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# The Components of the Bitumen in Athabasca Bituminous Sand and their Significance in the Hot Water Separation Process

BY

D. S. PASTERNAK AND K. A. CLARK



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## **THE COMPONENTS OF THE BITUMEN IN ATHABASCA BITUMINOUS SAND AND THEIR SIGNIFICANCE IN THE HOT WATER SEPARATION PROCESS**

### **Abstract**

Judging from the proportions of the components and the ultimate analyses, the bitumen throughout the Athabasca bituminous sand deposit had a similar origin. Moderate variations in the proportions of the components of the bitumen in bituminous sands which separate normally in the hot water process do not have any effect on the separation. There is evidence that some bituminous sand beds at Bitumount contain a bitumen whose components are in somewhat different proportions to each other than is the case with the bitumen in other beds in the section. The fine clay present in bitumen appears to be closely associated with the asphaltenes. A method is indicated for avoiding the formation of troublesome emulsions when determining the proportion of saponifiable material in the bitumen. Differences in the relative viscosity of the bitumen would appear to be due primarily to variations in the relative proportions of the oily constituents.

### **Introduction**

While carrying out a considerable amount of experimental work on the process of recovering bitumen from Athabasca bituminous sands by washing them with hot water, irregularities in the results appeared which did not seem to be due to changes in experimental conditions. These irregularities had to do mainly with the mineral content, and with the yield, of the recovered bitumen. It was also observed that the amount of water which became associated with the bitumen froth as it collected on the surface of the water often varied with bituminous sands from different localities and even from beds at different elevations at the same location. It was thought desirable to determine the relative proportions of the components of the bitumen contained in some of the bituminous sands to see whether there might be any relationship between the composition of the bitumen and the results obtained when these bituminous sands are put through the hot water separation process.

There has been very little previous work on the determination of the components of the bitumen in Athabasca bituminous sand. Krieble and Seyer (7) extracted the bitumen from bituminous sand and determined the components in the extracted bitumen but did not definitely indicate the solvent used for the removal of the resins from fuller's earth. Katz (6) and Bowles and Booth (3) made their determination of the components on bitumen which had been separated from bituminous sand in the hot water separation plant of the Research Council of Alberta during 1930. Separation by means of hot water results in the floating of a bitumen froth containing a considerable amount of water, and since this water was evaporated at the Research Council plant in an open dehydrator (4) there would have been some loss of light oil during the dehydration. Peterson and Gishler (10) made their determination on bitumen extracted from bituminous sand obtained from Bitumount, Alberta. Table I indicates the results obtained by these investigators.

TABLE I.  
Components of Bitumen in Athabasca Bituminous Sand as Determined by  
Other Investigators

	Krieble and Seyer	Katz*	Bowles and Booth	Peterson and Gishler*
Asphaltic acids and anhydrides .....	2.0	1.9	.....	0.9
Oily constituents .....	51.5	57.3	.....	57.7
Resins .....	24.0	15.6	.....	20.3
Asphaltenes .....	22.5	25.2	20.2	21.1

\*Data recalculated to an ash-free basis.

Krieble and Seyer, and also Katz, found that Marcusson's method for the determination of asphaltic acids and anhydrides led to the formation of troublesome emulsions and hence they employed other procedures. For the determination of the asphaltenes, resins and oily constituents they employed the method of Marcusson (8,9). Petroleum ether, b.p. 35-60°C., was used to precipitate out the asphaltenes. The resins were removed from the petroleum ether extract by adsorbing them on fuller's earth. Whereas Katz used chloroform to remove the resins from the fuller's earth, Krieble and Seyer mention the use of benzene or chloroform.

For their asphaltene determination Bowles and Booth employed cold solvents as indicated by Abraham (1) and the value they obtained represented the difference in the solubility of the bitumen in cold carbon disulphide and cold petroleum ether of 35-60°C. boiling range, calculated as a percentage of the water-free and mineral matter-free bitumen. However, as Abraham points out, the density and character of the petroleum ether as well as its boiling point range are important since heavy distillates or products derived from petroleum containing unsaturated or cyclic hydrocarbons will exert a greater solvent action upon the bitumen and hence will not precipitate the asphaltenes so completely. Peterson and Gishler did not indicate which solvents they used in making their determination.

