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Experiments Concerning the Thickening Process of Benzol Wash Oil

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During the carbonization process the coal is decomposed into coke, gas, tar, ammonia and light oil. By cooling the gas the tar is condensed and recovered as a dark brown or black liquid. Due to their vapor pressure recoverable hydrocarbons remain still in the gas, called benzene or light oil. Besides many other hydrocarbons the chief components of the light oil are benzene, toluene and xylenes. The light oil is a very valuable by-product of coal carbonization because it serves as raw material for chemical processes as well as a high octane fuel for Otto engines. There are three methods which are employed to recover the light oil from the gas:

- a) cooling to such low temperatures that the gaseous hydrocarbons are liquefied.
- b) absorbing the hydrocarbons by a solid (activated char coal, silica gel)
- c) absorbing the hydrocarbons by a liquid menstruum (wash oil)

Most of the light oil is recovered by the traditional liquid-absorbent system. In Europe, creosote oil which is prepared by the simple distillation of coal tar is almost entirely used for the absorption of the light oil, whereas in the United States petroleum oils (gas oil, straw oil, spindle oil) serve as the absorbing menstruum.

Both types of oil have their advantages and disadvantages. Creosote oils have a higher absorbent capacity than petroleum oils. However, during practical operation the viscosity of creosote oil increases quickly, whereas the petroleum oil maintains a more uniform viscosity. Basically, the formation of asphaltic material is responsible for an increase of the viscosity. Asphaltic substances are always formed when coal gas is stripped from light oil, however the difference lies in the fact, that the asphaltic substances are soluble in

creosote oil, thus increasing its viscosity, whereas the asphalt is insoluble in petroleum oils being deposited on heated surfaces unless precautions are taken to withdraw continuously the asphaltic substances from the oil. However, the asphalts either recovered from the creosote oil or deposited from the petroleum oil have similar properties in so far that they contain appreciable amounts of sulfur. The following article contains the results of some experiments, which were carried out by the author and one of his assistants in order to investigate the thickening process of creosote oil. The conclusions, drawn from the experiments, can be applied to the asphalt formation of petroleum oils too. Since the asphaltic substances contain high amounts of sulfur the experiments were restricted to the influence of sulfur or its compounds on the formation of asphalt. Another reason to make the experiments was to show that the asphalt formation can be retarded by a careful operation of the plant.

A creosote oil used for absorbing light oil from coal gas, during the course of the operation becomes more viscous and its content of asphaltic substances increases. The increase of the viscosity is not solely due to chemical reactions, the change of its boiling analysis is responsible as well. The lower boiling constituents of the wash oil as well as the naphthalene are vaporized, when the enriched wash oil is stripped from the light oil, thus increasing the viscosity of the recirculating oil. However, besides this physical influence, chemical reactions between constituents of the coal gas and those of the oil take place. The thickening of the oil is followed by an unsatisfactory distribution of the oil in the scrubber and the simultaneously increasing molecular weight requires a larger volume of the oil to be recirculated in order to maintain an effective extraction. In addition, practice has shown, that the proper debenzolization of the enriched oil becomes more difficult with an increasing thickening of the oil which in turn influences unfavorably the absorption of the light oil from the gas. In order to secure a uniform

quality of the wash oil, part of the spent oil must be discharged and replaced by fresh oil. Some plants are equipped with a wash oil regeneration system which removes the asphaltic substances from the wash oil by distillation. The wash oil consumption varies between 8 - 14% of the recovered light oil.

The following experiments were carried out using a spent and a fresh creosote wash oil.

The properties of the two oil-samples were as follows:

	fresh oil	spent oil
density 20°C	1.051	1.110
viscosity 20°C	1.39°E	7.92°E
Asphaltic substances %	0.0	25.3
Sulfur %	0.77	2.00
Ash (Fe ₂ O ₃) %	0.0014	0.0024
boiling analysis		
boiling point °C	242	240
250°C % vol.	14.0	1.5
260°C "	42.5	7.0
270°C "	63.5	25.0
280°C "	79.0	47.0
290°C "	87.0	61.5
300°C "	92.0	68.5
310°C "	94.0	72.0
320°C "	96.5	75.0

The table shows very instructively the changes to which a creosote wash oil is subjected during the operation. The asphalt content of the spent oil is much higher than that of the fresh one, sulfur has been absorbed by the oil, the viscosity is increased and the lower boiling constituents of the oil have disappeared.

Since the asphalt of the oil had so considerably increased, the influence of the removal of the asphalt on the properties of the oil was investigated.

The spent oil was dissolved in benzene and the asphalt was precipitated by ample addition of benzine and separated from the solution by filtration.

The benzine - benzene mixture was vaporized and the recovered oil was investigated. The following table represents the results of the analysis.

density	20°C	1.064
viscosity	20°C	1.51° E
asphalt	%	0.0
sulfur	%	0.94

boiling analysis

boiling point		250°C
260°C	% vol.	11.0
270°C	"	37.0
280°C	"	60.0
290°C	"	75.0
300°C	"	84.0
310°C	"	88.5
320°C	"	92.0
330°C	"	95.0

The refreshed oil is very similar to the fresh oil. However less low boiling oils are present because the low boiling oils, which were vaporized during the operation, cannot be restored by removing the asphalt.

