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by

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Changes of South-East Anatolian Bitumens and Their Main Fractions Under Various Oxidative Conditions

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Fractional analysis of South-East Anatolian bitumens were made by means of J. Marcusson's method and changes in fractional compositions and in functional groups under oxidative conditions were investigated. A more detailed study was carried out on the asphaltic resins fraction of the bitumen having Mağrip origin, since this bitumen proved to be the most susceptible one to oxidative conditions among others.

Introduction

The term bitumen denotes the basic mixture of heavy hydrocarbons in the generic sense, and is defined as mixtures of hydrocarbons of natural or pyrogenous origin or combinations of both, frequently accompanied by their nonmetallic derivatives, which may be gaseous, liquid, semisolid or solid, and which are completely soluble in carbon disulphide* by authoritative associations [1] [2].

Chemical composition of asphaltic bitumens is extremely complex; they are mainly mixtures of various broad groups of hydrocarbons which are more or less in colloidal solution in each other. The constituent hydrocarbons possess a wide range of molecular weight with varying paraffin, cycloparaffin and aromatic character. Elementary chemical analysis reveals that carbon and hydrogen are predominant elements that constitute asphaltic

* In fact this means that any organic substance based on hydrocarbons which is soluble in carbon disulphide may be regarded as a bitumen. The concern of this study is only that group of bitumens which are characterised not simply by their solubility in a certain solvent, but more specially by their adhesive character as a binder. To emphasise this group of bitumen the term of "Asphaltic bitumen" is used throughout the text.

bitumens. Nitrogen, sulphur and oxygen are also present in smaller amounts. Some rather simple hydrocarbon derivatives which may be considered most likely to be condensation and oxidation products of the hydrocarbons and compounds containing sulphur and nitrogen atoms also exist in asphaltic bitumens.

Although knowledge relevant to the rheological, physical and colloidal characteristics of asphaltic bitumens has advanced rapidly since the 1940s, the progress in obtaining information about chemical composition was not so rapid.

The colloidal nature of asphaltic bitumen is confirmed by the Tyndall effect as well as the Brownian movement which was first observed by F. J. Nellensteyn [3] who regards asphaltic bitumen as a protected system consisting of three components: (1) the oily constituents which form the dispersion medium, (2) the lyophilic phase which consists of asphaltic resins and which act as the protective body, (3) the disperse or lyophobic phase which most likely composed of collidal particles of elemental carbon.

The asphaltenes themselves are insoluble in the oils. They exist in asphaltic bitumen as a dispersion due to the peptization effect of asphaltic resins. The asphaltenes consist of higher molecular weight hydrocarbons and have a high carbon content at the inner core. An adsorption relevance exists between asphaltenes and asphaltic resins constituting micelles. The stability of the system primarily depends upon the relation between the micelles and the oily medium.

The adsorptivity of asphaltenes increases or decreases by temperature. The quantity of micelles may therefore increase or decrease. They appear at low temperatures and disappear with a rise in temperature. The layers of adsorbed hydrocarbons on the asphaltenes consist of resin molecules with gradually decreasing molecular weights in the outward direction, thus resins gradually assume the characteristics of the surrounding oils. This is why a sharp separation of these fractions could not be achieved yet. However, the line of demarcation between asphaltic resins and oily constituents becomes clearer as the new separation methods developed.

Asphaltic cements generally show relatively a low acidity. The presence of organic acids in asphaltic cements was first observed by Marcussou [4]. These acids are most likely similar to di-hydroxy monocarboxylic materials of $C_{20}H_{20}O_4$, the two hydroxy groups giving reactions similar to those of an acidic group. At temperatures as low as $120^{\circ}C$, the acids may lose water to form anhydrides [5].

In this study, fractionation of asphaltic cements with Turkish origin were made in order to separate them into the following five fractions: (1) Asphaltenes, (2) Asphaltic Resins, (3) Oily Constituents, (4) Free Asphaltous Acids, (5) Asphaltous Acid Anhydrides.

Changes of Asphaltic Cements Under Various Oxidative Conditions

Bitumens deteriorate with time at different rates depending on the conditions to which they are exposed and on their geographic origin. This deterioration took place more rapidly in thin films. The method of refining the crudes also affects the ageing characteristics of bitumen obtained.

Although considerable amount of research work has been carried out on the phenomena of deterioration of bitumens, the mechanism of ageing and the types of physical and chemical reactions that may occur in weathering of bitumens have not yet been completely explained.

Toch [6] exposed films of asphaltic cements under coloured glasses and found that rapid surface deterioration occurred when using violet, only slight deterioration was recorded beneath the green and red glasses. When air and moisture were excluded, no deterioration occurred beneath any of the glasses and deterioration by oxidation of the surface accelerated by light was postulated. Recent research works carried out by Yağız and Işıksalan [7] on various Anatolian bitumens have confirmed Toch's postulate by proving that light is one of the principle factors affecting oxidation. Alexander [8] found that light of various wavelengths

does not produce the same effect. Dubrisay [9] [10], who carried out extensive research on ageing under light, found iodine number of bitumens decreases during oxidation which probably be attributed to the disappearing of double bonds.

Graefe [11] showed that leaching by rain water occurred when bitumen coatings were exposed to atmospheric conditions and a bleached surface layer was produced which eventually cracks. Further studies [12] showed that cracking of the photo-oxidized surface is due to the thermal and mechanical strains*.

Recent investigations carried out by Gibson [13] showed that water-soluble degradation products were formed by asphaltic bitumens during oxidations. Although the nature of these water-soluble materials have not been identified, they probably include low molecular weight aldehydes [14].

The first extensive studies on the oxidation of bitumens were made by Dickinson and Nicholas [15] on coal tars in the dark from which it is concluded that two simultaneous first order reactions occurred: the conversion of phenols to resins and oxidation of hydrocarbons containing active hydrogen. It was later found that photo-oxidation extends to only 10 μ beneath the surface and light accelerates the absorption of oxygen by the asphaltic bitumens. Temperature also affects the rate of absorption of oxygen by asphaltic bitumens, the rate being approximately doubled for a temperature increase of 10°C. The Arrhenius relationship (exponential variation of absorption rate with absolute temperature) was obeyed [16]. Van Oort [17] showed that the amount of hardening was proportional to the amount of oxygen absorbed, and suggested that the best way to accelerate oxidation without changing the type of reaction was to increase the oxygen pressure. Lee and Dickinson [18] developed a pressure oxidation method to investigate the oxidation of coal tars. This method was used with modified test conditions for the investigation of Anatolian bitumens in this study.

* Some of the asphaltic bitumens with South-East Anatolian origin which were investigated in this study developed cracked surfaces (Fig. 1) when they were exposed to atmospheric conditions for a period of 3-6 months in thin layers [7].

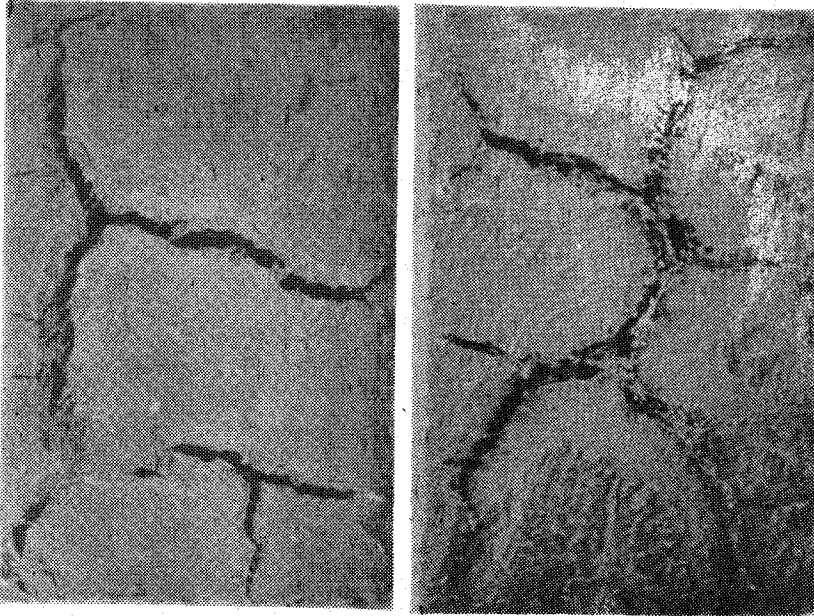
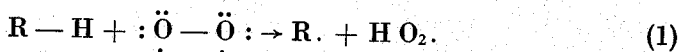


Figure (1) Cracked surfaces developed under atmospheric conditions.