Strieter (11) proposed a revised method of determining asphaltenes in which n-pentane was used in place of petroleum ether. Because n-pentane is of nearly constant composition and is a paraffin hydrocarbon, it should precipitate the asphaltenes almost completely. For the extraction of the resins from fuller's earth, Strieter's revised method substituted ethyl ether for the carbon disulphide or benzene ordinarily used. On a given sample he had found that "extraction of the resins with carbon disulphide yielded 8.3% and with benzene 13.2%, but extraction with ethyl ether yielded 22.7%. In these cases the sums of the components of the asphalt when using carbon disulphide, benzene, and ethyl ether were 88.1%, 94.7% and 99.4% respectively."

## Experimental

### *Method of Separating Components*

For the purpose of this investigation it was considered preferable to dispense with the determination of asphaltic acids and anhydrides and to follow Strieter's procedure as regards solvents. Thirty to forty grams of the bituminous sand, depending on its bitumen content, were weighed into a 33 x 94 mm. paper Soxhlet extraction thimble and the top of the thimble was plugged with cotton. The

thimble was placed in the Soxhlet extraction apparatus, covered with n-pentane and allowed to soak overnight to permit the asphaltenes to precipitate. Extraction with n-pentane was carried on for six hours, the thimble again allowed to soak overnight and then an additional extraction for six hours was carried out. The pentane solution was transferred to a 250-ml. beaker and allowed to evaporate slowly to dryness at room temperature. The residue was then dissolved in a total volume of 25 ml. of n-pentane, and the oily constituents separated from the resins by means of fuller's earth in the manner outlined by Strieter (11), n-pentane being used to extract the oily constituents and ethyl ether to extract the resins. In every case more than one treatment with fuller's earth was required to effect a complete separation of the oily constituents from the resins and to obtain oily constituents which were amber coloured.

After the extraction of the bituminous sand with n-pentane the thimble was allowed to air-dry without being removed from the soxhlet, and then the asphaltenes were extracted in the soxhlet apparatus with benzene. Since the extraction flask was only of 250-ml. capacity it was found necessary to keep the solution boiling continuously, even in the presence of glass beads, to prevent the solution from frothing over. With all the samples a small portion of the asphaltenes, varying in amount from sample to sample, was carried into the extraction flask during the initial stage of the extraction of the bituminous sand with n-pentane, but this settled out and adhered to the bottom of the flask. Hence the same flask was used for the benzene extraction after removal of the n-pentane solution. Following the benzene extraction an extraction with carbon tetrachloride was carried out, but only a trace of material was obtained from any of the samples.

Most of the benzene was distilled from the benzene solution and the residue was transferred to a crucible, dried on the water bath and later in the oven at 105°C., and weighed. Then it was ignited at 725°C. The weight after ignition was multiplied by the factor 1.15 to correct for the loss of water of hydration and the result was subtracted from the weight of the residue to obtain the net weight of asphaltenes. The amount of mineral matter present in the extracted asphaltenes appeared to vary somewhat with the clay content of the mineral aggregate in the bituminous sand. The fact that this mineral matter came through the pores of the paper thimble would indicate that it was material approaching colloidal dimensions.

In some cases a determination was made of the "difference resins" which represent that portion of the asphaltenes soluble in ethyl ether (2). In these instances the extraction in the soxhlet apparatus with ethyl ether was made just prior to the extraction with benzene, the sum of the two extracts being the content of asphaltenes.