Almost all of the sulfur which had been adsorbed by the wash oil is now present in the asphaltic substances as shown by the following sulfur balance.

Sulfur content of the products involved:

1. spent wash oil 2.00 % S
2. asphaltic substances 5.10 % S
3. refreshed wash oil 0.94 % S
4. fresh wash oil 0.77 % S

Sulfur balance:

Input:	g S	%
100 g spent wash oil with 2% sulfur	2.00	100.0
Recovered:		
25.3 g asphalt with 5.10% S	1.29	64.5
74.7 " refreshed oil with 0.94% S	0.70	35.0
total sulfur recovered	1.99	99.5

The asphaltic substances contain about $\frac{2}{3}$ of the total sulfur content of the spent oil. They contain almost the total sulfur which has been absorbed by the recirculating wash oil. The distribution of the sulfur between oil and asphalt indicates that sulfur is more or less responsible for the formation of the asphaltic substances.

The separation of the benzol soluble substances from the benzol insoluble ones showed equal sulfur content of the two classes of asphalt.

It was now tried to reproduce the thickening of the wash oil in the laboratory, i. e. to produce asphaltic substances in a fresh oil.

It is known that creosote oils contain constituents (mono - and polyhydric phenols) which easily will absorb oxygen, whereby high molecular compounds are formed. Hydrogen sulfide is likewise easily oxydized to sulfur and water by means of oxygen. The elementary sulfur is an active polymerizing agent. Both ingredients, oxygen as well as hydrogen sulfide are always present in coal gas. The thickening of the wash oil will be slow at normal temperatures as well as due to the low partial pressure of the reacting gaseous agents. In order to

speed up the polymerization the tests were carried out at elevated temperature (120°C) and with almost pure polymerizing agents.

Test run 1

At first the influence of oxygen at elevated and normal temperature was investigated. Oil samples of about 1/2 liter were heated in an oil bath to the desired temperature. One sample was treated with inert nitrogen in order to investigate the influence of the heating procedure. Another sample was treated with oxygen and the third one with oxygen too, but with the difference that iron filings were added which were supposed to act as a catalyst. The velocity of the gas travelling through the oil was so low, that practically no vaporization of the oil took place.

The change of viscosity, the density and the asphalt content indicated the effect of the respective treatment.

The composition of the original oil was as follows:

viscosity 20°C : 1.39°E

density 20°C : 1.051

asphalt content: 0,0%

Color and appearance: bright, dark, greenish-yellow, without deposits.

The results are represented by table a).

Table a) Reaction-Temperature 120°C

Kind of treatment	after hours of exposure	12	24	36	48	60	72	84
Nitrogen	viscosity °E	1,39	1,39	1,39	1,39	1,39	1,40	1,40
	density	1,051	1,051	1,051	1,051	1,051	1,051	1,052
	asphalt %	0,31	0,37	0,39	0,35	0,38	0,45	0,51
Oxygen	viscosity °E	1,43	1,46	1,50	1,55	1,58	1,64	1,67
	density	1,055	1,058	1,061	1,064	1,066	1,068	1,071
	asphalt %	2,65	4,79	6,21	6,45	6,60	7,51	9,06
Oxygen + iron filings	viscosity °E	1,43	1,46	1,50	1,55	1,57	1,61	1,64
	density	1,055	1,058	1,061	1,064	1,066	1,068	1,070
	asphalt %	2,53	5,11	5,62	5,85	5,86	7,42	8,48

The represented figures indicate that at an elevated temperature (120°C) almost no change in the properties of the oil results, although the asphalt content is slightly increased. The appearance of the oil did not change either. However, oxygen attacks the oil after a short period of time. The asphalt content increases very rapidly whereby viscosity and density are slightly raised. In addition some asphalt was deposited on the walls of the reaction vessel which is not included in the represented analytical figures. Considering those deposits, the actual asphalt content of the treated oil would be 2 - 3% higher. The addition of iron filings did not speed up the asphalt formation which indicates that the steel tubes or cast iron bubble caps of the heat exchangers and stripping column have no deleterious effect on the quality of the wash oil.

Since wash oil and gas are brought to an intimate contact during their passage through the scrubber at normal temperatures of about $20 - 25^{\circ}\text{C}$, the influence of oxygen on the asphalt formation at room temperature was therefore investigated. The result of the experiments is represented by table b).

- Table b) Reaction Temperature $20 - 25^{\circ}\text{C}$

Kind of treatment	after hours of exposure	24	48	72	96	120	144
Oxygen	viscosity $^{\circ}\text{E}$	1.35	1.37	1.38	1.38	1.38	1.38
	density	1.052	1.052	1.051	1.052	1.054	1.058
	asphalt %	0.05	0.12	0.18	0.21	0.52	0.62

The experiments indicate that even at normal temperature oxygen produces asphaltic substances in the wash oil.

The asphalt content of the spent wash oil was as high as 25.3%, while the regenerated oil was free from asphalt. It had now to be investigated whether a repeated treatment of the asphalt free oil with oxygen would form again

asphaltic substances. For that reason the regenerated wash oil was treated with oxygen at 120° C.

Properties of the regenerated oil.

Viscosity at 20° C = 1.51^oE

density at 20° C = 1.064

asphalt content = 0.0%

Table c) represents the results of the experiment.

