_2$O)$_n$-H $\rightarrow$ Nafol 20$^+$(AN)

CH_3 COOR

CH COOH

$CO_2-(CH_2CH_2O)_{23}H$

PEG= polyethylene glycol
RAm = Rosin amide
AN = Abietic Nafol 20$^+$
EAMN= Ethoxylated abietic-maleic
anhydride Nafol 20$^+$

7,EA$_{23}$-MN
8;AM$_2$N {(CH$_2$CHO)-H}=R
where, R is coming from Nafol 20$^+$

Scheme (2.2): Scheme for synthesis of Rosin derivatives

2.4   EVALUATION TESTS: -

The prepared PEAA grafts were tested for their effectiveness as flow improvers for the QPC crude oils. In this respect, three Egyptian wax crudes, viz, Benisuif mixture (BS), Karama mixtures and Wadi Rayan crude oil, were used for evaluating the performance of the synthesized polymeric additives. The mixed Bensuif is based on mixing BS and different weight percentages (0- 25 wt %) of Wadi Rayn crude oil which have low pour point (-3 $^{\circ}$C). The composition of Karama mixed crude oils, pour point and the location of production in QPC are listed in **Table (2.3)**. The physicochemical characteristics of mixed Benisuif and mixed Karama are given in **Table (2.4)**. Asphaltene contents were determined by using IP43/84 in which toluene and n-heptane were used as solvent and non-solvent for asphaltene, respectively. Wax content of these crude oils was determined using the UOP method 46-85 in which urea was used to separate wax contents after isolation of asphaltene.

2.4.1 Actual Pour Point Testing (PPT)

PPD additives were formulated as 10% (wt %) in Diesel fuel. The physico-chemical characteristics, such as density, viscosity and flash point, were determined and listed in **Table (2.5)**. Test procedures are trying to simulate the system temperature

designed by Qarun Petroleum Co. (QPC) laboratories as possible. The most important parameters are designed as:

- Injection the PPD at well head temperature (65 °C)
- cooling down to the storage tanks temperature (48 °C)
- running pour point test

In this respect, the tested crude oils (50 ml) were heated up to 65 °C and the PPD additives were added at different concentration. The solution was shacked for 3 minutes and the temperature was kept constant to 5 minutes according to QPC procedure. The solution was transferred to bottle test tube in water bath cooled at 48 °C. The tube was transferred to another cooling bath cooled down to 24 °C.

The tube was transferred to cooling bath cooled down to 0°C.The pour point temperature was measured at temperature 48 °C.

2.4.2. Evaluation of Crude Oil Viscosity: -

The prepared additives based on PEAA waste were evaluated as flow improver for wax crude through rheological measurements at concentrations of 100, 250, 500 and 1000, 2000, 5000 and 10,000 ppm.

Table (2.3): Compositions Pour Point and Location of Production Field of Mixed Karama Crude Oil.

Name of Field Zone	Volume Percentage (%)	Pour point (°C)	API Gravity at 60 °F	Kinematic Viscosity at 40 °C cSt
South west karma (SWK8)	25	30	41	12.3200
SOUTH WEST Karama (SWK9)	4	30	41.7	14.28
SWK11	19	27	41.6	13.8
(KARAMA) K5	17	21	37.4	8.2
RABO-1X	5	21	41.8	6.0200
FARASHA-1X	5	21	43.5	5.9000
AQSA-1X	4	24	41.3	6.6
AMMANA-E-1X	10	27	41.6	13.8
Karama north west (KNW-1X)	11	24	38.6	8.3436
Mixed Karama (Total)	100	33	-	-

Experimental

Table (2.4): Physicochemical Properties of the Tested Crude Oils.

