EXPERIMENTAL

Experimental

Materials and Methods

Materials Used

Glacial acetic acid, Acetic anhydride, Diethanol Amine Acetone, Maleic Anhydride, Hydrochloric Acid, (36% conc.), Hydrogen Peroxide, (Chemically pure, strength determined precisely by the thiosulfate method and found to be 25 percent), Potassium Hydroxide, Potassium Iodide, Pyridine, (redistilled and stored in dark bottle with added KOH plates); Sodium hydroxide, Sodium sulphate anhydrous, Sodium thiosulphate, Starch Indicator, Conc. Sulphuric acid, nitric acid Phenolphthalein Indicator. Xylene, and toluene. These chemical were analytical grade and used as received without further purification

Asphalt used

The used Asphalt has 60/70 Penetration grade, and the oxidized asphalt were supplied from Refinery Suez Company, Egypt. Their physical properties are shown in Table (1).

Table: (1) Physical Properties of Asphalts (L), and Oxidized Asphalt

Physical Properties (ASTM D 946)	Asphalt 60/70 (Suez Co.)	Oxidized Asphalt (Suez Co.)
- Softening point, Ring&Ball, °C	47	88
- Penetration, at 25 °C, 0.01mm	65	15
- Ductility, at 25 °C, cm	+150	98

Natural Rubber (NR), Malisian rubber in the form of rubber smoked sheets RSS-1, d 0.913 ± 0.005 $g.cm^{-3}$, and moony viscosity ML(1+4) at 100 °C, 60-90.

Styrene Butadiene Rubber (SBR), Heilopolis Military and Civil Co. of Chemicals, Cariflex –S1712.

EBCA Emulsifier B, nonionic asphalt emulsion; from Egyption British Co. general characteristic:-

-Transparent medium, viscous liquid.

-Miscible with water and produce no excessive foam on mixing with water.

-pH of 1% solution is 7-7.5

Polyacrylic acid (sodium salt) from Egyption British Co. general characteristic:-

-Pale yellow and viscous liquid.

- pH = 7-7.5

-Solid content =40%

Preparation of Peracetic Acid [91]:

Peracetic acid was prepared by reacting hydrogen peroxide and acetic acid, using sulfuric acid in small quantities as catalyst to speed up the reaction. Glacial acetic acid (1.6 mol ≈ 96 g) was added to 22.5% hydrogen peroxide solution (4 mol ≈ 136 g) in presence of sulfuric acid approximately 2-3%. Equilibrium was obtained in approximately 12-16 h, at room temperature. Such solutions contain some unconverted hydrogen peroxide and water, which was eliminated by addition of small aquantity of acetic anhydride (5-7 ml), to shift the equilibrium toward the formation of additional peracetic acid. Then the produced peracetic acid was estimated.

Determination of Peracetic Acid Concentration [92]:

In conical flask (250 ml), prepared peracetic acid (0.1 g) was dissolved in glacial acetic acid (25 ml). Saturated aqueous KI (2 ml) was added and the reaction mixture was allowed to stand for 10 min. Then distilled water (25 ml) was added, and starch solution (2%, 1 ml conc.), was introduced as an indicator. The titration was carried out directly against (0.1 N) sodium thiosulfate ($Na_2S_2O_3.5H_2O$) solution.

Calculation:

peracetic acid concentration was calculated by the following equation:-

$$\text{peracetic acid concentration,\%} = \frac{V_1 N_1 M}{W \times 1000}$$

Where;

V_1: Volume of $Na_2S_2O_3.5H_2O$ (ml).