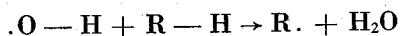
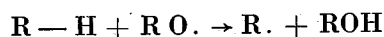
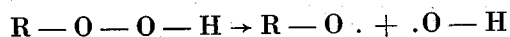
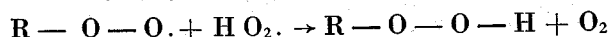
Most of the reports on the weathering of bitumens from a chemical point of view are concerned with chemical additives to inhibit or retard the ageing. Abraham [19] lists a number of additives for improving durability. A research work carried out on the improvement of durability characteristics of Turkish bitumens, by Tüzün and Yağız [20] showed that α -naphthol, β -naphthol and ammonium sulphate could effectively be used as anti-oxidants.

It is generally accepted that photo-chemical reactions produce free radicals and the acceleration effect of light on oxidation is the evidence of a free radical chain process. Dickinson and Nicholas [15] were also considered the oxidation to be a free radical chain process. This chain reaction may be described as follows:

It initiates by

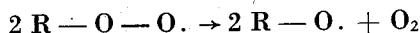


and propagates by

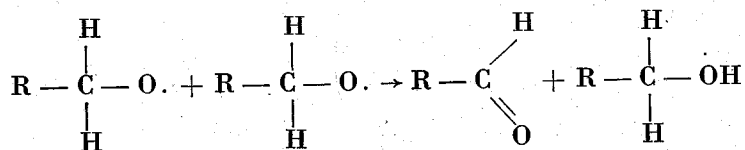
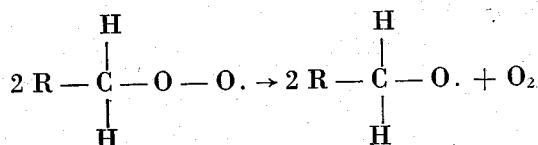
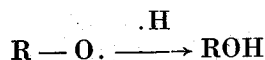


Thus R. radicals thus produced react again in accordance to the reaction shown in (2) above.

The chain reaction terminates by combination of free radicals or by inhibitors that capture peroxy radicals. A number of workers have observed that the final products of oxidation include carboxylic acids, carboxyl and hydroxy compounds and esters. The existence of carboxyl and hydroxyl groups show that not only peroxy radicals decompose to alkoxy radicals but rearrangements are also occur via transfer of hydrogen atoms:



peroxy radical alkoxy radical



Formation of esters have been observed in air-blown bitumens [21]. Goppel and Knotnerus [22] found that ester linkages in air-blown bitumens largely contributed to formation of materials of higher molecular weight. They have observed that all of the oxygen taken up by the asphaltic bitumen can be accounted for as hydroxyl, carbonyl, carboxyl and esters groups.

Sergiyenko and Garbalinsky [23] performed extensive research on the oxidation reaction during the air-blowing operation and found that the distribution of oxygen after 60 hours of oxydation as 11 % carboxyl groups, 25 % carbonyl groups and 64 % ester groups.

The tests that may be used for prediction of the asphaltic bitumen's behavior during the service life may be grouped as shown below:

(1) Heating bulk samples at application temperatures. A test method of this type has been developed by the A.S.T.M. [24], but a modified process [25] is now included in most of the specifications of asphaltic bitumens.

(2) Oxidation of thin films in the dark. Such a test has been developed for coal tars [18] but has also been used for asphaltic bitumens later [26], [27]. A modified version of this test is used for the investigation of South-East Anatolian bitumens as will be explained later on.

(3) Oxidation of thin films in the light, with washing of the surface by water when necessary. A test method of this type has been developed by the National Bureau of Standards [28] which requires accelerated weathering machines.

For this particular study which was carried out on South-East Anatolian bitumens, ultra violet exposure was applied to thin films of bitumen samples in an atmosphere where relative humidity was 100 %, since the ultra violet exposure conditions were proved to be the most severe among the other exposures.

Since the chemical nature of asphaltic bitumens are very complex, chemical changes during oxidation are not completely understood so far and rather general trends have only been revealed for the types of molecules that are present.

Fractional Compositions of Asphaltic Bitumens

Fractionation methods can be grouped under two basic type: physical separations on the basis of different physical properties of the fractions and chemical separations on the basis of chemical

properties. But in many cases fractionation methods based on combination of physical and chemical separation such as solvent extractions, azeotropic distillations and chromatographic separations are used [29].

It is generally accepted that asphaltic bitumens may sharply be separated into two broad fractions known as asphaltenes and malthenes. By further separation, malthenes may be fractionated into asphaltic resins and oils, but this sub-division is not sharp enough, the reason being that neither resins nor oils have been definitely described.

The five principal procedures used for fractionation today are distillation, solvent extraction, adsorption, chromatography and chemical precipitation.

Distillation for fractionation can be considered as the first step in determining fractional composition of bitumens. Cracking at high temperatures and overlapping of boiling ranges are the limitations of this operation.

Solvent extraction was suggested by Clifford Richardson [30] for the first time. He separated native bitumen from inorganic matters by carbon disulphide. Hoiberg, Hougen and Zapata [31] were the first investigators to suggest fractionation of asphaltic bitumens into three fractions by means of hexane and propane. These fractions were asphaltenes, asphaltic resins and oily constituents. Later, Hoiberg and Garris [32] developed a new method which utilizes polar solvents for separation of asphaltic bitumens into five fractions.

Traxler and Schweyer [33] devised a fractionation method to separate asphaltic bitumens into three fractions in which separation of asphaltenes was eliminated. Since all three fractions obtained by this method contain asphaltenes, it is considered as an inconvenient method for fractionation. The modified version of his method [34] was not a less confusing procedure. The fractionation procedure devised by Knowles et al. [35], was intended to separate asphaltic bitumens into four main fractions, two of which (resins and oils) were to be subdivided into further fractions.

Adsorption procedures for separation of asphaltic bitumens have been in use since the early 1900s. Today, new adsorbents provide very efficient tools for fractionation of asphaltic bitumens.

Chromatographic operations are very promising as separation procedure and numerous methods have been proposed since its invention by Tswett. Zechmeister [36] quotes that Day was the first investigator who applied chromatographic principles in separation of light fractions of crude oils in Pennsylvania.

Kleinschmidt's [37] method (which is a rather new procedure) separates asphaltic bitumens into four main fractions. Kleinschmidt first precipitated asphaltenes by n-pentane and then eluted the n-pentane soluble fraction by various eluants through a chromatographic column of fuller's earth in order to separate white oils, dark oils and asphaltic resins. Watson's [38] method was devised to separate asphaltic bitumens into two main fractions called resins and oils. The method suggested by Eby [39] provides separation of petroleum oils into three main fractions. Both methods use silica gel as the adsorbent. A similar method is proposed by Dunkel et al. [40] which is more suitable for asphaltic bitumens since it provides separation of asphaltenes too. Methods devised by Glasgow and Termini [41], and Hubbard and Stanfield [42] and O'Donnell [43] are also used for separation of asphaltic bitumens, but none of them can be considered perfect for the purpose. Even by O'Donnell's method (which employs a combination of fractionation operations such as distillation, chromatography and thermal diffusion) the fractions obtained overlapped in composition as shown by Simpson et al. [44].

Chemical precipitation methods are based on separation of fractions by stepwise precipitation with excess of reagents.