Test	Method	Crude Oils	
		BeniSuif	Karama
API Gravity at 60 °F	ASTMD-1298	42.6	41.1
Specific Gravity at 60/60 °F	ASTM D-1298	0.8128	0.820
Wax content, (Wt %)	UOP 46/64	22	16
Asphaltene content, (Wt%)	IP 143/84	5	3
Water content vol%	IP 74/70	0.4	0.23
Kinematic Viscosity (cSt) at 50 °C 60 °C	ASTM D-445	9 5.8	7 4.3
Pour Point °C	QPC procedure	39	33

Table (2.5): Physicochemical characteristics of PPD:

Characteristics	PEAA-1	PEAA-2	PEAA-3	PEAA-4
Chemical structure	Modified Ethylene-EthylAcrylate Copolymers Blend with HDRA	Modified Ethylene-MethylAcrylate Copolymers Blend with HDRA	Modified Ethylene-EthylAcrylate -Vinyl Acetate Polymers Blend with HDRA	Modified Ethylene-MethylAcrylate - Vinyl Acetate polymers Blend with HDRA
Solvent	Diesel fuel	Diesel fuel	Diesel fuel	Diesel fuel
Weight %	10	10	10	10
Viscosity at 50 °C (cSt)	280	250	200	380
Density at 23 °C (g/cm^3)	0.843	0.872	0.813	0.945

Measurements were carried out at different temperatures above and below pour point of crude oils ranging from 48 to 15 °C. The experimental procedure starts when the additives were mixed with crude oil at the prescribed concentration at 65 °C. Meanwhile, the viscometer cup is preheated to the same temperature, then loaded with 25 ml of the treated sample, and then the temperature is brought down to a constant temperature, at which the measurements will be achieved, at a low shear rate of 7.29 S^{-1} (dynamic cooling). Shearing was continued for 15 minute at the test temperature before evaluation. The shear stress-shear rate relationship was recorded for the tested samples. Shear-rate, shear stress, and viscosity can be calculated by the following equations:

1) Shear-rate (D):

$$D = M \times n \ (S^{-1}) \qquad\qquad 2.1$$

Where; M is shear –rate factor, depending on sensor system, and n is actual test speed. The actual test speed is calculated as following:

$$n = \frac{\text{Set test speed}}{\text{Reduction factor "R"}} \quad \dots \qquad 2.2$$

2) Shear-stress (τ):

$$\tau = A \times S \ (\text{Pascal [Pa]}) \qquad\qquad 2.3$$

Where; A is shear –stress factor, depending on time of measuring drive unit and sensor system, and S is measuring value (scale grade).

3) Apparent Viscosity (η):

$$\eta = (G \times S)/n \ (mPa.S) \qquad\qquad 2.4$$

Where; G is "instrument factor", depending on the type of measuring drive unit and sensor system.

2.4.3. Evaluation of Wax Deposition:

The lab test, cold finger test, for the selected PPD has been described by Smith and Josue et. al [35, 117]. They make use of a deposition surface cooled under controlled conditions to a temperature below the cloud point and the crude oil solution temperature. This method is called static cold finger test. This method allows control over the variables of oil solution temperature, deposition surface, temperature differential and time.

The cold finger experiments **Figure (2. 1)** were made by heating the petroleum samples in several different temperatures in a heating bath in contact with a cold surface kept at different temperatures. For that, the heating bath temperature was fixed initially with a predefined temperature of 90 °C and the cooling bath was set at a pre-established temperature for the beginning of the tests.

Figure (2.2) shows the apparatus before the experiment and **Figure (2.3)**, after the experiment, shows clearly a typical paraffin deposition.

The samples from the petroleum fields were previously submitted to the thermal treatment in an oven during 1 h in order to make the sampling of the amount of petroleum to be used in the experiments. The samples were stored in stainless-steel recipients (vessel), the vessel and the petroleum were weighed, being the net weight of 500 g each vessel containing petroleum. The recipient with the petroleum was then conditioned inside the heating bath and heated up to the pre-established temperature of 90 $^{\circ}$C, in order to eliminate the influence of the thermal history. While the petroleum was heated up, it was preceded by the connections of the cold fingers in the cooling bath circulation system. After reaching the thermal equilibrium between the heating bath and the recipient with petroleum (vessel) at a high temperature for elimination of the thermal history, a new adjustment in the heating bath temperature controller was made until a new low temperature to that previously established was reached for the accomplishment of the next steps of the experimental procedure.

Reaching this new thermal equilibrium of the bath and vessel in the test temperature, the cold fluid valves were opened to condition the cold finger at the test temperature.