N_1: Normality of $Na_2S_2O_3.5H_2O$,

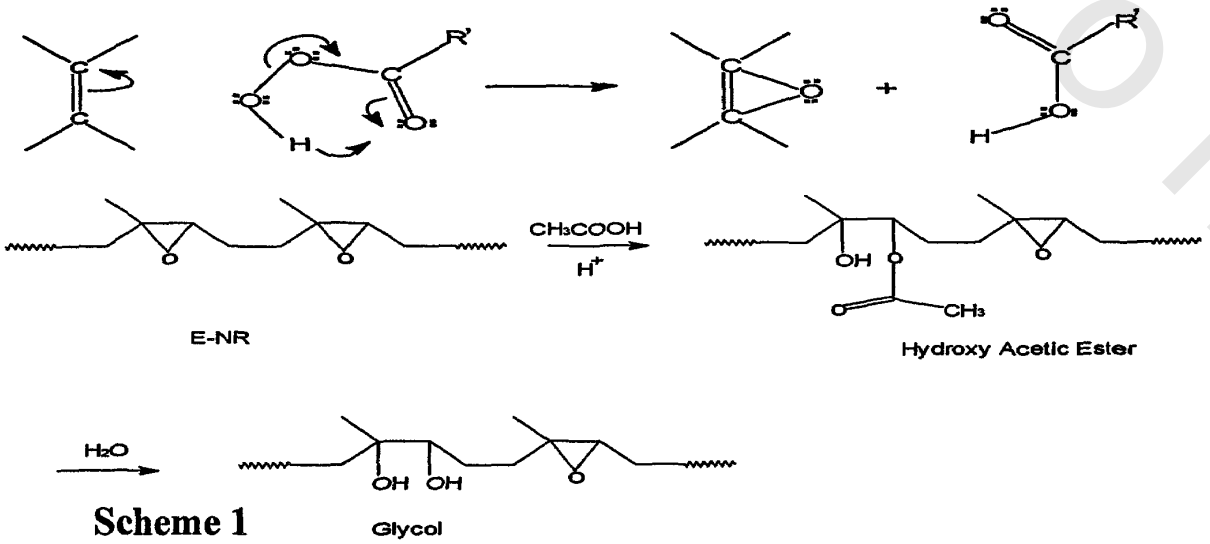
M: Molecular weight of peracetic acid sample,

W: Weight of peracetic acid sample (g).

Epoxidation of Diene Rubbers with Preformed Peracetic Acid [93]:
Three necked round bottom flask (1L) fitted with a thermometer, reflux condenser, dropping funnel, magnetic stirrer, solution of natural rubber (NR), or styrene butadiene rubber (SBR) (10 g) in toluene (500 ml) was introduced. Appropriate amount of freshly prepared peracetic acid solution (59%) (19, 38, 76, and 114 ml respectively) was added slowly for 2 h to obtain the suitable amount of the required peracetic acid to give epoxy rubber with higher hydroxyl, and epoxy group content. The temperature was maintained at about 20-25 °C over a total reaction time of 4 h. The product was then washed three times with a saturated solution of sodium chloride, twice with a saturated solution of sodium chloride containing potassium hydroxide to neutralize the residual acid in the mixture and finally washed three times with distilled water. The upper layer was decanted and the lower organic layer was dried in a vacuum desiccator.

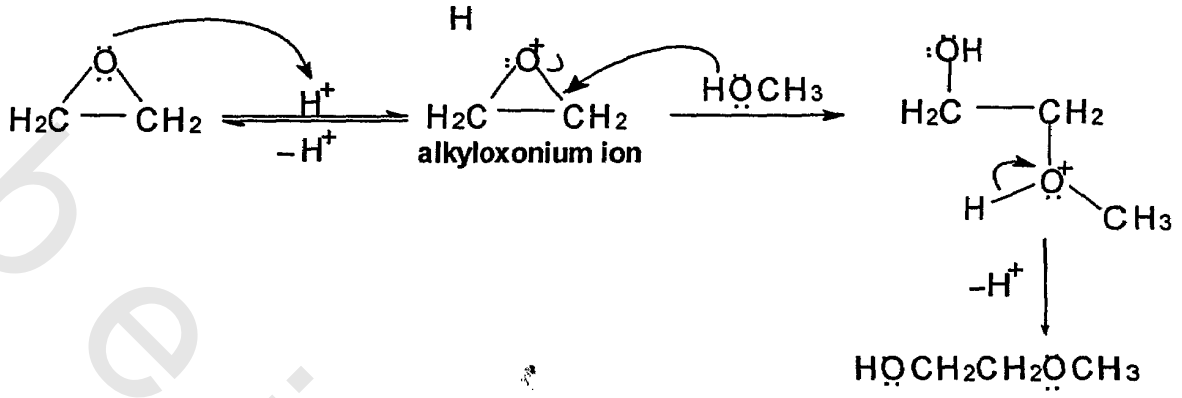
Some characteristics of the epoxidized natural rubber (ENR) prepared via the above-mentioned such as total iodine value, hydroxyl number, and epoxy group content were calculated.