Table c) Reaction temperature 120° C

Kind of treatment	after hours of exposure						
		24	48	72	96	120	144
Oxygen	viscosity ^o E	1.57	1.62	1.67	1.69	1.72	1.76
	density	1.065	1.070	1.075	1.075	1.076	1.078
	asphalt %	2.48	5.52	5.78	6.32	7.10	7.53

The obtained results indicate that a refreshed oil is again able to form asphaltic substances if subjected to a repeated treatment with oxygen. Although the asphalt formation is not as rapid as before, the wash oil still contains substances which are thickened under the influence of oxygen.

The results of the tests show that oxygen at elevated and normal temperatures is responsible for the formation of asphalt, which increases the viscosity and the density of the wash oil.

Since it is well known that elementary sulfur sometimes exercises polymerizing effects and that hydrogen sulfide which is always present in the coal gas is easily oxidized to elementary sulfur, the simultaneous effect of elementary sulfur was admixed to the oil and the oxygen treatment was repeated. The results of the experiments are represented by the attached diagram No. 1.

Properties of the employed wash oil

Viscosity at 20°C = 1.39°E

Density 1.051

Asphalt content 0.0%

Temperature 120°C

Kind of treatment	after hours of exposure								
		12	24	36	48	60	72	84	
Nitrogen + 1% sulfur	visc. °E	1.40	1.40	1.40	1.40	1.42	1.41	1.42	
	density	1.057	1.057	1.057	1.057	1.057	1.058	1.059	
	asphalt %	0.54	0.66	0.77	0.84	0.87	0.83	1.02	
Oxygen + 1% sulfur	visc. °E	1.46	1.51	1.60	1.60	1.61	1.62	1.63	
	density	1.062	1.066	1.070	1.070	1.071	1.072	1.073	
	asphalt %	3.76	5.20	7.10	8.00	8.30	8.00	9.08	
Oxygen + 1% sulfur + Fe filings	visc. °E	1.44	1.51	1.57	1.60	1.62	1.64	1.65	
	density	1.062	1.067	1.069	1.070	1.071	1.073	1.077	
	asphalt %	3.87	6.78	8.05	8.12	8.58	8.64	9.48	

Comparing the figures with those of test run No. 1 it is evident that no fundamental difference of the asphalt formation was observed when 1% elementary sulfur was admixed to the oil. Although the asphalt content of the nitrogen treated sample is somewhat higher, the difference is not so large as to indicate an important influence of the admixed elementary sulfur. The same conclusions may be drawn from the oxygen treatment without or with an additional admixture of iron filings, although the asphalt formation is a little faster in the beginning of the experiments than before.

Diagram No. II represents the results of the experiments and shows very instructively that elementary sulfur exercises only a slight influence on the formation of asphalt.

The coke oven gas which is passed through the benzol scrubbers contains besides small amounts of oxygen, more or less hydrogen sulfido. Gas analyses

drawn before and after the benzol scrubbers, indicate that the wash oil absorbs oxygen as well as hydrogen sulfide. Since the preceding experiments illustrate the influence of the oxygen on the asphalt formation it is now necessary to investigate the effect of hydrogen sulfide alone or in combination with oxygen.

Test run 3: Influence of hydrogen sulfide without or in combination with oxygen on the formation of asphalt.

Properties of the employed oil:

Viscosity at 20°C = 1.39°E

Density " " = 1.051

Asphalt content 0.0%

a) The oil was treated with pure hydrogen sulfide for 120 hours applying a temperature of 120°C.

The treated oil had

a viscosity of 1.43°E

an asphalt content of 0.90%

Hydrogen sulfide has only a very slight tendency to form asphalt, which is almost equal to the influence of nitrogen in the presence of a small percentage of elementary sulfur.

b) The following table represents the influence of hydrogen sulfide in combination with oxygen on the asphalt formation at temperatures of either 120°C or 20 - 25°C.

Kind of treatment	after hours of exposure	hours of exposure					
		24	48	72	96	120	144
Oxygen + hydrogen sulfide at 120°C	visc. °E	1.47	1.52	1.56	1.60	1.63	1.64
	density	1.059	1.064	1.069	1.072	1.076	1.076
	asphalt %	4.36	6.10	7.84	8.00	8.34	8.80
Oxygen + hydrogen sulfide at 20 - 25°C	visc. °E	1.40	1.41	1.43	1.45	1.45	1.46
	density	1.049	1.056	1.065	1.071	1.073	1.074
	asphalt. %	0.07	0.25	1.76	1.88	2.14	2.46

After a short time a visible change of the oil took place; the color changed from greenish--yellow to brown and black and a pitch like deposit was formed at the walls of the glass vessel. Since it was impossible to determine exactly those deposits the actual asphalt content of the oil is supposed to be a little higher than listed. When applying a reaction temperature of 120°C . the increase of the asphalt content is similar to that when the oil was treated with oxygen. However, there is a great difference when the oil was treated at normal temperatures. After a treating time of 72 hours the asphalt content of the oil was 4 - 5 times as high as when oxygen alone was employed. Since gaseous hydrogen sulfide had almost no effect the conclusion can be drawn that the sulfur in statu nascendi originating from the reaction of hydrogen sulfide with oxygen is responsible for the rapid asphalt formation.

The results of the experiments are represented by diagram No. III. A comparison of the curves Nos. 3 and 4 shows very instructively the influence of the combined oxygen - hydrogen sulfide treatment on the asphalt formation in wash oil.