The cold finger was immersed in the vessel already conditioned at the test temperature, using an electric elevator. Turned on, the agitator speed rotation was adjusted at 300 rpm and was introduced into the recipient.

The temperatures of the system were monitored in intervals of 2 min through a Lab View program, for a period of 5 h. The adjusted temperatures for the tests were: 60, 50 and 40 °C for the hot bath and 7, 3 and -1 °C for the cold bath. A total of nine tests were made, combining temperature of the hot bath and cold bath, in two equal recipients to test repeatability.

The interval between the beginning of the experiment and the increase of the temperature due to the formation of the deposit is called the critical time of deposition. This means that the deposition begins to be formed when it was elapsed that time.

The manometer was inclined at an angle of 35° to the horizontal and the manometric fluid is water. Because water and oil have densities that are close to each other, this maximizes the manometer reading. The temperature increase, due to the formation of the deposition, as a function of time, can be approximated by the equation [96, 97]:
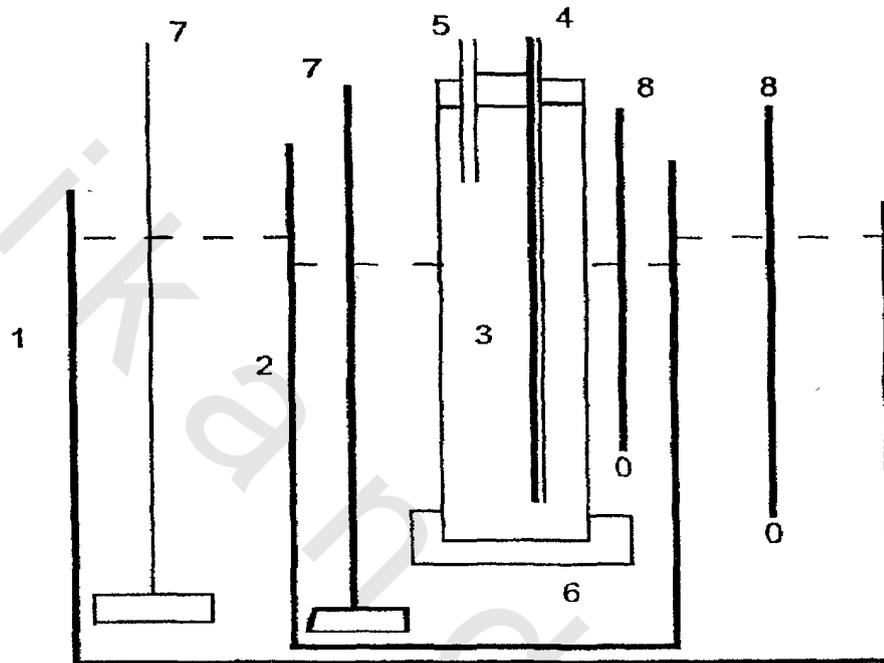
$$\log T = \log a + b \log t \tag{2.5}$$

Figure (2. 1): Apparatus with cold finger for encrustation studies.