#### *Factor of 1.15*

Clay from a clay parting in the bituminous sand beds occurring in the neighbourhood of the Abasand Oils Ltd. plant was pulped with water, washed through a 100-mesh sieve and then dispersed in water by stirring. The portion which did not settle out in 16 hours was dried and ignited. The loss on ignition was 12.7%. To convert the ash to mineral matter would require multiplication by the factor 1.15. The clay which did not settle out in 16 hours

was considered to be similar to the mineral matter passing through the paper thimble when the asphaltenes are extracted by benzene. Hence the factor 1.15 was used in converting the ash from the asphaltenes to mineral matter. Bowles and Booth (3) arrived at the same value for this factor.

### Experimental Results and Discussion

The component analyses of the bitumen in nine bituminous sands along with the results obtained from the hot water separation of these sands are shown in Table II. This table merits study. The main difference between the analyses of the samples is variations in the proportion of asphaltenes with corresponding variations in the proportion of oily constituents. Bitumen obtained from bituminous sand at Abasand is considerably more viscous than that obtained from normal bituminous sand at Bitumount 50 miles further north, and the difference in component analyses appears to be an increase in the content of asphaltenes and resins with a corresponding decrease in the content of oily constituents. By normal bituminous sand is meant one that releases its bitumen readily during the hot water separation process yielding a bitumen froth containing less than 10% of mineral matter, dry basis.

TABLE II.  
Comparison of Various Athabasca Bituminous Sands as Regards the Components of Their Bitumen and Their Separation by Hot Water

Bituminous sand*	Components				Asphaltenes as % of asphaltenes plus resins	Bitumen recovered on separation by hot water		
	Asphaltenes, %	Resins, %	Oily constituents, %	Water content, %		Mineral matter content (dry basis), %	Yield (pure basis), %	
Bitumount 1A	20.1	25.0	54.9	44.6	39.3	8.2	76.0	
" 1B	16.0	25.6	58.4	38.5	37.7	5.8	75.4	
" 3	20.4	25.1	54.5	44.8	35.7	6.1	80.3	
" 4	16.9	26.0	57.1	39.4	37.8	4.5	76.1	
" 5	19.3	25.9	54.8	42.7	32.6	25.0	80.0	
" 6A	19.4	24.8	55.8	43.9	.....	.....	.....	
" 6B	20.3	26.2	53.5	43.7	.....	78.5	26.2	
" 6C	22.8	29.0	48.2	44.0	.....	.....	.....	
Abasand .....	23.4	29.0	47.6	44.6	27.7	6.5	77.1	

\*The numbers Bitumount 1 to 6 inclusive represent different depths in the deposit at Bitumount; the larger the number the greater the depth. Bitumount 3 to 6 inclusive came from one locality whereas Bitumount 1 was collected half a mile away. Bitumount 1B was taken from a section directly below that from which Bitumount 1A was collected. Bitumount 4 was collected directly below Bitumount 3, and Bitumount 5 directly below Bitumount 4 along the side of the old quarry. Bitumount 6A, 6B and 6C were collected at the bottom of this quarry from bituminous sand which appears to be somewhat weathered. Bitumount is 50 miles north of Abasand.

The separation of the bitumen from bituminous sand by the hot water separation process does not appear to depend on the relative amounts of the various components present in the bitumen. Bituminous sand from Abasand containing 23.4% of asphaltenes released its bitumen just as effectively as Bitumount 1B material containing 16.0% of asphaltenes.

The high content of mineral matter shown by the bitumen recovered from Bitumount 5 bituminous sand as compared to that shown by the bitumen recovered from Bitumount 3 material does not appear to depend on the relative amounts of the various components since the proportion of these components are quite similar for the two bitumens. The reasons for such variations in the cleanliness of the bitumen recovered by the hot water separation

process as well as for variations in the yield, have been reported by the authors (5).