The epoxidation reaction of organic peracid may be explained by transfer an oxygen atom to the double bond in the alkene. The following mechanism has been proposed as shown in scheme1.



Scheme 1

The proposed mechanism of acid - catalyzed ring opening is as follows:



Tests for Evaluating The Epoxidized Rubber :

- Determination of Epoxy Group Content [94]:

A weighed sample of epoxidized compound (0.5g) was introduced to 200 ml round bottom flask, and then 25 ml of pyridine solution (16ml. conc. HCL per 1 liter of pyridine) was added. The solution was refluxed until being the sample completely dissolve (for 30 min), heating gently. Then the solution was cooled with the condenser, and then 50 ml of methyl alcohol and 15 drops of phenolphthalein indicator were added. The mixture was titrated with 0.5N methanolic NaOH to a pink end point. Beside the epoxy sample a blank experiment was carried out under the same conditions.

Calculation :-

$$\text{Epoxy group content, \%} = \frac{(A - B) \times K \times 0.028 \times 100}{W}$$

Where:

A = Quantity of NaOH in ml taken for titrating the acid (blank).

B = Quantity of NaOH in ml taken for titrating the acid (sample).

K = 0.9998.

W = Weight of the sample (g).

- Determination of Hydroxyl Group Content [95]:

A sample (0.1– 0.2g) was introduced to round bottom flask quick fit (cap 250ml) then about 25 ml of the reagent (2.5g acetic anhydride in 25ml pyridine) was transferred to the flask which connected with aquick-fit condencer. The ingredients were heated gently for 3 hrs. At the end of the reaction, (50ml) distilled water was added through the upper part of the condenser and the heating was continued for 1-2min. The solution was titrated against (0.5N) NaOH in presence of phenolphthalein till the end point was appeared.

A parallel blank experiment was carried out. The hydroxyl group content, X % was calculated from the formula:

$$X = \frac{0.0085(V_1-V_2)\,K \times (100)}{g}$$

V_1 = Quantity of NaOH taken for titrating the acid in the blank experimental.

V_2 = Quantity of NaOH taken for titrating the acid in the sample.

K = 0.9998.

g = Weight of the sample.

-Total Iodine Value [96]:

Iodine value is the amount of halogen in gm, expressed as iodine which reacts with 100gm. of material under specified conditions.

Scope: This method for determination of iodine value for mixtures, the results obtained gave only an indication and not an accurate measure of the degree of unsaturation of the sample.

A known quantity of sample is dissolved in carbon tetrachloride and allowed to react with excess iodine chloride in acetic acid.

The excess reagent is then converted into free iodine by the addition of KI, and the liberated iodine was determined by titration with thiosulphate solution.

Procedure:

-20 ml. of carbon tetrachloride was added to 0.1— 0.2 g. of the sample in 250 ml round flask and shacked until the sample is dissolved, then 25 ml. of iodine solution was added.

-The flask was shacked and allowed to stand in the dark for 120 minutes at a temperature of 20 ± 3°C. At the end of the reaction period 20ml of potassium iodide solution was added and well mixed. 200ml of water was added and shacked well again.

-The excess iodine was titrated with thiosulphate solution, using starch as an indicator near the end (from blue to colorless) of the titration.

$$I = \frac{12.7 \text{ X N X V } (B - A)}{W}$$

Where;

I = Iodine value.

V = Volume of thiosulphate solution consumed with sample (A) in ml used for the sample, B for the blank experiment A for the sample.

N = Normality of the thiosulphate solution.

W = weight of the sample in g.

Infrared Spectroscopic Analysis

IR-spectra of the epoxidized and non-epoxidized natural rubber samples were recorded using ATI Mattson-Genesis Series FTIR™ infrared spectroscopy. The wave number and intensities of the IR

bands of the different types of the functional groups were determined in a range of 4000-500cm^{-1}

Modification of Asphalt

Asphalt 60/70 penetration grade was modified by epoxidized rubber to improve the paving asphalt. The blending technique of asphalt with (epoxidized rubber) employed involved heating the asphalt sample to 60-80 °C then was mixed with specific amount of (ENR), (SBR) and molten cross-linker (MA) in a beaker untill achieve a homogenous blends. The mixture was placed in an oven at 150-170 °C. The curing time and hardener concentration were estimated.