The method proposed by Marcusson and Eickmann [45] can be used to separate asphaltic bitumens into two or three fractions by using solvent naphtha and sulphuric acid successively. The method devised by Julius Marcusson [46], provides separation of asphaltic bitumens into five main fractions as free asphaltous acids, asphaltous acid anhydrides, asphaltenes, asphaltic resins and oily constituents. Later, Hans Pöll [47] suggested an addi-

tion to provide further fractionation of asphaltenes into hard asphaltic carboids and hard asphaltic resins. The method suggested by Rostler and Stenberg [48], [49] was intended to separate asphaltic bitumens into asphaltenes and maltenes by n-pentane, after which maltenes fraction was to be subdivided into four further broad fractions which are different in chemical reactivity.

As a conclusion it may be said that all separation operations and methods available today have their limitations and by none of them may fractionation of asphaltic bitumens with sharp demarcation be achieved.

Although it is rather an old method, Julius Marcusson's procedure for fractionation of asphaltic bitumens is used for this study for the following reasons: (1) Marcusson's method provides separation of asphaltic bitumens into five main fractions which are identified by a terminology widely accepted by investigators, and names of some of the fractions indicate certain chemical property and reactivity (for instance, free asphaltous acids and acid anhydrides). (2) Preliminary studies proved that Marcusson's method gives reproducible results. (3) It is very elaborate; employing a combination of extraction, chemical precipitation and adsorption procedures. (4) It provides the capability of the separation of asphaltic bitumens into three main fractions only (asphaltenes, asphaltic resins and oily constituents) whenever it is required.

As it will be seen later, chromatographic procedures were also used for more detailed studies of asphaltic resin fractions in this investigation.

Experimental

This investigation was performed on asphaltic bitumens produced from crudes of Mağrip, Raman and Batı Raman oil fields in South-East Anatolia. "Distillation at Reduced Pressure" procedure [50] was employed for the production of asphaltic cement samples from crude oils.

The behaviors of these three asphaltic cements under oxidative conditions were studied and changes both in fractional com-

positions and physical properties were determined. It is concluded that the asphaltic bitumen from Mağrip is the most susceptible bitumen to oxidative conditions. After this conclusion, detailed studies concentrated on the asphaltic resin fraction of the Mağrip asphaltic bitumen.

The properties of asphaltic bitumens investigated are shown in Table 1.

TABLE 1

Properties of Asphaltic Bitumens having Mağrip, Raman and Batı Raman Origins, as obtained by Standard Test Methods of Road Bitumens.

Test Method	Origin of the Bitumen		
	Mağrip	Raman	Batı Raman
Specific Gravity, 25/25°C, (ASTM D 70-52)	1.012	1.035	1.039
Flash and Fire Points, °C (ASTM D 92-66)	243, 272	252, 287	215, 257
Penetration, 100 g, 25°C, 5 sec, (ASTM D 5-65)	165	148	154
Ductility, 25°C, cm, (ASTM D 113-68)	40	84	116
Loss on Heating, 163°C, 5h, %, Penetration, of residue, percent of original	0.41 83	1.59 84	1.17 75
Solubility in CCl ₄ , % (ASTM D 2042-66)	99.69	99.82	99.91
Spot Test, (AASHTO T 102-57)	(+)	(+)	(+)
Softening Point, R and B, °C, (ASTM D 2398-68 T)	48	43	44

I. Investigations made on Asphaltic Bitumens

1. Fractionation of Asphaltic Bitumens with Mağrip, Raman and Batı Raman Origins.

Julius Marcusson's method [46] was applied to separate the asphaltic bitumen samples into their main fractions. Results obtained are given in Table 2.

TABLE 2

Fractional Compositions of Asphaltic Bitumens having Mağrip, Raman and Batı Raman origins, as obtained by Marcusson's Method

Main Fractions	Origin of the Bitumen		
	Mağrip	Raman	Batı Raman
Free Asphaltous Acids, %	1.63	2.21	3.51
Asphaltous Acid Anhydrides, %	0.28	0.49	0.52
Asphaltenes, %	21.50	28.36	28.25
Asphaltic Resins, %	9.10	5.98	10.65
Oily Constituents, %	63.30	59.48	54.00
Balance of the Sample, %	4.19	3.48	3.07

2. Effect of Ultra Violet Radiation.

a) Changes in chemical compositions

Asphaltic bitumens with Mağrip, Raman and Batı Raman origins were subjected to ultra-violet radiation in thin films* after which their fractional compositions were determined by means of J. Marcusson's method.

Results obtained are given in Table 3.

TABLE 3

Fractional Compositions of Asphaltic Bitumens having Mağrip, Raman and Batı Raman Origins, after they were subjected to UV Radiation

Main Fractions	Origin of the Bitumen		
	Mağrip	Raman	Batı Raman
Free Asphaltous Acids, %	1.38	1.97	1.24
Asphaltous Acid Anhydrides, %	0.28	0.39	0.45
Asphaltenes, %	36.17	36.86	39.36
Asphaltic Resins, %	20.29	19.24	18.03
Oily Constituents, %	37.60	36.87	37.90
Balance of the Sample, %	4.28	4.67	3.02

* Thin films of asphaltic bitumens of approximately 50 μ , were formed on glass plates by spreading a solution of bitumen in CS₂ and evaporating the solvent afterwards. Specimens prepared in this manner were then subjected to ultra-violet radiation for 24 hours at a medium where relative humidity was 100 %.

Increases and decreases in the percentages of the main fractions after UV radiation, for all asphaltic bitumens investigated are shown in Table 4 for comparison purposes.

TABLE 4

Increases and Decreases in the Percentages of Main Fractions of Asphaltic Bitumens with Mağrip, Raman, and Batu Raman Origins after they were subjected to UV Radiation

Origin of the Bitumen	Changes in the Amount of Main Fractions of				
	Free Asph. Acids %	Asph. Ac. Anhyd. %	Asphaltenes %	Asphaltic Resins %	Oily Constituents %
Mağrip	15.34(—)	...	68.23(+)	122.97(+)	40.60(—)
Raman	10.86(—)	20.41(—)	29.97(+)	221.74(+)	38.01(—)
Batu Raman	64.67(—)	13.46(—)	39.33(+)	69.29(+)	29.81(—)

(+) Increases, (—) Decreases

b) Changes in the Consistencies

The penetration values and softening points of all asphaltic bitumens studied were determined before and after they were subjected to UV radiation in thin films as described previously and changes in these properties were recorded. Results are shown in Table 5.

TABLE 5

Changes of Consistency Properties of Asphaltic Bitumens with Mağrip, Raman and Batu Raman Origins, due to UV Radiation

Origin of the Bitumen	Property					
	Penetration, 0.1 mm			Softening Point, °C		
	Before UV	After UV	Difference	Before UV	After UV	Difference
Mağrip	165	33.5	79.7 % drop	48	85.5	37.5
Raman	148	20	86.5 % drop	43	79	36
Batu Raman	154	21	86.4 % drop	44	75.5	31.5

3. *Effect of Oxygen.*

Asphaltic bitumens with Mağrip, Raman and Batı Raman origins were subjected to pressure oxidation test [51] in thin layers* before and after which their absolute viscosities were determined by means of a sliding-plate microviscometer [52]. Results are shown in Table 6.

TABLE 6

Changes of Absolute Viscosities of Asphaltic Bitumens with Mağrip, Raman and Batı Raman Origins, due to the Pressure Oxidation Test

Origin of the Bitumen	Absolute Viscosity, 10 ⁷ poise		Increase in Abs. Vis. (In folds of the Original)
	Before Pr. Ox. Test	After Pr. Ox. Test	
Mağrip	0.027	0.269	10
Raman	0.048	0.267	5.5
Batı Raman	0.093	0.137	1.5

As it is seen from the results given in Table 4, 5 and 6 the asphaltic bitumen from Mağrip is the most susceptible bitumen among others, to oxidative conditions. Therefore, more detailed and extensive investigations were concentrated on the Mağrip bitumen and particularly on the asphaltic resins fraction of this bitumen, because this fraction has a very important role in the general properties and behaviours of asphaltic bitumens [53], [54], [55], [56], [57].

4. *Formolite Reaction*

As it is known asphaltic resins contain considerable amount of unsaturated hydrocarbons. The cyclic unsaturated hydrocarbons undergo the formolite reaction [58, 59, 60] which is actually a type of aldehyde condensation, and producing insoluble condensation products. These products are essentially high-molecular-weight resins with varying softening points.