Another interesting point shown in Table II and corroborated by the data in Tables III and IV, is the constancy of the asphaltenes when calculated as a percentage of the asphaltenes plus resins. With the slight exceptions of Bitumount 1B and 4, the percentage for the Abasand is substantially the same as for the Bitumount samples. Considering this in conjunction with the "difference resins" (Table V) and the ultimate composition (Table X) makes it appear that the bitumen throughout the extensive Athabasca bituminous sand deposit had a similar origin. Abasand and Bitumount are 50 miles apart. The bitumen at Abasand could thus be considered as differing from the bitumen at Bitumount primarily through a decrease in the proportion of oily constituents. This decrease could have happened in two ways—either through conversion of the missing oily constituents into resins and asphaltenes in such a manner as not to change the relative proportions of the resins and asphaltenes already present, or through evaporation of the missing oily constituents at some period in the history of the bitumen. Either happening, or a combination of the two, would provide the same net result.

TABLE III.  
Components of Bitumen After Subjecting Athabasca Bituminous Sand to Mild Weathering

Bituminous sand	Components			Asphaltenes as % of asphaltenes plus resins
	Asphaltenes, %	Resins, %	Oily constituents, %	
Bitumount 3*.....	20.4	24.8	54.8	45.1
" 4*.....	19.6	25.9	54.5	43.1
" 5*.....	18.8	25.2	56.0	42.7
Bitumount 6A**.....	20.2	26.0	53.8	43.7

\*Washed with tap water at room temperature and air-dried indoors for four weeks.

\*\*Air-dried indoors for three months.

Material from the supplies of Bitumount 3, 4, 5 and 6A bituminous sands were submitted to artificial weathering in the hope that analyses of the contained bitumen before and after weathering would shed some light on the question of what happens when a bituminous sand weathers. For a reason that has no bearing on the present study, Bitumount 3, 4, and 5 sands were washed in cold water before being spread out in a thin layer, indoors, to dry and thus to weather. The washing in cold water had little or no effect on the Bitumount 3 and 5 sands. But when Bitumount 4 was stirred in the cold water about 30% of its bitumen separated from the sand and adhered to the paddle. This bitumen could not be put back into the bituminous sand except as a gob so it was thrown away. The component analysis was made, subsequently, on the 70% of the bitumen that was not washed out. Table III in conjunction with Table II shows that, with the exception of Bitumount 4, the changes in the proportions of the components due to the mild weathering were small. In the case of Bitumount 4, however, the percentage of asphaltenes in the bitumen from the weathered bituminous sand is definitely up and the percentage of oily constituents is down. It is not reasonable that the weathering had any more effect on this bituminous sand than it had on the other

three sands. The only explanation, then, for the change in component analysis is that the bitumen which was washed out of Bitumount 4 was higher in oily constituents and lower in asphaltenes. This explanation would mean that Bitumount 4 was not a homogeneous bituminous sand. It was collected by taking a uniform cut across five or six feet of bituminous sand in the face of a quarry. There must have been, in this thickness, some bed impregnated with a bitumen which was somewhat higher in oily constituents and lower in asphaltenes than the bitumen in the other beds making up the section sampled. The analyses given in Table II show that there is variation in the composition of the bitumen in the bituminous sand at different elevations in the beds at Bitumount. It appeared that if the analyses had been made on bitumen from individual, and often quite thin, beds instead of on bitumen from composite samples representing five or six feet of beds, wider variations might have been revealed. At a later date 14 samples were obtained over a 30-foot elevation at the location of Bitumount 3, 4, and 5, some beds being a few inches apart and others several feet. The asphaltene content was found to vary between 14.9 and 20.5%.

TABLE IV.  
Components of the Bitumen Retained by the Tailings When a Poor Separation Occurred

	Components			Asphaltenes as % of asphaltenes plus resins
	Asphaltenes, %	Resins, %	Oily constituents, %	
Air-dried tailings from Bitumount 6B .....	26.5	32.8	40.7	44.7

Bitumount 6B was not a normal bituminous sand. It gave very poor results in the laboratory separation plant. After pulping it for 45 minutes and then washing it with hot water it gave a yield of 26% of extremely sandy bitumen froth. The rest of the bitumen was found to be coating the mineral particles in the tailings. The component analysis of the bitumen in the tailings is given in Table IV. Comparing this analysis with that of Bitumount 6B in Table II it is seen that the ratio of asphaltenes to asphaltenes plus resins is virtually the same. But the asphaltenes and resins are up and the oily constituents are down for the tailings bitumen. The oil which floated as sandy froth in the separation test must have been higher in oily constituents and lower in asphaltenes and resins. Here, apparently, is another example of a composite bituminous sand sample containing material from a bed whose bitumen content is distinctly lower in asphaltenes and higher in oily constituents.