- Softening Point (Ring and Ball):

The standard test was carried out according to ASTM D36-76.In this test a warmed brass ring was filled with hot asphalt or (modified asphalt) blend and allowed to cool in air for 30 minutes. Any surplus of sample is then cut off level with the top of ring. The apparatus is assembled and filled to a height of 5 cm above the upper surface of the ring with freshly boiled distilled water at a temperature of (4 ± 1) °C. This temperature is maintained for 15 min, a steel ball previously cooled to 4°C is placed in the center of the disc and then the temperature is raised by 5°C per min.

The temperature at which the sample surrounding the ball touches the lower plate is recorded as the ring and ball softening point.

- Penetration:

The standard test was carried out according to AASHTO T 49-78. In this test the asphalt or (modified asphalt) blend was heated and mixed thoroughly then poured into a standard small cup. The sample is allowed to cool in air from 1 to 1.5 hr, then transferred to a water bath maintained at precisely 25°C from 1 to 1.5 hr. Standard needle is allowed to penetrate into the surface for 5

seconds under the correct loading and constant temperature. Three or four penetrations are taken and the average value of penetration is recorded.

-Vulcanization [39]:

Oxidized asphalt was mixed with natural rubber in different percent (5, 10, 20, 30, 40, 50, 100, and 200). The additive concerned with vulcanization properties (see Table 2) at room temperature on a two rolls mill (LABSCO, Laboratory Supplied by Company Ollmann & Co KG, D-6360 Friedberg/H-Germany, Collin type SWW 150) 380 v, 50 Hz and length of roll 300 mm, 170 mm diameter with speed of slow roll 18 rev. min. The prepared compounded rubbarized asphalt was left for at least 1h before vulcanization.

The vulcanization process was conducted at (153±2) °C under a pressure of 10 ton/mm^2 for 20 min by (CARVER Laboratory Press, Model M, FREDS. Carver INC-USA Protected by US and foreign patents). Components of the mixture and their ratio are listed in Table (2).

Table (2): (Vulcanization) Recipe for Rubber Loaded Mixing Ratio with Different Types of Modification.

Ingredients	phr
Rubber	100
Stearic Acid	1
Zinc Oxide	5
Sulfur	1.5
Carbon Black	40
TMTD	1
MBT	1.5

phr: Parts per hundred parts by weight of rubber
TMTD: tetramethylthioramedisulfide
MBT: mercaptanbenzothiazolmonosulphide.

Evaluation of Vulcanized Sample
-Stress-Strain Measurements [39]:

Four individual dumbbell shaped specimens for tensile test were cut using a steel die of standard (Punch Press model 1701 Germany width 4 mm). The stress strain behavior of the test specimens prepared from vulcanized rubbers film samples (with thickness approximately 1-2 mm measured by micrometer) were determined at room temperature using Tension Machine type M-10(HUNG-TA INST R-UMENT Co. LTD), connected with data analysis, at cross head speed 100 mm/min.

Elongation at Break

$$\text{Elongation at break} = \frac{L - L_1}{L_1} \times 100$$

L_1: length of the specimen before extension.
L_2: length of the specimen after extension.

The average results of four samples were calculated and presented in the form of stress-strain diagram.

Young's Modulus

Young's modulus can be calculated from values of stress and strain by using the following equation:
Young's modulus = Stress / Strain = Ts / Eb

- Determination the Degree of Swelling [39]:

Swelling measurements of the vulcanized rubber were carried out using both Kerosene and Benzene as solvents. These solvents were chosen in view of their dailyused in different applications. The physical properties of these solvents are in Table (3).

Table (3): Chemical and Physical Properties of Solvents Used

Solvent	Formula	Mol.wt	Sp.gravity g/cm^3	Melting Point, C	Boiling Point,°C
Kerosene	$C_{10}H_{22}$ to $C_{16}H_{34}$	144-194	0.816-0.797	-150-60	150-300
Benzene	C_6H_6	78.11	0.875-0.878	5.5	79.6

Square samples of 0.5x0.5 cm length and 0.3 cm thickness were cut from the prepared vulcanized rubber sheets. Each sample was weighed by a sensitive balance of 10 g accuracy.