* For this test, asphaltic bitumen samples were spread in shallow aluminium containers in films of about 1 mm thick and were placed in a stainless steel oxidation bomb as shown in Fig. 2, where they were exposed to oxygen at 90°C, under a pressure of 25 atmosphere, for a period of 6 hours.

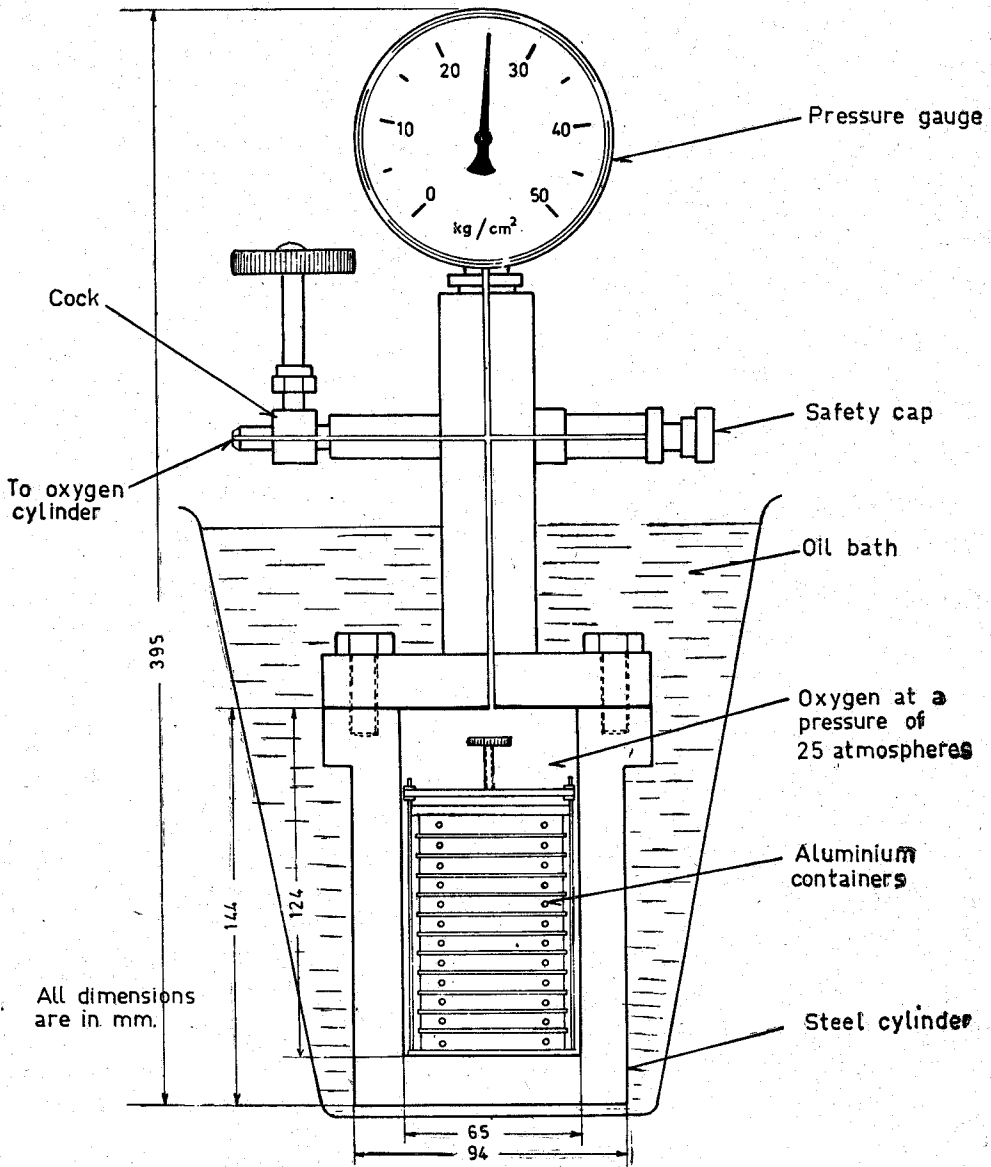


Figure (2) Pressure vessel assembly for oxidation test

Asphaltic resins fractions separated from asphaltic bitumens of Mağrip, Raman and Batı Raman by Marcusson's method, were subjected to formolite reaction (see Fig. 3). Softening points of asphaltic resins were determined* before and after this reaction. Results obtained are given in Table 7.

TABLE 7

Effect of Formolite Reaction on the Softening Points of Asphaltic Resins Fractions

Origin of Asphaltic Resins	Softening Point, °C		Increase in Softening Point, °C
	Before Formolite Reaction	After Formolite Reaction	
Mağrip	38.2	46.0	7.8
Raman	36.7	40.5	3.8
Batı Raman	39.1	42.0	2.9

Same reactions and tests were performed on the asphaltic resins fractions separated from asphaltic bitumens which were previously been subjected to ultra-violet radiation. Results obtained are given in Table 8.

TABLE 8

Effect of Formolite Reaction on the Softening Points of Asphaltic Resins separated from Irradiated Asphaltic Bitumens

Origin of Asphaltic Resins	Softening Point, °C		Increase in Softening Point, °C
	Before Formolite Reaction	After Formolite Reaction	
Mağrip	37.3	40.5	3.2
Raman	35.2	38.6	3.4
Batı Raman	32.7	33.4	0.7

* ASTM D 2398-68 T Method was applied with all dimensions reduced to 1/20 th, since asphaltic resins subjected to formolite reaction were as small as 100 mg in quantity.

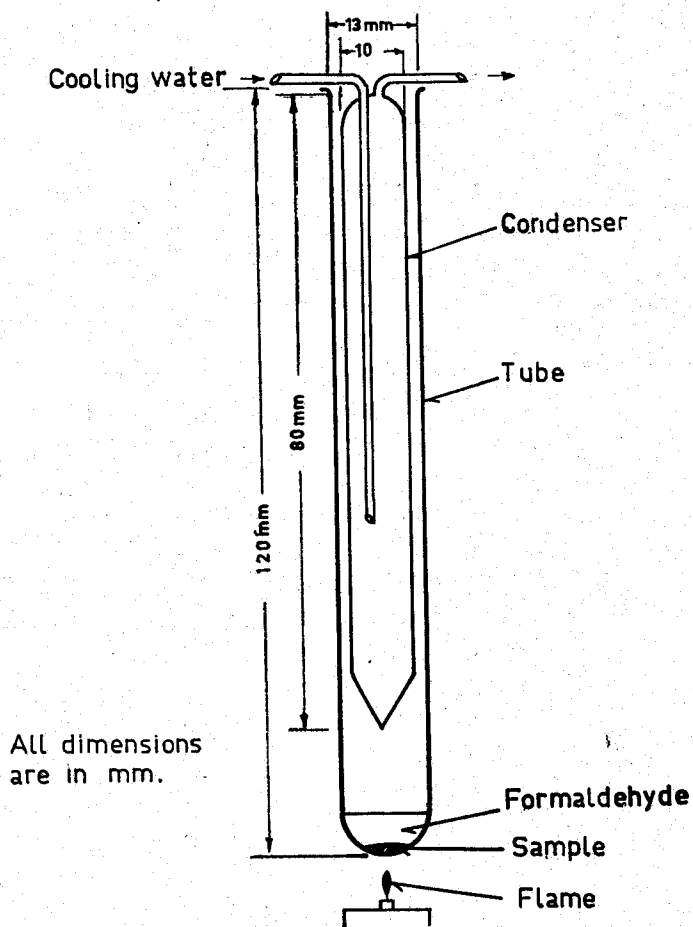


Figure (3) Assembly for formolite reaction.

II. Investigation of Asphaltic Resins Fraction Separated From Asphaltic Bitumen of Mağrip Origin

Sufficient amount of asphaltic resins were separated from asphaltic bitumen of Mağrip origin and collected in a suitable glass container with ground glass stopper. About half of these resins were subjected to pressure oxidation test and asphaltic resins oxidized in this manner collected in a similar container.