When Bitumount 6B was pulped for three hours preparatory to separation in the laboratory plant, a yield of 90% of bitumen as froth was obtained. The long period of pulping apparently was required to cause the floating as froth of the greater part of that portion of the bitumen which, in a previous run, had stayed with the tailings after a pulping period of 45 minutes and was found to have a relatively low proportion of oily constituents. The assumption might thus be made that a long period of pulping is required to enable the bitumen with a relatively low proportion of oily constituents to separate itself sufficiently from the mineral aggregate so that it can form a bitumen froth when subjected to the hot



water separation process. However, this assumption leads nowhere. The 90% yield following three hours of pulping was not satisfactory since the recovered bitumen retained a 30% content of mineral matter. The 26% yield following 45 minutes of pulping was still less satisfactory as it had a 78.5% content of mineral matter; yet it had been deduced that it must have been bitumen with a higher content of oily constituents. On the other hand Abasand bituminous sand contains bitumen with a low content of oily constituents and it separates normally after a short period of pulping. As has been commented already, the relative proportions of the components in a bitumen appears to have little if any bearing on how the bituminous sand containing it will behave when subjected to the hot water separation process. Other factors are the important ones in determining how a bituminous sand will separate.

Other work by the authors (5) has shown that the clay content of a bituminous sand is the important factor in determining its separation behaviour. Some clay is necessary for normal separation. However, it is also responsible for the dispersal in the plant water of the bitumen which fails to appear in the froth. In one separation run on a bituminous sand whose bitumen had been analysed for percentages of components, the clay and associated bitumen in the plant water were collected. A component analysis of the bitumen content of this bitumen-clay aggregate showed that the proportion of the components was essentially the same as that in the bitumen in the bituminous sand.

TABLE V.  
Proportion of "Difference Resins" in the Bitumen of Athabasca Bituminous Sand

Bituminous sand	Difference resins as % of asphaltenes
Bitumount 1B .....	32.1
"    3 .....	33.6
"    4 .....	33.1
"    5 .....	33.8
Mildred-Ruth .....	33.4
Abasand .....	34.8
Bitumount bitumen recovered by hot water process and dehydrated .....	33.3
Bitumen seepage at Bitumount .....	32.5
Bear Oil Co.* .....	31.8
Vermilion crude oil .....	29.3
Wainwright crude oil .....	30.3

\*Sample from core of bituminous sand from a well about 75 miles south of Abasand.

In some samples the "difference resins" were determined. Table V shows that the "difference resins" are, quite uniformly, about 33% of the asphaltenes irrespective of the locations from which the bituminous sands come. The data for Vermilion and Wainwright crude oils are simply shown for comparison, and in this respect they appear not much different from the bitumen in the Athabasca bituminous sands.

#### *Association of Clay with Asphaltenes*

No mineral matter was carried through the pores of the paper thimble during the extraction of bituminous sand with n-pentane and only a trace was carried through during the extraction of "difference resins" with ethyl ether. It would thus appear that the very fine mineral matter which is carried through the pores of the paper thimble during the extraction of the asphaltenes with benzene is closely associated with the portion of the asphaltenes

which remain after removal of the "difference resins". When bitumen has been obtained from Athabasca bituminous sand by the hot water separation process with subsequent evaporation of the water and settling out of mineral matter at elevated temperature, there always remain in the bitumen varying amounts of fine mineral matter depending on the clay content of the bituminous sand. For example, bitumen which had been separated at Bitumount and dried and settled in the laboratory showed a mineral matter content of 3.2%. Of this mineral matter, 68% of it passed through a paper thimble on extraction with benzene. Since this fine mineral matter appears to be closely associated with the asphaltenes it is understandable why it does not settle out from hot bitumen.