The tested pieces were completely immersed in the solvent individually. The swelling was allowed to take place in stoppard glass bottles at room temperature. The samples were removed from the solvent at time intervals (15, 30, 60, ... min).

The excess of solvent on the surface of the tested sample was removed by blotting with filter paper. Then the samples were weighed again. After 24 hours (total immersion time) the tested pieces were removed when the swelling equilibrium was obtained [39].

The degree of swelling is calculated from the formula:

$$Q = (m - m_o) / m_o$$

Where:

m_o: is the weight of initial rubber sample, and

m: is the weight of swollen rubber sample.

Determination the degree of swelling is used to test thefinished polymeric articles intended for service in theliquid and gaseous media.

Chemical Resistance

This method is carried out according to ANSI/ASTM D543-67. The chemicals used in this test were in the technical grade. All solutions were made with freshly prepared distilled water. Specified concentrations are on a weight percent or specific gravity basis. The standard reagents were as follows:

. Distilled water, freshly prepared.

. Acid (H_2SO_4 10%).

. Solvents (Acetone, Benzene).

. Petrol (Kerosene).

- Preparation of Asphalt Polyurethane Foams [97]

A) First Nonionic asphalt emulsion (50-60% solid content) was prepared from asphalt 60/70 Alex. As follows:-

*heating the bitumen until being completely melt(not more than 10 °C over the m.p.).

*The non-ionic emulsifier (EBCA emulsifier) was added to the bitumen at lowstirring speed.

*The water was added to the mixtureat the same temperature slowly with continous stirring

After 30 min to 1h stirring the bituminous emulsion shoud be obtained.

B) Second, Add to 55g of nonionic asphalt emulsion (50-60% solid content) castor oil which reacted before with dimethyl diphenyl diisocyanate (MDI) to give different ratios of NCO/OH (1.1, 1.2, 1.3, and 1.4) individually at 60/70 °C

Modification of Asphalt Polyurethane Foams

asphalt –polyurethane foam sample with NCO/OH ratio =1.2, was chosen from the economical point of view to be modified with different percentage of commercial rubber (Addibond 65),

polyacrylic acid water base, and polyurethane based on (epoxidized natural rubber + MDI) at different ratios of NCO/OH (1, 2, 3, 4, and 5) which were added during the preparation of asphalt polyurethane foams.

Tests carried out on the Prepared Formulations:

- Sound Proofing Test

It is measured by using a special apparatus, precision integration sound level (Bruel and Kjaer, Type 2236), Denmark. A sound proofing box (60x20x60 cm). The final foam sample noise sources in addition to the microphone were put at equal distances from both sides of the sample.

The sound pressure level (SPL) was measured for every sample by the sound level meter at frequency of 31.5Hz and constant noise level.

- Vibration Damping Test

The vibration damping performance is generally represented by the velocity level (VL). The test method of the velocity levels mainly encounters attaching the sample. The velocity level is measured by using the Integrating Vibration Meter, Type 2513 (Denmark) for all samples with the same vibrator source.

Thermal Stability [98]:

Each of the prepared vulcanized sample, and asphalt polyurethane foam were placed in furnace at 200 °C, and then withdrawn from the furnace after a time intervals; (for 100h) cooled untill room temperature, weighed The weight loss of the cold sample after each time interval was recorded.

Differential Scanning Calorimetric Analysis
TGA, and DSC (Shimadzu TGA-50H, and Shimadzu DSC 50) Laboratories of Micro analytical center, Cairo University.

Marshall test [99]
Preparation of Test Specimens.
- Number of specimens prepared. The used percents of asphalt by weight of aggregate were 4.5, 5, 5.5, 6, and 6.5.
Three samples of each percent were prepared to take the mean value of the test.

- Preparation of aggregates; aggregates dried to constant weight at (110 ±5) °C were separated by dry sieving into the desired mesh size.

- Determination of mixing temperature: the used method was carried out according to Asphalt Institute [99] which recommends that it is necessary to made benefit of the temperature-viscosity relationship for asphalt in order to arrive at the proper viscosity for the construction process. The temperature of mixing was in the range of 155 °C to 175 °C.