The preceding experiments show the effect of oxygen and/or hydrogen sulfide on the asphalt formation of creosote oil whereby temperatures of either 120°C . or $20 - 25^{\circ}\text{C}$ were applied. As may be expected a more rapid asphalt formation takes place at higher temperatures.

However, during practical operation of a light oil recovery system the absorption of the light oil vapors is carried out at temperatures of $20 - 25^{\circ}\text{C}$ whereas the enriched oil during its passage through the following stripping system is heated to $150 - 200^{\circ}\text{C}$. Especially when led through the heat exchangers, the oil is slowly heated, whereby the absorbed oxygen and hydrogen sulfide is expelled. It was therefore necessary to try to reproduce the commercial operation by laboratory tests.

The oil was subjected to a treatment with oxygen and hydrogen sulfide for approximately 30 minutes and subsequently heated to 200°C for a short period of time, using a reflux condenser. After every three completed cycles a sample was drawn and tested as before.

Properties of the applied wash oil

Viscosity at 20°	1.39 E
Density at 20°	1.051
Asphalt content	0.0%

The following table contains the results of the experiments.

Oil x times processed	3	6	9	12	15	18	21	24
Viscosity° E						1.68	1.72	1.75
Density	1.052	1.052	1.055	1.057	1.059	1.062	1.067	1.074
Asphalt %	0.20	0.46	0.67	1.04	1.90	2.62	4.06	5.10

The obtained figures show that the asphalt content rises very quickly under a combined cold - warm treatment with oxygen and hydrogen sulfide.

Diagram No. IV represents the results of the experiment.

It is evident that the highly reactive constituents which are present in the wash oil are responsible for the formation of asphaltic substances. Removing such type of substances by a treatment with sulfuric acid and caustic should effect a decreasing asphalt formation.

The fresh wash oil was twice treated with 1% concentrated sulfuric acid 5 - 15°C and at 15 - 25°C respectively and neutralized by means of 20% caustic soda.

The results of the refining process were as follows:

	ccm	%
Employed losses due to acid treatment	600	100.0
losses due to caustic soda treatment	85	14.2
yield of refined oil	9	1.5
	506	84.3

Properties of the refined oil:

viscosity at 20°C	1.32 E
density at 20°C	1.046
asphalt	0.0%

Boiling analysis:

Boiling point	244°C
250°C	10.0 % vol.
260 "	40.0 "
270 "	61.0 "
280 "	77.0 "
290 "	87.0 "
300 "	91.0 "
310 "	94.0 "
320 "	96.0 "

Test run 5

The refined oil was treated with oxygen at 120°C. The results of the experiments are represented by the following table.

Kind of treatment	after hours of exposure							
		24	48	72	96	120	144	
Oxygen at 120°C	visc. E	1.34	1.33	1.35	1.36	1.37	1.37	
	density	1.051	1.048	1.053	1.051	1.051	1.052	
	asphalt %	0.21	0.87	1.25	1.54	1.90	2.56	

The asphalt formation has been greatly reduced. While the original oil after twenty hours of exposure contained already 4.79% asphalt, the refined oil contains but 0.21% after an equal period of exposure; after 72 hours the respective figures are 7.51 and 1.25%. Refining a creosote wash oil by means of acid and caustic will greatly extend the useful life of the oil. Diagram No. V represents the results of the experiment, whereas diagram No. VI compares the asphalt formation of the refined oil with that of the crude one.

Summary and conclusions.

Analytical determinations showed that a spent creosote wash oil contains more sulfur than a fresh one. Almost all of the absorbed sulfur is present in the asphaltic substances of the spent oil. Numerous experiments were carried out in order to investigate the thickening process of the creosote wash oil. Oxygen effects a strong asphalt formation, whereas hydrogen sulfide results in a slowly increase of the asphalt content. The formation of asphalt is accelerated by a combined attack of oxygen and hydrogen sulfide. Reactive and unsaturated compounds of the creosote oil are responsible for the thickening process. The useful life of a creosote oil can be extended by removing its reactive compounds by means of acid and caustic. Due to the mostly inevitable presence of hydrogen sulfide in coal gas, the oxygen content of the gas should be kept at a minimum. Should a dry box desulfurization system be installed prior to the light oil recovery system the necessary oxygen admixture to the gas must be carefully supervised in order to maintain the lowest oxygen concentration possible in the gas. The utilization of a wet sulfur extracting system which does not need any admixture of oxygen is preferable. Modern coke oven plants extract sometimes the light oil from the compressed coal gas which has been partly liberated from hydrogen sulfide prior to the light oil extraction. If such a procedure is used the oxygen