Bowles and Booth (3) found that 4% of the mineral matter present in the bitumen they used was carried through an alundum thimble on extraction with carbon disulphide. The thimble they employed was made of alundum mixture No. RA 98 which, according to the manufacturer's specifications, retains minimum sized particles of 20 microns.

*Effect of Clay When Determining Asphaltic Acids and Anhydrides*

Preliminary work on the determination of components included the determination of asphaltic acids and anhydrides by the method outlined by Katz (6). Due to the formation of troublesome emulsions which caused difficulty and loss of time, their determination was discontinued. This preliminary work, however, had verified the findings of the investigators shown in Table I, that the proportion of asphaltic acids and anhydrides contained by the bitumen in Athabasca bituminous sand was about two per cent. The amount of emulsion appeared to vary somewhat with the clay content of the bituminous sand, being considerable with Bitumount 3 whose mineral aggregate contained 7.5% passing 200-mesh of which a considerable proportion was clay.

Fine clay appeared in the extract when the extraction of bitumen from bituminous sand with benzene was carried out either in a paper thimble or in a Gooch crucible. It seemed likely that the fine clay was responsible for the formation of troublesome emulsions after saponification. Consequently samples of three bituminous sands were extracted from a paper thimble in a Soxhlet apparatus with acetone. This solvent tended to leave behind in the thimble the asphaltenes and the fine clay associated with the asphaltenes. On removal of the acetone, benzene was added to the extract and saponification with alcoholic potassium hydroxide was carried out. After pouring into 40% ethyl alcohol a negligible quantity of emulsion was formed during the subsequent separation and washing of the two layers.

TABLE VI.  
Proportion of Asphaltic Acids and Anhydrides in the Bitumen of Athabasca Bituminous Sand

Bituminous sand	Bitumen extracted with benzene		Bitumen extracted with acetone	
	Asphaltic acids and anhydrides as % of bitumen	Dry weight of emulsion, grams	Asphaltic acids and anhydrides as % of bitumen	Dry weight of emulsion, grams
Bitumount 3 .....	1.6	0.055	1.8	0.001
" 4 .....	1.8	0.024	2.0	0.001
" 5 .....	1.9	0.016	1.8	0.001

Table VI contains a comparison of the results obtained when the asphaltic acids and anhydrides are determined by the two methods. Variations in the proportion of this component in the bitumen of these bituminous sands are of a small order. The negligible formation of emulsion when the bituminous sand is extracted with acetone is noteworthy.

#### *Migration of Bitumen During Storage of Bituminous Sand*

On storing samples of bituminous sand in quart sealers at room temperature for about six months or more, visual examination indicated that in some of the samples a portion of the bitumen had migrated towards the bottom. Table VII indicates the variation in the bitumen content of the upper and lower portions of representative samples after such a storage period.

TABLE VII.  
Migration of Bitumen During Storage of Bituminous Sand

Bituminous sand	Original bitumen content, %	Upper half of sealer after storage		Lower quarter of sealer after storage	
		Bitumen content, %	Asphaltene content of bitumen, %	Bitumen content, %	Asphaltene content of bitumen, %
Bitumount .....	16.7	13.5	14.9	19.1	15.4
" .....	11.8	8.9	15.3	15.9	15.6
" .....	11.2*	10.7	.....	11.6	.....
" .....	13.0	12.0	17.5	17.0	16.8
" .....	16.2	13.3	19.9	19.0	17.9
Ells River .....	11.3	11.4	16.0	11.2	15.9
Abasand .....	15.6	15.5	23.9	15.6	23.6

\*Asphaltene content of bitumen 16.9%.