Both of the containers were stored in a nitrogen atmosphere and also kept away from light throughout the investigation.

1. *Changes in Molecular Weight of Asphaltic Resins due to Oxidation.*

Molecular weight of the asphaltic resins fraction was determined* before and after it was subjected to the pressure oxidation test. To see the further effect of oxidation, the duration of the test was doubled and tripled. Results obtained are shown in Table 9 and Fig. 4.

TABLE 9
Effect of the Duration of Pressure Oxidation Test on the
Molecular Weight of Asphaltic Resins

Molecular Weight	Unoxidized Asphaltic Resins	Oxidized Asphaltic Resins		
		Duration of Oxidation, hours		
		6	12	18
	492	555	566	567

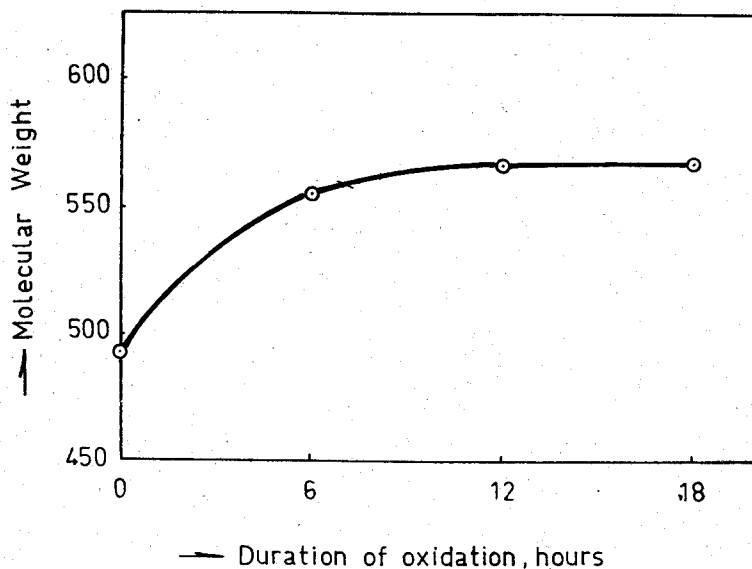


Figure (4) Effect of duration of oxidation on the molecular weight of asphaltic resins.

* The Apparatus used was a Molecular Weight Apparatus, Model 115, Coleman Inst.

2. *Formation of Carbon dioxide and Water*

Observations were made to identify possible formations of reaction products such as CO_2 and H_2O . For this purpose the oxygen was discharged* through a U tube containing CaCl_2 , followed by a wash-bottle containing a clear solution of $\text{Ba}(\text{OH})_2$. U tube was weighed accurately before and after discharging oxygen and it is seen that there is an increase in the weight of U tube proving that a very little amount of water was formed during oxidation, (the amount being 0.076 % by weight of the asphaltic resins placed in the bomb). On the other hand, the wash-bottle containing $\text{Ba}(\text{OH})_2$ solution remained clear, showing that no CO_2 was formed during oxidation.

Figure 5 gives a diagram of the apparatus used in the test.

3. *Spectrophotometric Investigations*

Samples from both unoxidized and oxidized asphaltic resins with Mağrip origin were studied by means of a spectrophotometer in order to determine the presence of various chemical functional groups by their distinctive infra-red absorption spectrum characteristics**. The spectra obtained are given in Figures 6, 7 and 8.

4. *Chromatographic Analysis*

Samples of both unoxidized and oxidized asphaltic resins of Mağrip origin were separated into five sub-fractions by means of column chromatography and by flowing chromatogram method***

In fact these five sub-fractions were also separated into further sub-divisions by collecting the percolates from each eluant

* To ensure filling the bomb with dry oxygen, the gas was forced to pass through a steel U tube containing CaCl_2 , before entering the bomb.

** The apparatus used was a Perkin-Elmer 337, double-beam, grating, null adjusting spectrophotometer with an operation range of $4000-400\text{ cm}^{-1}$ (2.5—25 microns).

*** A glass column of 1 cm in diameter and 40 cm in length was filled with silica gel (Merck, 0.05-0.20 mm) evenly. A small amount of Hyflo (J. M. Hyflo Super Gel) was then placed as a top layer 5 mm thick. The asphaltic resins to be adsorbed were dissolved in CCl_4 and passed through the column. In order to separate the adsorbed compounds, the chromatogram formed was then eluated with Carbon tetrachloride, Benzene, Toluene, Pyridine and Propionic Acid, in accordance to the elutropic order.