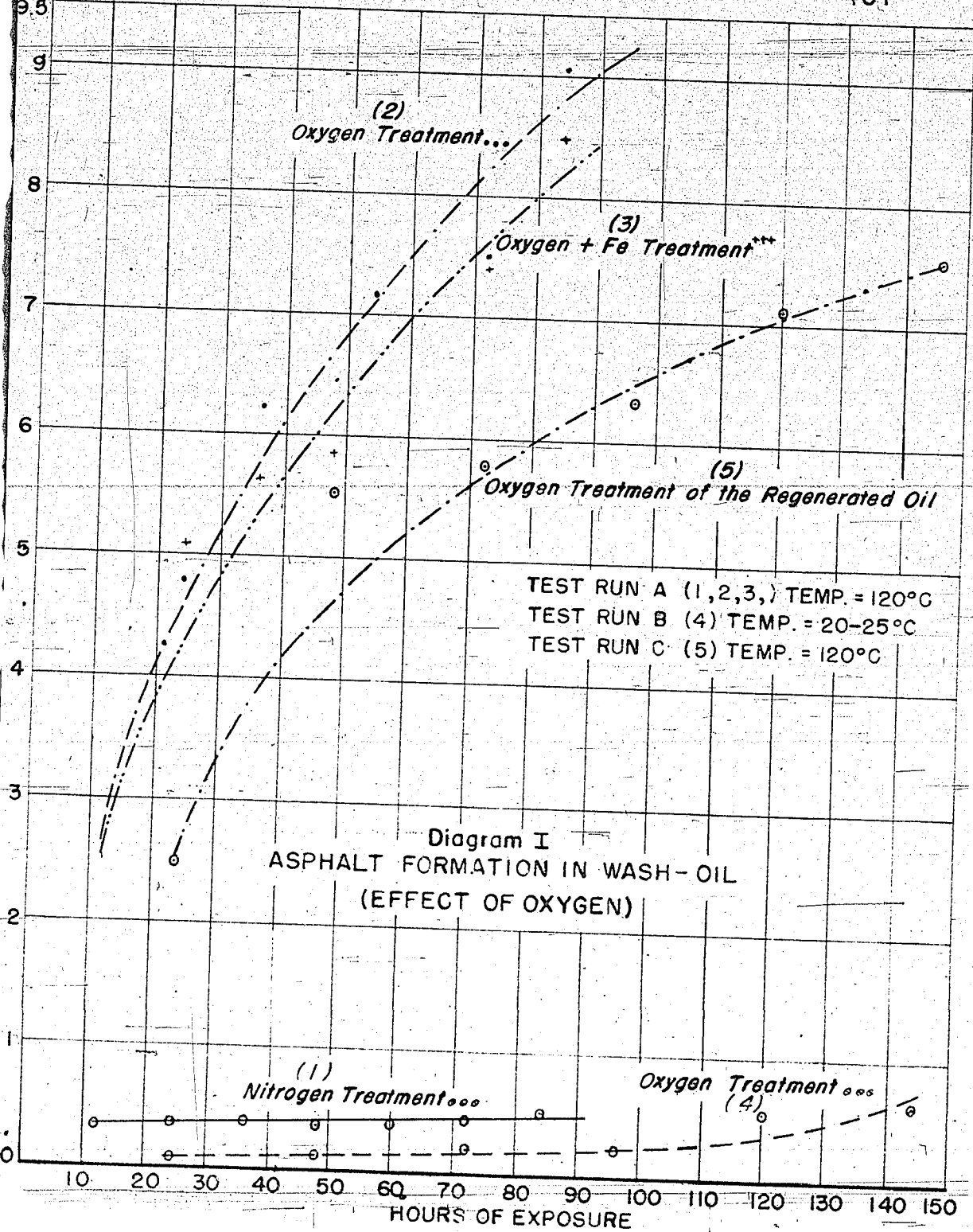
admixture should be very carefully controlled since with an increasing pressure of the gas the partial pressure of the excessive oxygen is raised too, hence increasing the probability of an accelerated formation of asphaltic substances. It should be pointed out that besides oxygen and hydrogen sulfide still other components of the gas are able to form asphaltic substances, however analyses of the asphaltic material indicate that hydrogen sulfide in combination with oxygen is one of the main sources of the formation of asphalt.