In a number of the Bitumount samples a distinct migration downwards of a portion of the bitumen took place. In some of these cases the migrating bitumen appeared to have a lower asphaltene content since the asphaltene content of the bitumen in the lower quarter of the sealer was distinctly lower than that in the upper half of the sealer. In other cases the asphaltene content of the bitumen appeared to have been uniform within the limits of experimental error. A necessary requirement for migration of the bitumen is not necessarily a low asphaltene content since the bitumen in Ells River bituminous sand showed no migration; however, the mineral aggregate of the latter consists of a relatively large proportion of fines which apparently exerts a restraining influence on migration. The non-migration of bitumen in Abasand bituminous sand is probably due to its relatively high asphaltene content which makes its bitumen considerably more viscous than that from Bitumount. It should be emphasized, however, that not all the samples from Bitumount showed migration.

#### *Uniformity of Asphaltenes*

It has been mentioned previously that during the extraction of the bituminous sand with n-pentane a small portion of the asphaltenes, varying in amount from sample to sample, was carried into the extraction flask during the initial stage of the extraction. This portion of the asphaltenes contained about 75 to 84% of "difference resins" whereas the overall content of "difference resins" in the total asphaltenes is about 33%. Similarly, in those instances in which the "difference resins" were determined by subsequent extraction with ethyl ether a relatively small proportion of the

asphaltenes (exclusive of "difference resins"), varying in amount from sample to sample, was carried into the extraction flask. This portion of the asphaltenes contained about 81 to 95% of "difference resins". Table VIII shows some representative results.

TABLE VIII.  
Proportion of "Difference Resins" in the Asphaltenes Removed During the N-Pentane and Ethyl Ether Extractions

Bituminous sand	Total asphaltene content of bitumen, %	Content of "difference resins" in the asphaltenes removed during n-pentane extraction, %	Content of "difference resins" in the asphaltenes removed during ethyl ether extraction, %	Content of "difference resins" in the asphaltenes removed by both the n-pentane and ethyl ether extractions, %	Asphaltenes (exclusive of "difference resins") removed by both the n-pentane and ethyl ether extractions as % of asphaltene content of bitumen exclusive of "difference resins"
Bitumount .....	16.1	75	81	79	10.5
" .....	16.8	...	...	83	5.5
" .....	19.3	84	95	94	9.9
" .....	19.9	...	...	96	9.0
Ells River .....	16.0	...	...	83	3.3
Mildred-Ruth .....	17.2	...	...	86	3.1
Abasand .....	23.6	...	...	96	5.5
Bitumount bitumen recovered by hot water process and dehydrated* .....	18.2	...	...	88	6.9
Bitumen seepage at Bitumount† .....	16.0	...	...	86	3.0
Vermilion crude oil .....	10.7	...	...	81	9.7
Wainwright crude oil‡ .....	11.0	...	...	89	5.2

\*During the dehydration 3% of light ends were removed.

†The gasoline and kerosene fractions amounting to 21% by weight of the original dry crude oil had been previously removed.

‡The bitumen seepage at the foot of the 60-foot river bank contained only 0.9% water and 1.2% mineral matter.

NOTE: The Mildred-Ruth lakes area and Ells River are, respectively, 20 and 40 miles north of Abasand.

It is apparent that, generally speaking, the higher the total asphaltene content of the bitumen the lesser the tendency for the asphaltenes (exclusive of the "difference resins") to be carried into the extraction flask by the ethyl ether, and the same feature was noted for the asphaltenes (including the "difference resins") during the n-pentane extraction. It would appear that the oily constituents and resins extracted by the n-pentane, and the "difference resins" extracted by the ethyl ether, exert a solvent action on a portion of the asphaltenes during the early stages of the soxhlet extraction while the concentration of extract inside the thimble is still relatively high. In the extraction flask, where there is a greater dilution of the extract, these asphaltenes are precipitated out. Judging by the content of "difference resins" the portion of the asphaltenes removed during the n-pentane extraction appears definitely different from the remaining portion. It is altogether likely that the portion of the asphaltenes removed during the ethyl ether extraction is also somewhat different from the remaining portion. In both instances a part of the apparent difference may be due to the solvent action exerted by the extracted material on the remaining material during the early stages of the soxhlet extraction. For example, during the extraction with n-pentane the oily constituents and resins would have, presumably, a greater solvent action on the "difference resins" than on the balance of the asphaltenes, thus

increasing the content of "difference resins" in the asphaltenes which show up in the n-pentane extract.