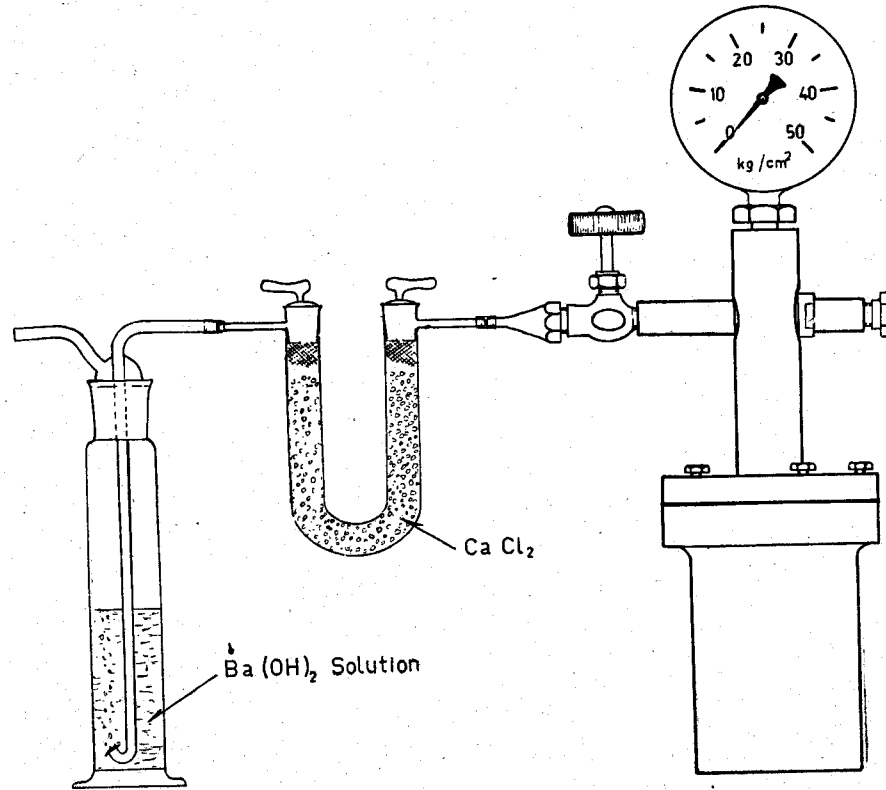


Figure (5) Assembly for identification of CO₂ and H₂O

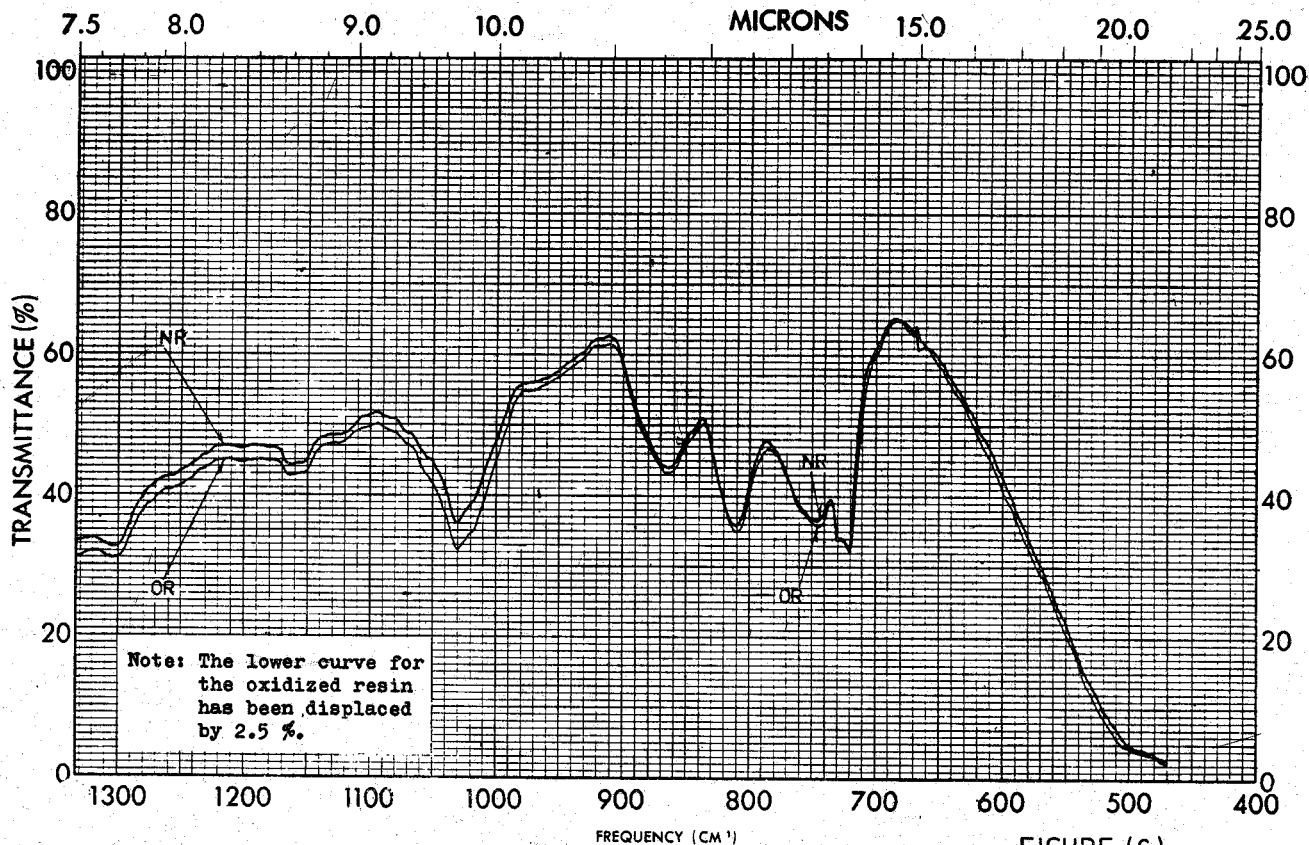


FIGURE (6)

SAMPLE NR - Normal Resin	CURVE NO _____	SCAN SPEED 150 cm ² /min	OPERATOR _____
OR - Oxidized Resin	CONC _____	SUIT Normal	DATE _____
ORIGIN Magrip Asphaltic Bitumen	FILM PATH < 0.015 mm	REMARKS _____	
SOLVENT None	REFERENCE Air	_____	

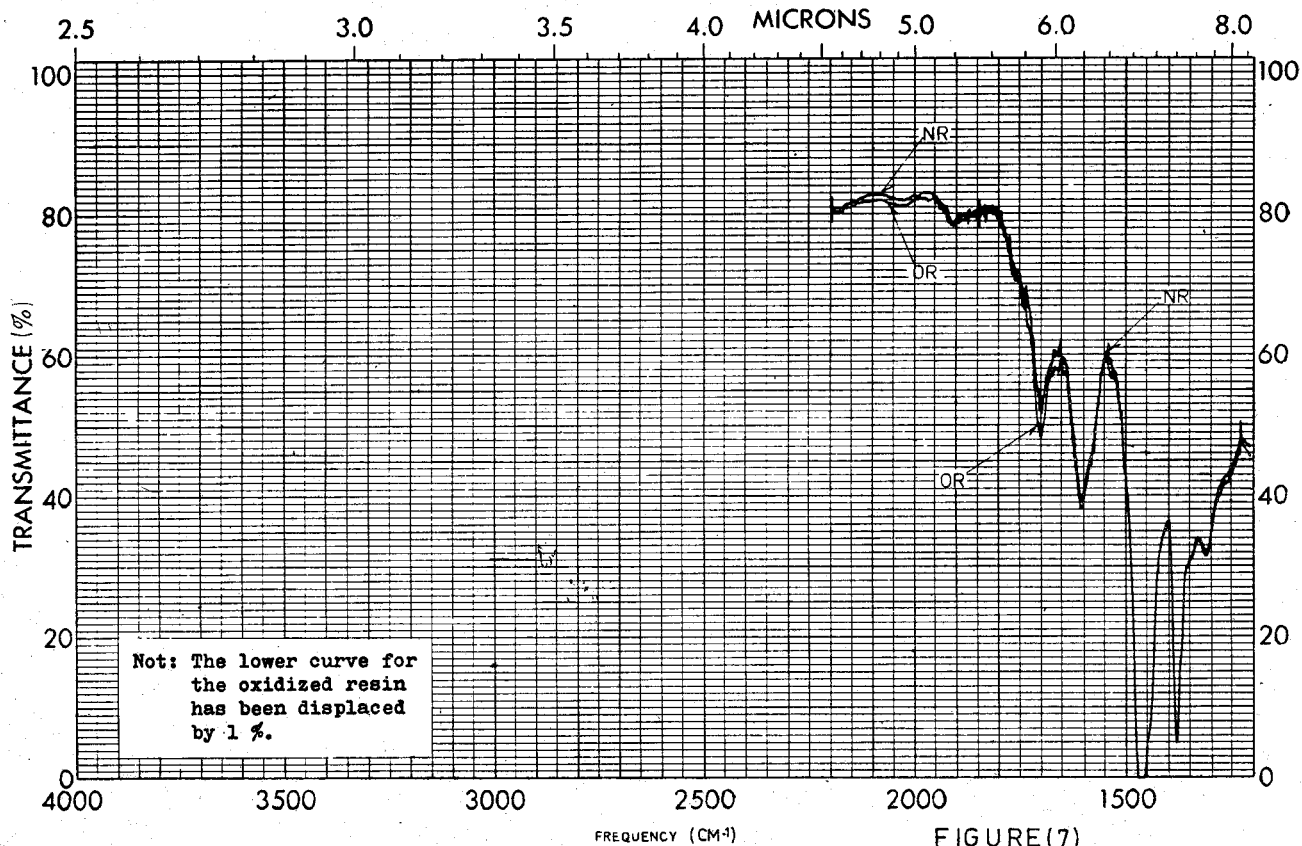


FIGURE (7)

SAMPLE	NR - Normal Resin	CURVE NO	SCAN SPEED 150 cm ² /min	OPERATOR
	OR - Oxidized Resin	CONC	SLIT Normal	DATE
ORIGIN	Magrip Asphaltic Bitumen	FILM PATH 0.05 mm	REMARKS	
SOLVENT	None	REFERENCE Air		