(1) Thermostatted vessel, (2) vessel with fluid, (3) cold finger, (4) cooling water inlet, (5) cooling water outlet, (6) insulated bottom, (7) stirrers, (8) thermometers.
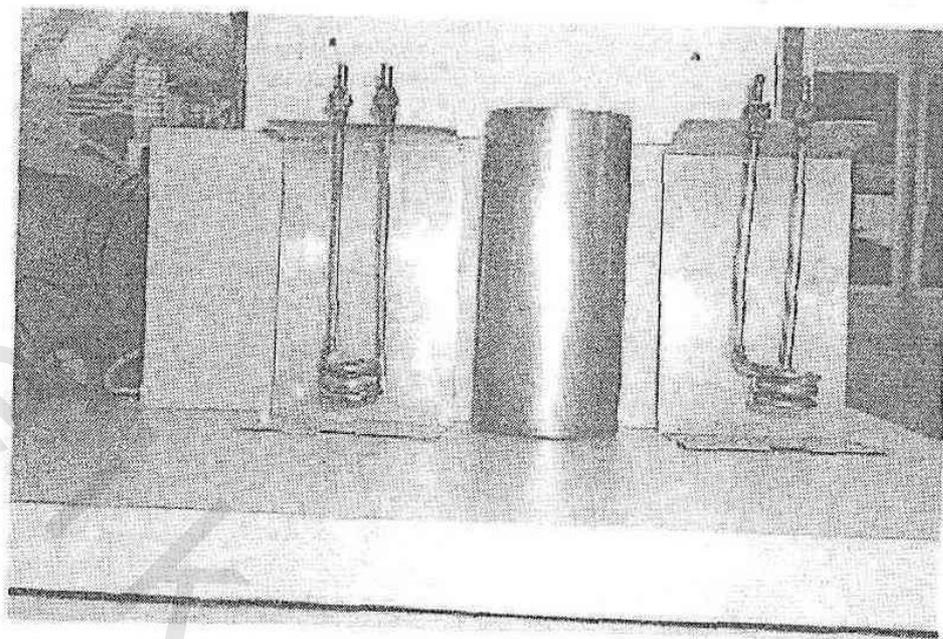
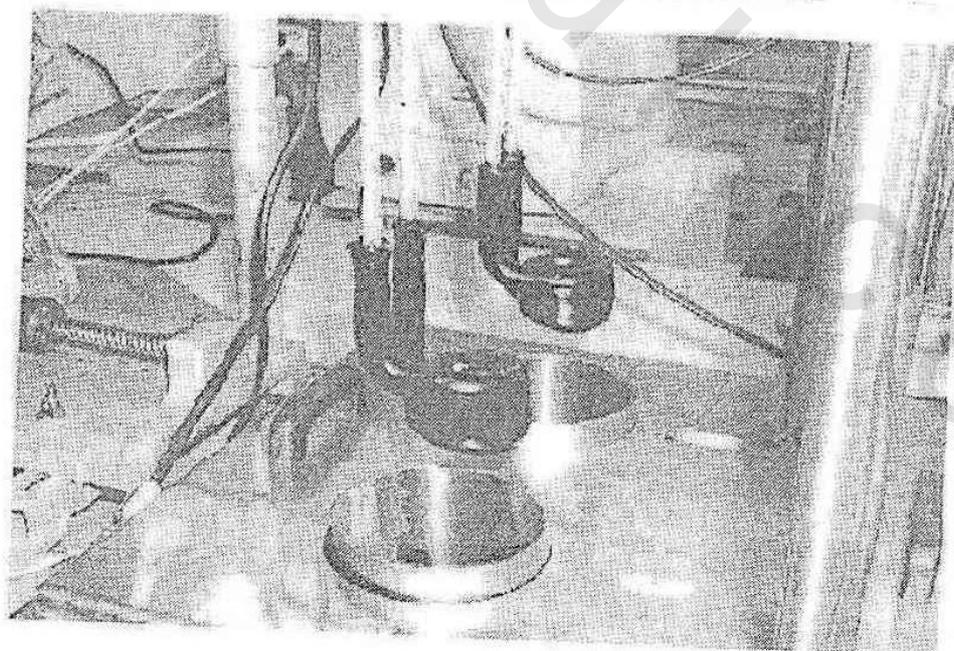**Figure (2.2). Cold finger and recipient of stainless steel (vessel).**

Figure (2. 3). Cold finger with paraffin deposit.

The value of the parameter b depends on the given mean temperature difference, and this dependence can be approximated by a straight line. Extrapolation of this plot for b=0 enables a more exact evaluation of the critical temperature difference as shown later.

2.4.4. Evaluation of Flow Characteristic by Pipe-loop:

A laboratory-scale paraffin deposition flow system was constructed to simulate the deposition of paraffin in the transfer pipeline. A schematic diagram of the system is shown in **Figure (2.4)**. The equipment consists of two concentric galvanized tubes with a facility to measure the pressure drop between the ends of the inner tube that is called the test section. The crude that is used to conduct the experiments is stored in a reservoir, with a capacity of 20 gallons (0.0756m^3). The crude can be pumped through the test section and back into the reservoir. The flow rate is adjusted using a flowmeter and a bypass valve. An inclined manometer is used to measure the pressure drop.