#### *Aging of Bituminous Sand During Storage*

When the 14 samples were collected at the location of Bitumount 3, 4 and 5 a portion of each sample was stirred with water at 75°F. With some samples little or no bitumen separated from the sand while with other samples there was almost complete separation. The amount of separation appeared to depend to some extent on the bitumen content of the bituminous sand and on the nature of the mineral aggregate. Sample 6 showed almost complete separation, a small portion of the bitumen floating while the balance lay as a coagulated mass on top of clean gray sand. Table IX compares the components of the bitumen which floated in sample 6 to the components of the bitumen in the entire sample. The portion of the bitumen which floated had a somewhat lower asphaltene content, but there was no appreciable variation in the content of "difference resins".

TABLE IX.  
Components of Bitumen Which Floated at 75°F. as Compared to Components in Entire Sample

Sample	Components		Difference resins as % of asphaltenes
	Asphaltenes, %	Resins plus oily constituents, %	
Bitumen which floated .....	16.9	83.1	33.1
Bitumen in entire sample .....	18.5	81.5	33.7

A portion of sample 6 had been placed in a bottle when collected and wet-proof tape placed around the screw cap. After storing in the dark at room temperature for nine months there was not the slightest sign of bitumen separation when stirred with water at 75°F. The storage at room temperature (about 75°F) had caused the bitumen to become firmly attached to the mineral aggregate. This had not occurred in the bituminous sand deposit where the formation temperature may be as low as 36°F (5). The latter publication by the authors also described the effect of storage on the hot water separation process.

#### *Ultimate Composition of Bitumen and B.t.u. Value*

There does not appear to be any appreciable difference in the ultimate composition and the B.t.u. value of the bitumen throughout the Athabasca bituminous sand area. This tends to substantiate the deduction that this bitumen had a similar origin. Table X contains the analyses.

#### *Viscosity of Bitumen versus Components and Ultimate Composition*

It has been indicated previously that the bitumen throughout the Athabasca bituminous sand area appears to show no appreciable variation as regards their ultimate composition and the "difference resins" content of their asphaltenes. Furthermore, with slight exceptions, the ratio of asphaltenes to asphaltenes plus resins appears reasonably constant. Hence the relatively viscous bitumen at Abasand could be considered as differing from the more fluid bitumen at Bitumount primarily through a decrease in the relative proportions of the oily constituents.

TABLE X.  
Ultimate Composition of Bitumen and B.t.u. Value

Bituminous sand	Bitu- mount	Ells River	Mildred- Ruth	Abasand (3)	Bear Oil Co.*
Ultimate Composition:					
Carbon .....	83.3	83.3	83.3	83.3	83.4
Hydrogen .....	10.4	10.4	10.4	10.4	10.4
Sulphur .....	4.6	4.6	4.5	5.1	4.7
Nitrogen .....	0.4	0.4	0.5	0.4	0.6
Oxygen, etc. (by difference)%	1.3	1.3	1.3	0.8	0.9
	100.0	100.0	100.0	100.0	100.0
Carbon/Hydrogen Ratio .....	8.0	8.0	8.0	8.0	8.0
Calorific Value, gross B.t.u. per lb.	17,900	17,700	17,800	.....	17,850

(3) See Bowles, K. W., and Booth, F. L. Bureau of Mines, Ottawa. F.R.L. Report No. 76. 1947.

\*Sample from core of bituminous sand from a well about 75 miles south of Abasand.

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