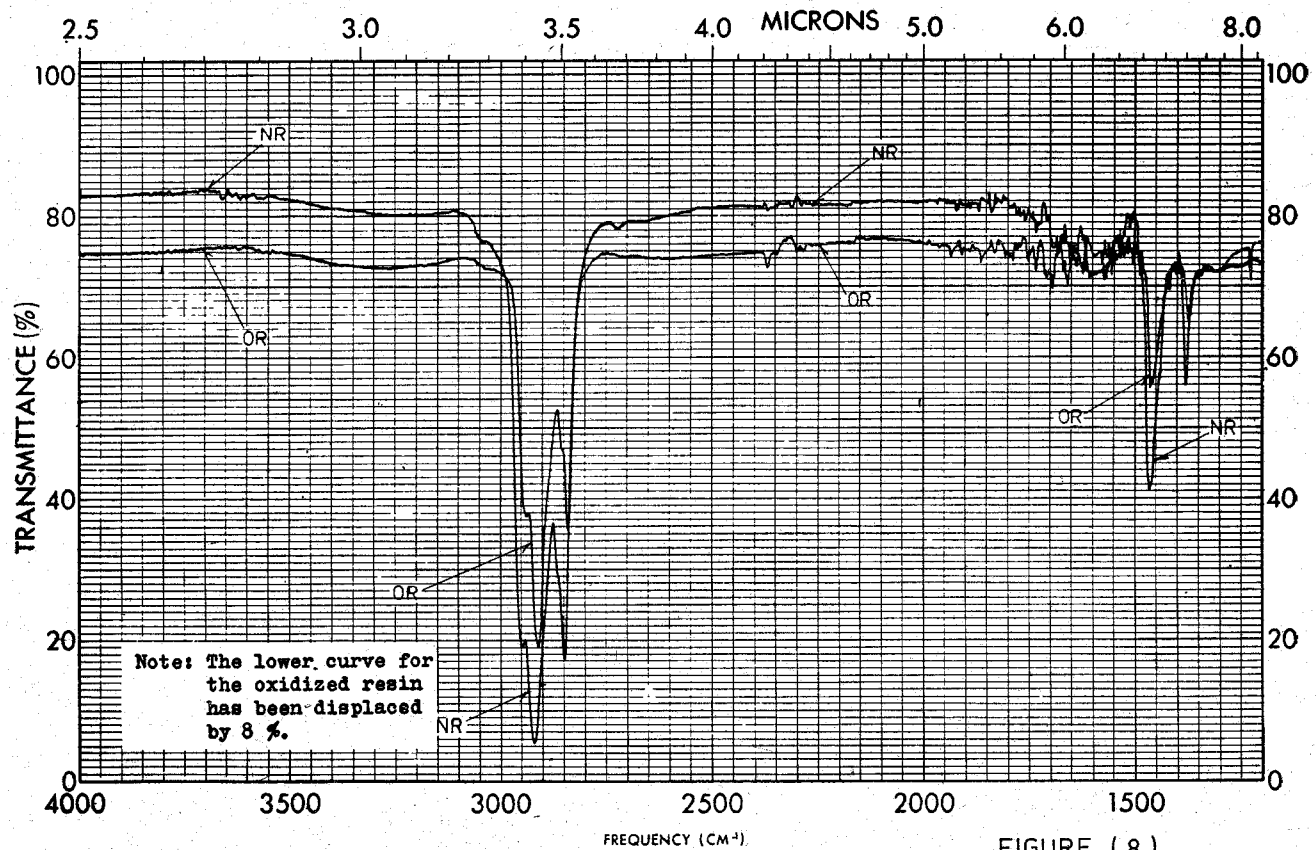


FIGURE (8)

SAMPLE <u>NR - Normal Resin</u>	CURVE NO _____	SCAN SPEED <u>150 cm¹/min.</u>	OPERATOR _____
<u>OR - Oxidized Resin</u>	CONC _____	Slit <u>Normal</u>	DATE _____
ORIGIN <u>Magrip Asphaltic Bitumeh</u>	FILM PATH <u>< 0.015 mm</u>	REMARKS _____	
SOLVEN <u>None</u>	REFERENCE <u>Air</u>	_____	

into 10 separate containers. However, the number of subdivisions from the same eluant was brought down from 10 to either 1, 2 or 3 by combining them among themselves according to either the similarity of their visible colors or the color or type of spots they formed on a filter-paper, as seen under UV light.

The combined sub-divisions were first classified into two broad groups and marked as follows:

Unoxidized Asphaltic Resins	Oxidized Asphaltic Resins
1a _n , 1b _n , 1c _n	1a _{ox} , 1b _{ox} , 1c _{ox}
2a _n , 2b _n	2a _{ox} , 2b _{ox}
3a _n	3a _{ox}
4a _n , 4b _n , 4c _n	4a _{ox} , 4b _{ox} , 4c _{ox}
5a _n , 5b _n	5a _{ox} , 5b _{ox}

where 1, 2, 3, 4 and 5 denote the percolates obtained from the eluants in the order of elutropic serie, that is 1 for Carbon tetrachloride, 2 for Benzene, 3 for Toluene, 4 for Pyridine and 5 for Propionic Acid. Indices of "n" and "ox" indicate normal (unoxidized) and oxidized asphaltic resins. Finally, a, b and c emphasise the combined sub-divisions of the same eluant.

After these 22 percolates were evaporated down to 5 cc, identifications of functional groups, existence of which were considered possible, were made by means of micro spot tests. Results obtained are given in Table 10.

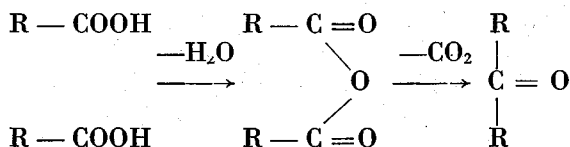
Results and Conclusions

Conclusions drawn from this investigation may be summarized as follows:

1. The results given in Tables 2, 3 and 4 show that the amounts of main fractions of all asphaltic bitumens tested were changed considerably due to the effect of UV radiation. The amounts of asphaltic resins and asphaltenes were increased markedly, while the amount of oily constituents were decreased at the same rate. Likewise, smaller decreases in the percentages of free asphal-

Functional Groups	Sub-divisions Obtained by Collecting the Percolates From Different Eluants																						
	Percolates of carbon tetrachloride						Percolates of Benzene				Percolates of Toluene		Percolates of Pyridine						Percolates of Propionic Acid				
	1a _n	1b _n	1c _n	1a _{ox}	1b _{ox}	1c _{ox}	2a _n	2b _n	2a _{ox}	2b _{ox}	3a _n	3a _{ox}	4a _n	4b _n	4c _n	4a _{ox}	4b _{ox}	4c _{ox}	5a _n	5b _n	5a _{ox}	5b _{ox}	
Alcohols	+	+	-	-	-	-	+	-	-	+	-	+	-	-	+	+	-	?	?	?	?		
Phenols	-	+	-	-	-	+	+	+	+	+	+	+	-	-	+	-	-	-	-	-	-	-	
Phenol Esters of Carboxylic Acids	-	-	-	-	-	+	+	+	-	-	+	-	-	-	-	-	-	-	-	-	-	-	
Alkyl Phenol Ethers	+	-	-	-	-	-	-	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	
Polyhydroxybenzenes	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Anthraquinones and their Derivatives	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Enols	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	
Carbonyl Groups	-	-	-	-	-	-	+	+	-	+	-	?	?	?	?	?	?	?	?	?	?	?	
Aldehydes	+	+	+	+	+	-	+	-	+	+	-	-	+	-	+	-	-	-	+	+	+	+	
o-Hydroxyaldehydes and -ketones	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Methylene Ketones	?	?	?	?	?	?	?	?	?	?	?	?	+	?	?	?	?	?	+	+	?	?	
Carboxylic Acids	-	-	-	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	?	?	?	?	
Esters of Carboxylic Acids	+	+	+	+	-	+	?	?	?	?	?	?	+	+	-	+	-	+	?	?	?	?	
Carboxylic Acid Anhydrides	-	-	-	-	-	-	-	-	-	-	+	-	-	+	-	-	+	-	-	-	-	-	
Aliphatic Esters of Carboxylic Acids	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	
1-2 Dicarboxylic Acids	+	+	+	+	+	-	-	-	-	-	+	-	+	-	+	+	+	+	-	-	-	-	
Halogenoalkyls, Halogenoaryls	-	+	-	-	+	+	-	-	+	+	?	?	-	+	-	+	+	+	-	+	+	-	

tous acids and asphaltous acid anhydrides were also observed. These results support the contention that oils form first the resins, then carboxylic acids and eventually the asphaltenes during oxidation [61]. On the other hand, the decrease in the asphaltous acids and acid anhydrides may be attributed to conversion of asphaltic acids first into anhydrides by dehydration and then to ketones by decarboxylation as below:



2. Rheological properties of all bitumens studied were modified considerably due to the effect of UV radiation: Marked increases in softening points and considerable decreases in penetration values were recorded. This is obviously due to the conversion of less viscous fractions such as oily constituents into more viscous, even solid fractions such as asphaltic resins and asphaltenes, (Table 5).