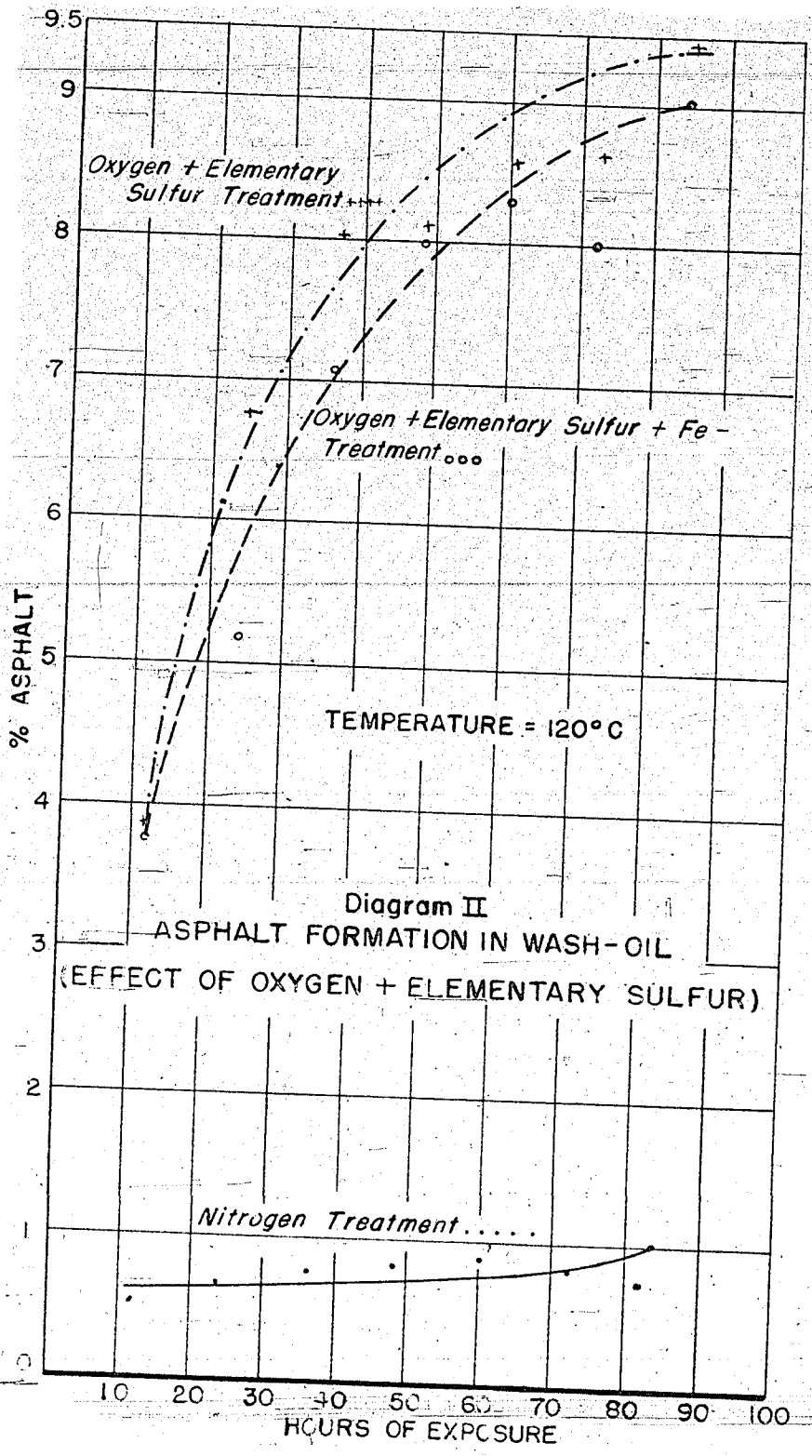
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