- Preparation of mold for compaction hammer test: Throughly clean the specimen mold assembly, and also the face of the compaction hammer and heat them on hot plate to a temperature near the mix temperature. Place a piece of filter paper toweling cut to size in the bottom of the mold before the mixture is placed in the mold.

- Preparation of the mixtures: Weight in to separate pans for each test specimen the amount of each size fraction required to produce a batch which will result in a compacted specimen 2.5±0.05 inches in highest. This will normally be about 1100gm. Place the pans in the oven and heat to temperature approximately 10 °C

above the mixing temperature. Weight the required amount of asphalt cement (previously heated to the mixing temperature). Mix the aggregate and asphalt cement by hand with a trowel for 2 min to yield a mixture having a uniform distribution of asphalt throughout.

- Compaction of specimen: place the entire batch in the mold and apply 75 blows to each side of the mold with special compaction hammer.

- Remove the specimen from the mold by means of an extrusion jack, and then the specimens are allowed to cool over night.

- The previous work was also repeated with when epoxidized natural rubbercurred with malic anhydride, (MA) resin was added to asphalt.

Apparatus:

An electrically powered testing device was used to apply loads to test specimens, the Marshall stability testing head was used to testthe specimens, and a Marshall flow meter was used to determine the amount of strain at the maximum load for the test.

Test procedure

In Marshall Method, each compacted test specimen was subjected to the following tests according to ASTM D 1559-89

a- Bulk specific gravity according to ASTM D2041-00

b- Stability and flow determination.

c- Voids analysis.

Stability and flow determination

The standard test was carried out according to AASHTO T 245-78.

After the bulk specific gravity of the test specimens had been determined, the stability and flow tests were performed as follows.

Test specimens were immersed in the water bath at 60 ±2 °C for 30 min before thetest.

Thoroughly clean the inside surfaces of testing head, and zeroed for the no-load position.

Remove the test specimen from thewater bath and dry the surface. Place the specimen in the lower testing head and center; then fit upper the testing head into position and center complete assembly in the loading device.

Set the flow meter to zero. The same assembly of testing head and flow meter then is used in testing the specimens. Flow meter is required for the determination of the flow value. The point of failure is defined by the maximum load reading obtained.

The deformation or strain undergone by the specimen during loading to maximum value was measured by the flowmeter and reported as flow value.

Specific gravity and voids analysis

Specific gravity

Bulk specific gravity of Compacted Mixtures:

There are three standard methods according to AASHTO T 166-789, one of them which were used in this work (or rapid test for dense graded mixtures). In this test, the specimens may be either laboratory scale-molded mixtures or from asphalt pavement.

The mixtures may be surface or wearing course binder or leveling course, or hot mix base.

In this test, the dry specimen is weighed (Wa). The specimen is immersed in water at (25°C) for one minute and recorded the immersed mass (Ww). Remove the specimen from the water surface, dry by blotting with damp towel and determine the surface dry mass.

Bulk specific gravity = Wa / (Ws-Ww)

Wa =weight of sample, gm.
Ws =weight of surface-dry sample, gm
Ww =weight of sample in water, gm

Hot mix dense-grade asphalt concrete mixture conforming the gradation requirements of the American Asphalt Institute type IV-C and used successfully and extensively by the road and Brides

The stability, flow, specific gravity and void analysis were carried out for each series of test specimens as follow:

*(G mm) maximum theoretical specific gravity, and
*(G) Specific gravity

From these values the following parameters can be determined the asphalt lost by absorption into aggregate particles, effective asphalt content of paving mixture, percent of densification, percent of air voids in mix, percent of voids in mineral aggregate, and percent of voids filled with bitumen.

Tabulation of equations:

Gmm measured maximum theoretical specific gravity.

$$\text{Gmm (gm/cm}^{3)} = \frac{(100 + \text{Bt. \%})}{\{\text{Bt.\% / density Bt.} + 100 \text{ /density of mix. agg.}\}}$$

Bulk Specific gravity (unit wt.) G gm/cm^3 =wt. / volume.