Thermocouples to monitor the temperature in the test section and in the reservoir were installed. A blower was required to keep the pump from overheating as the experiments were run for periods of 72 h.
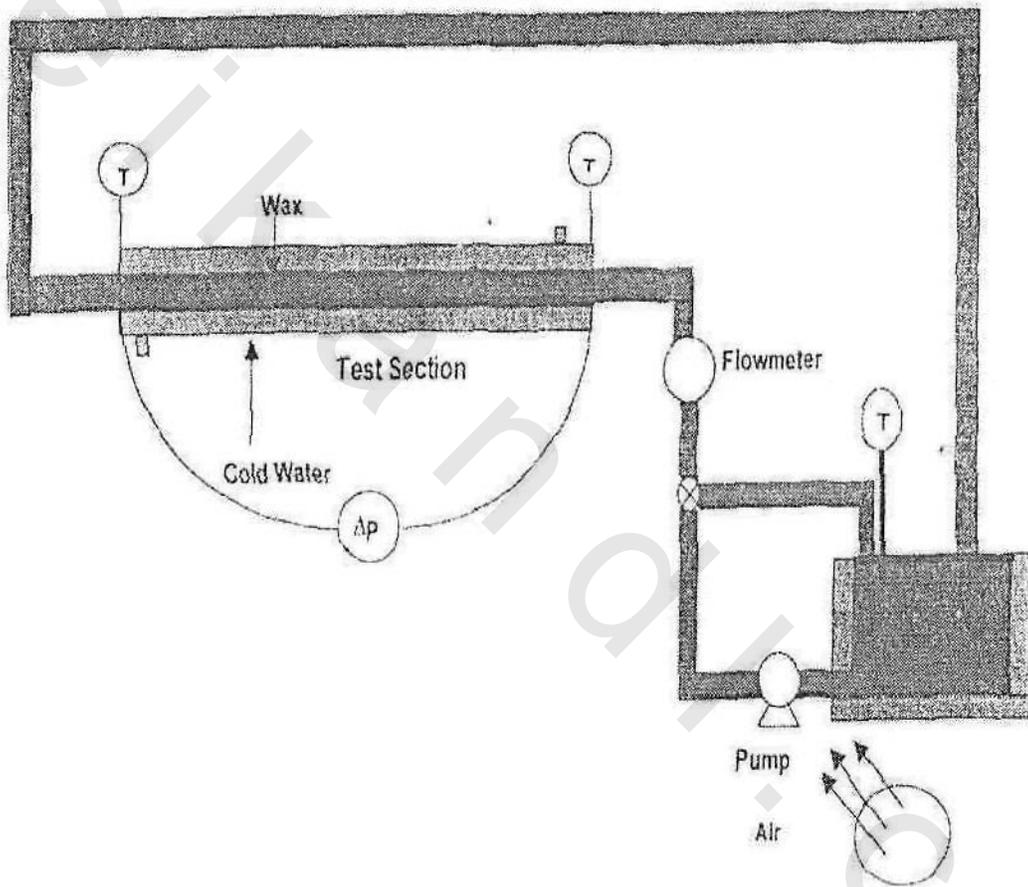
T= thermocouple and thermometer

Figure (2.4): Flow Chart of Laboratory Flow Loop.

A water bath attached to a refrigeration unit was used to provide the cooling for the outer wall of the inner tube. The water was maintained at a constant temperature as required by the experiment. Water is pumped into the outer tube and back into the water bath. This keeps the walls of the test section at the required temperature throughout the experiment. At the start of the each experiment, the manometer is checked to ensure zero reading, and the flow rate adjusted using the bypass valve. Manometer readings are noted at regular intervals until the end of the experiment. At the end of each experiment, all the pumps and coolers are switched off, and the test section disassembled. Paraffin wax that is deposited in the test section is removed using scrapers and the amount of paraffin is measured using a measuring jar.

This experiment was repeated for both crude oil with and without additives after replacement of the test section (one meter), which connected to cold system, with a new section having the same length and internal diameter but it was cooled at room temperature. On the other hand, the restart ability test was carried out for each crude oil with and without additives. In this respect, the flow rate was detected after switch off the pump and restart after 15 minute.