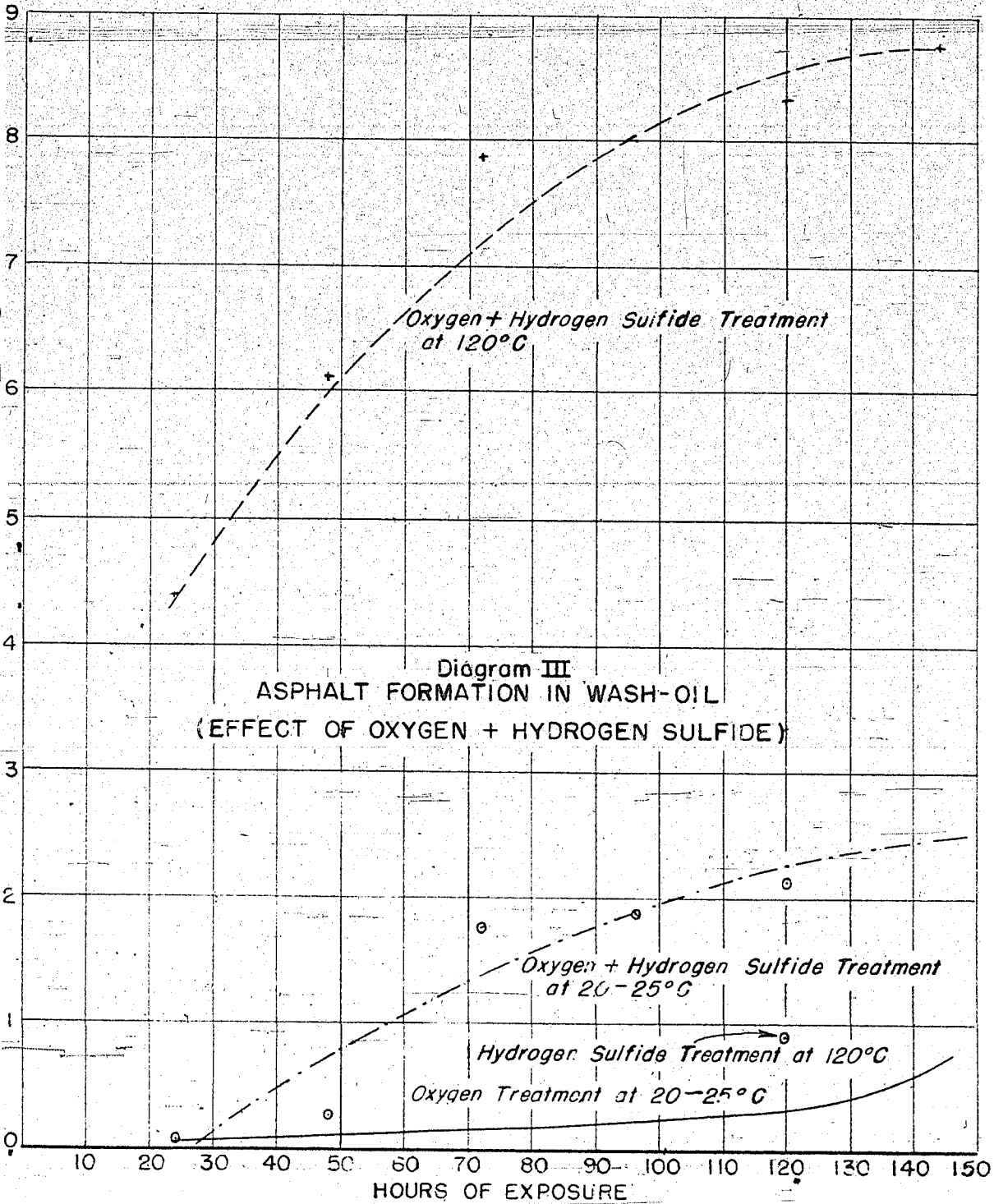
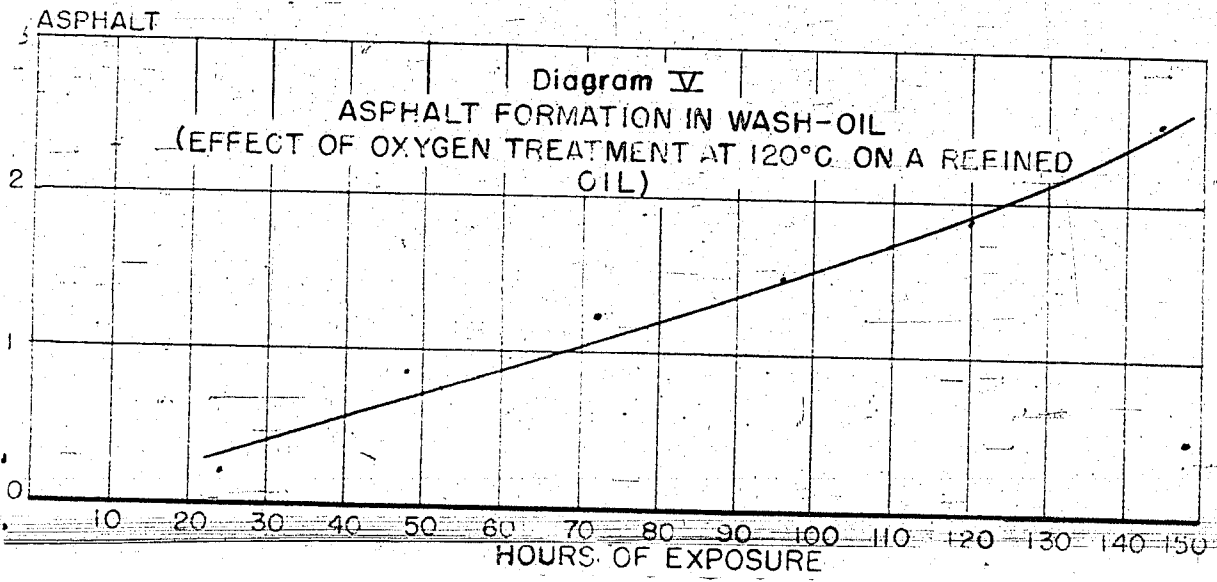
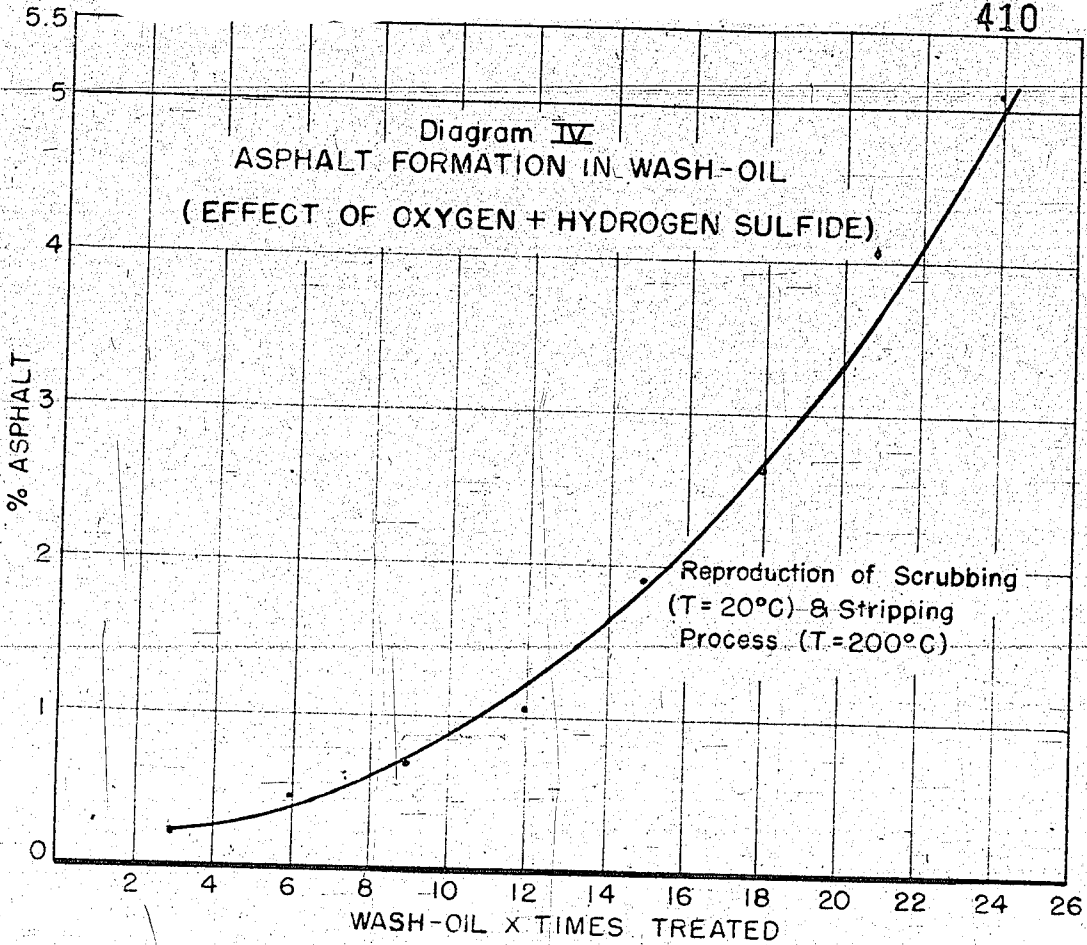