Air voids % = {(Gmm-G)/Gmm }X 100

Mineral voids % = Bt. volume + air voids

Bt. volume = (Bt % X G)/1.02

$$\text{Voids filled with bitumen \%} = \frac{\textbf{(Bt \% X G/1.02)}}{\textbf{Mineral voids X 100}}$$

Determination of optimum asphalt content [99]:

The optimum asphalt content of the asphalt paving mix were determined from data obtained as out lined in graph consideration is given to the test property curves.

From these data curves, asphalt content is determined to determine the following properties.

- maximum stability
- midian of limits 3 to 5 percent of air voids in mix.

The optimum asphalt content of the mix is then the numerical average of the values for the asphalt content determined as noted above the optimum asphalt must be satisfactory with the curves illustrated in (Fig 5)

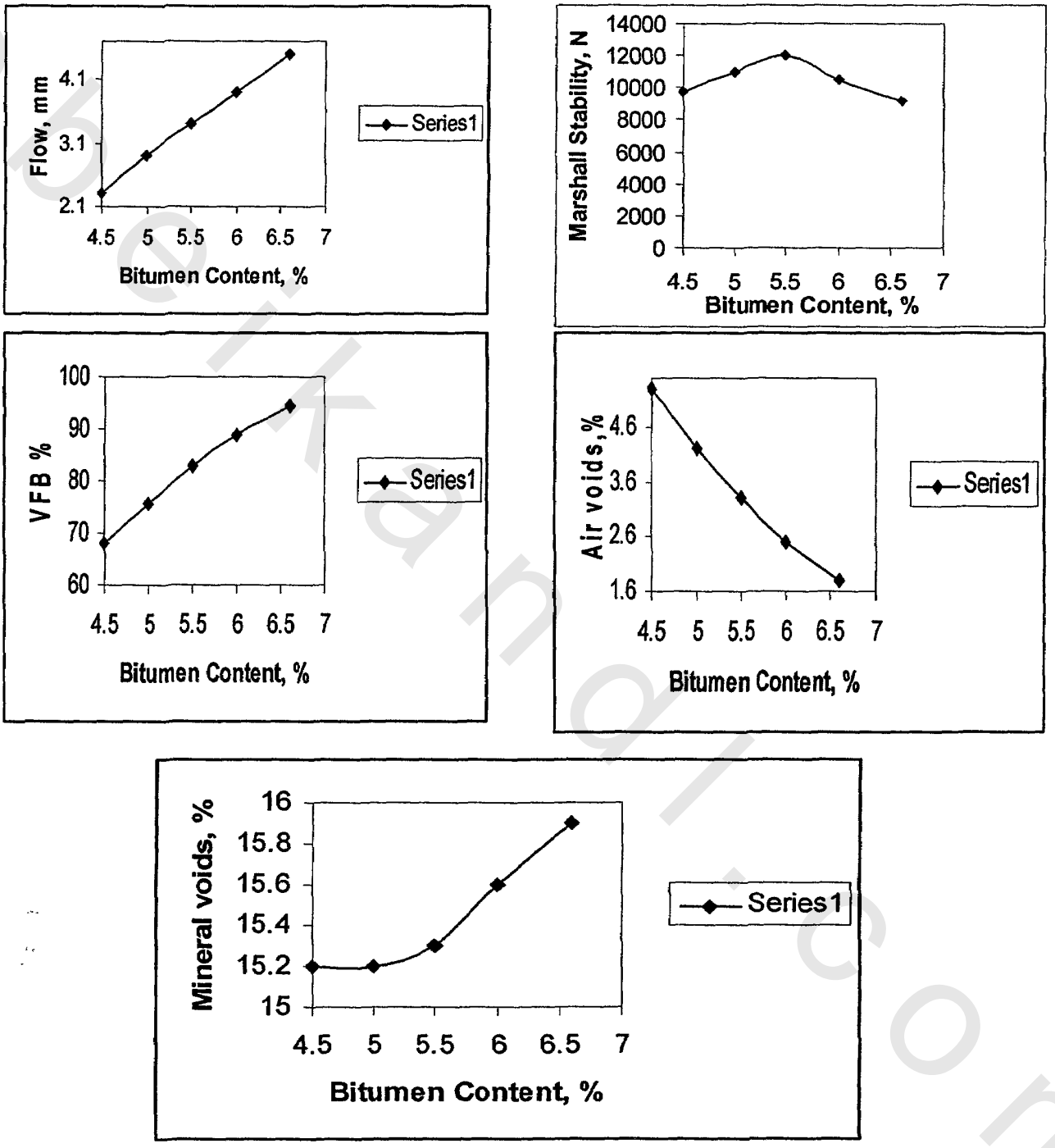


Fig (5): The Optimum Asphalt Curves

SCANNING ELECTRON MICROSCOPE (SEM)