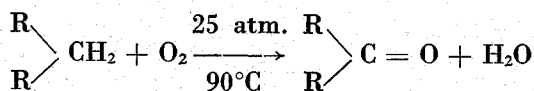
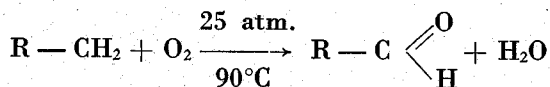
3. Pressure Oxidation Test is also affected in a similar manner on asphaltic bitumens and considerable increases in absolute viscosities were observed (Table 6), which again can be attributed to the conversion of less viscous fractions into more viscous ones.

4. Results of Formolite Reaction given in Table (7) and (8) show that asphaltic resins having Mağrip origin contain more cyclic unsaturated hydrocarbons than resins with other origins. The same results may also be interpreted as the asphaltic resins having Mağrip origin is the most susceptible one to UV radiation among the others.

5. As seen from Table (9), Pressure Oxidation Test caused increases in the molecular weight of asphaltic resins; the rate of increase being 12.8 % for 6 hours oxidation. When the duration of oxidation was increased to 12 hours, the increase in the molecular weight reached to 15 %. A further increase of 6 hours in the duration of oxidation had no further effect on the molecular weight.

6. It was observed that a very little amount of water (0.076%) was formed during oxidation of asphaltic resins. The formation of carbon dioxide, which would cause a decrease in molecular weight was not observed. These findings indicate that a dehydration reaction occurs during oxidation, but no decarboxylation reaction at all. These observations were in agreement with the recorded increase in molecular weight of asphaltic resins due to the oxidation conditions.

From the facts of the formation of water and the increase in molecular weight, it can be concluded that during the pressure oxidation the following reactions should have occurred:

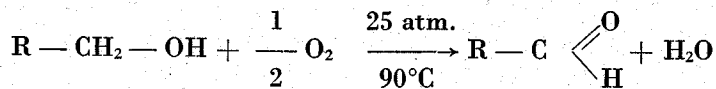


The reactions given above are also confirmed by the results obtained from spectrophotometric and chromatographic analysis, which indicated increases in carbonyl groups and decreases in methyl and methylene groups. (See paragraphs 7 (b) and 8 (c), (e), (f), (h) below).

7. Results of the spot tests which were made to identify the functional groups in the sub-fractions of asphaltic resins separated by chromatographic means are shown in Table 10. Following conclusions were drawn from these results:

a) Alcoholic groups exist in asphaltic resins. However the amount of these groups decreases with oxidation. (This conclusion was also confirmed by spectrophotometric findings. See paragraph 8 (j) below).

This indicates that the following type of reaction should have happened:



and alcohols oxidized to aldehydes. Observations mentioned in paragraph 7 (b) also support this conclusion.

b) The amount of carbonyl groups, the presence of which were recorded, increases with oxidation. This is also confirmed by spectrophotometric evidences. (See paragraph 8 (h) below).

c) The amount of phenolic groups, the existence of which were recorded, does not change with oxidation. This is reasonable since phenols do not react with oxygen under these conditions. Spectrophotometric evidences also corroborate these findings.

d) Likewise, halogenoalkyls and halogenoaryls remained unchanged after oxidation.

e) No definite conclusion could be reached about the presence of enols, methylene ketones and aliphatic esters of carboxylic acids.

f) It may be said that alkyl phenol ethers, polyhydroxybenzenes, anthraquinones and their derivatives, o-hydroxyaldehydes and ketones were not found to exist in asphaltic resins.

g) Although slight indications were recorded regarding to the presence of carboxylic acids and their derivatives, it may be said that they also do not exist in asphaltic resins.

8. The results of spectrophotometric investigation can be seen in Figures 6, 7 and 8. By studying these spectra and comparing spectrums of oxidized and unoxidized resins, the following conclusions were reached: [62], [63], [64], [65], [66], [67], [68].

a) Small decreases in the absorbance at 720 cm^{-1} and at 730 cm^{-1} were observed after oxidation, which may be interpreted as oxidation reducing the compounds having paraffinic straight-chain character with four or more methylene groups.

b) Oxidation reduced the amount of aromatic rings with two or four adjacent hydrogens as indicated by the decreases in the absorption at 750 cm^{-1} and at 820 cm^{-1} .

c) Oxidation caused a slight increase in the absorption at 1030 cm^{-1} , which can be attributed to the fact that the amount of $\text{C}=\text{O}$ bonds were slightly increased.

d) The equal amount of absorption shown by both oxidized and unoxidized resins near 1310 cm^{-1} may be attributed to aromatic and olefinic esters and it can be said that their amounts remained unchanged after oxidation. Results of Spot Tests (Table 10) also support this conclusion.

e) Marked decreases in the absorption at 1380 cm^{-1} and at 2960 cm^{-1} were observed which indicate that the amount of methyl groups were decreased considerably due to oxidation.

f) The amount of methylene groups, which show distinct absorptions at 1460 cm^{-1} , 2850 cm^{-1} and 2926 cm^{-1} were reduced considerably after oxidation, as indicated by marked decreases in absorptions of the wavenumbers mentioned above. Likewise, marked decreases in absorptions at 1465 cm^{-1} and 1471 cm^{-1} indicated that C — H bonds in methylene groups and the amount of methylene-methylene groups were reduced considerably due to oxidation.

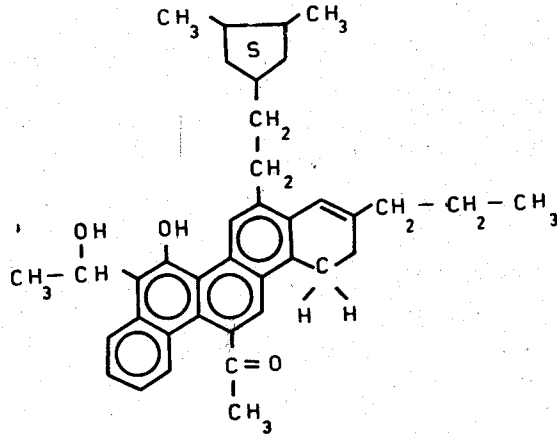
g) The distinct absorption at 1600 cm^{-1} due to olefinic carbon bonds that are either conjugated with or belong to aromatic systems remained unchanged after oxidation which indicates that the amount of these bonds was not influenced with oxidation.

h) Oxidation caused a distinct increase of absorbance at 1700 cm^{-1} which indicates that the amount of carbonyl groups were increased due to oxidation.

i) A small absorption peak at 3610 cm^{-1} which can be attributed to phenolic hydroxyl groups, remained unchanged after oxidation which indicates that the amount of these groups was not affected by oxidation. This conclusion is corroborated by the results of spot test analysis too.

j) Small absorption peaks at 3600 cm^{-1} and at 3670 cm^{-1} , which can be attributed to alcoholic hydroxyl groups, disappeared after oxidation, which indicated that these groups were oxidized probably to aldehydes. The results of spot test analysis also support these findings.

9. By taking into account all of these findings, the following hypothetical average structure for asphaltic resins was deduced.



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 Z E T

Bu alıřmada, Gney Doęu Anadolu menřeli ham petrolerden elde edilen asfaltik bitmlerin ve bunları teřkil eden ana fraksiyonların ykseltgen řartlar altında uęradıkları deęiřiklikler incelenmiřtir. nce asfaltik bitmlerden hangilerinin ykseltgen řartlardan en ok etkilendięi arařtırılmıř, bunun Maęrip menřeli asfaltik bitm olduęu tesbit edildikten sonra, arařtırmalar bu asfaltik bitmn asfaltik reineler fraksiyonu zerinde yoęunlařtırılmıřtır. Elde edilen sonular, ykseltgen řartların asfaltik bitmlerin fraksiyonel bileřimlerini nemli derecede deęiřtirdięini ve zellikle yaęlı bileřenlerin miktarının azaldıęı ve asfaltik reineler ve asfaltin miktarlarının arttıęını gstermiřtir. Ykseltgen řartların asfaltik bitmlerin penetrasyon derecelerini dřrdę ve yumuřama noktaları ile mutlak viskozitelerini ykselttięi yani bitmleri nemli derecede sertleřtirdięi gzlenmiřtir

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