Diagram III
ASPHALT FORMATION IN WASH-OIL
(EFFECT OF OXYGEN + HYDROGEN SULFIDE)



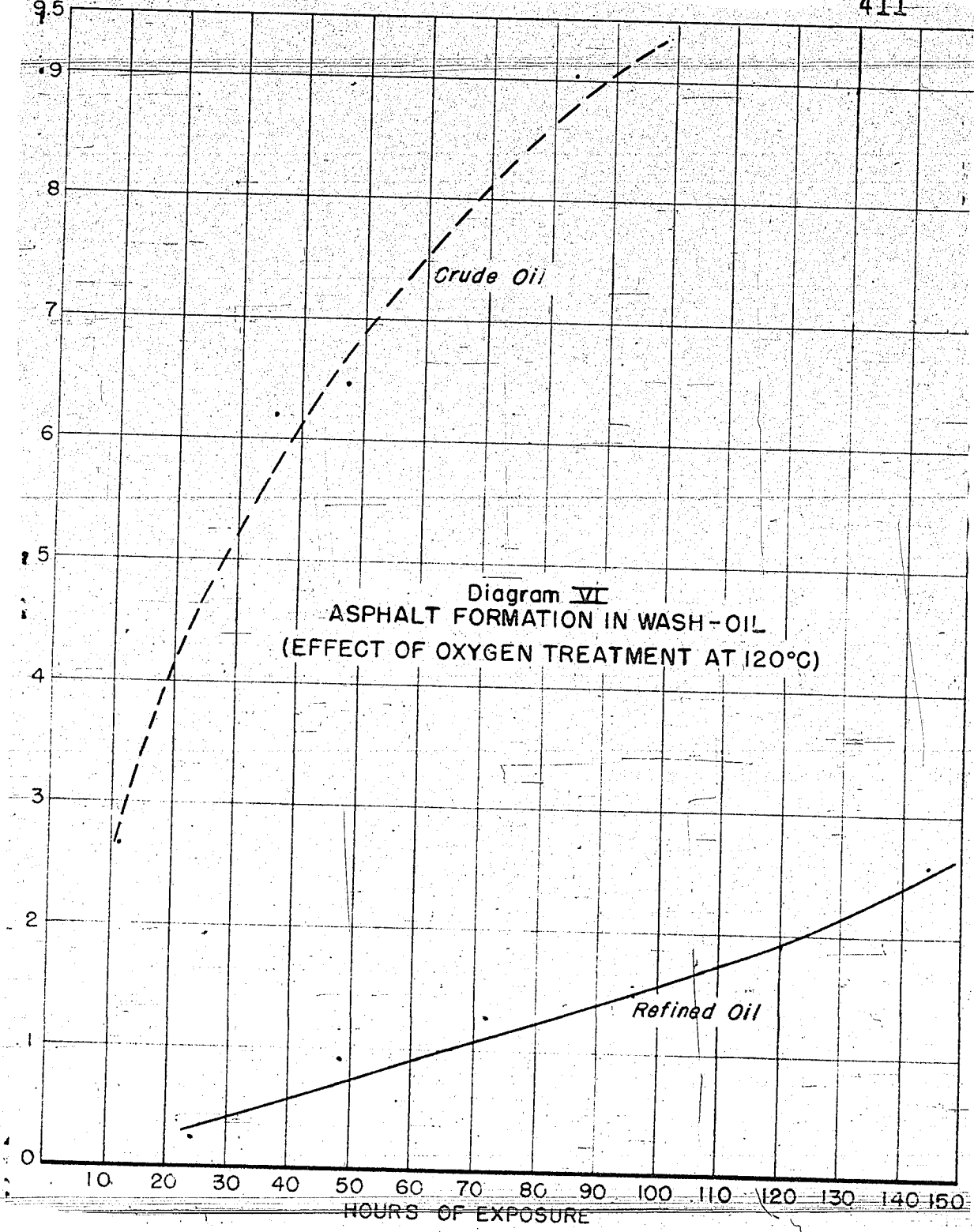


Diagram VI
ASPHALT FORMATION IN WASH-OIL
(EFFECT OF OXYGEN TREATMENT AT 120°C)

Crude Oil

Refined Oil

HOURS OF EXPOSURE