SEM was used to determine the particle size

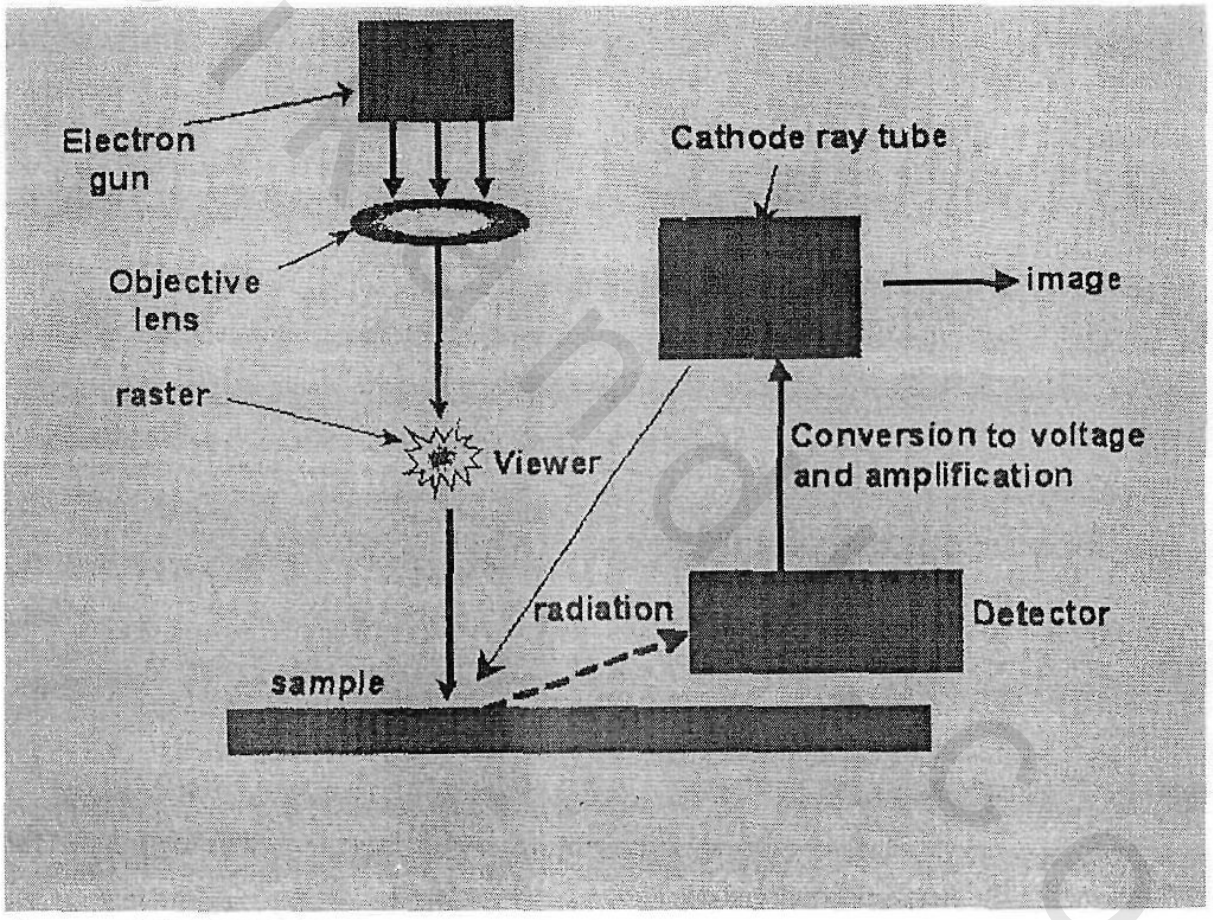


Figure (6) SEM Apparatus