(D)

Experiments on the Mutual Solubilities of Tar Oils

By

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The tar oils from the distillation of hard coal tars (middle, heavy and anthracenoil) are miscible, due to their similar chemical composition, in all proportions with one another. The above oils, however, contain crystalline substances which at any time after blending can settle out in large or small quantities, resulting in objectionable deposits. This is due particularly to the naphthalene contained in the middle and heavy oil and the various compounds making up the residue in the anthracene residue. The amount of these crystalline materials remaining in solution after the blending of the oils is a function of their composition and temperature.

The middle oil fraction boiling between 180° - 240°C is able to hold much larger quantities of anthracene residue if it is saturated with naphthalene. Conversely, if an anthracene oil is saturated with anthracene residue, it can hold much higher quantities of naphthalene without raising the temperature.

This property of tar oils was of considerable practical importance to the operating section of the North German Coal and Coke Co. Without injuring the properties of this oil, the largest possible amounts of naphthalene and anthracene residues were held in solution. The work of W. Demsn on the mutual solubilities of various oils, done during his years of work at this plant confirms the content of this report.

The purpose of these experiments was to determine what conditions of temperature and blends will result in keeping the largest amounts of anthracene and naphtaline residues in solutions of middle and anthracenoils.

In an early experiment, as shown in Table 1, a blend of anthracene oil (which had been taken from a centrifuged anthracene product and which after a 24-hour cooling period at 0°C still contained 6% anthracene residue) and a sediment free at 0°C middle oil were mixed in various proportions. As shown in Table 1, the oil mixtures were cooled to 0°C for 24 hours and examined at this temperature. The resulting sediment was weighed and expressed in °C of the original mixture. These values were compared with the calculated values at each mixture ratio. The difference between the calculated and observed values is explained in each case by the extra material remaining in solution.

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The results indicate that, with ratios of middle oil to anthracene oil of 100/1 to 30/70, all material remains in solution. The variation of this phenomenon is shown in Figure 1. The line AB gives the calculated residue content in the mixture as soluable sediment. The area ACD represents the anthracene in solution and the area BCD gives the quantity of anthracene sediment dropping out of solution.

If one computes the amount of anthracene residue remaining in solution based on middle oil contained in the mixture, the optimum ratio is seen to exist at a mixture of middle oil 1/anthracene of 20/80, as shown in Figure 1a. Raising the amount of middle oil 1 over the ratio causes the amount of residue held in solution to drop off.

Holding residues in solution does not require that either of the mixture component be free of sediment, as is shown in Table 2 to Figure 2. To illustrate this, in place of the residue-free middle oil I used in the first experiment was substituted a Middle Oil 2, which contained 22.7% raw naphthalene @ 0°C. This was mixed with an Anthracene Oil - 2 which at 0°C contained 11% anthracene residue. A comparison of the calculated and measured residue quantities indicate that considerable quantities of naphthalene and anthracene remained in solution. It should be particularly noted that with a mixture of 50/50, no residue was found, so that at this ratio, the optimum exists. At ratios greater than this anthracene crystalizes out, and at ratios less, naphthalene settles out. In Figure 2, the total calculate residue in solution is represented by line AB, while the areas ACD and BCE represent the zones of measured naphthalene and anthracene which crystalized out. The area DCE shows the quantity of naphthalene and anthracene residues remaining in solution.

The curve DCE shows that larger proportions of either oil are needed to completely prevent the crystalising out of either naphthale e or anthracene residues for between C & C, the curve DCE touches ACB. Within the segment CC, is a zone between ratios of anthracene oil and middle oil 2 of 40/60 to 50/50 which is optimum for both oils. It is also seen that the solubilizing ability of middle - 2 on the anthracene residue in the anth acene oil, despite its own high raw naphthalene content which contradicts the results in Table 1 and Figure 1. On the other hand, the experiment also shows the corresponding effect of anthracene residue on the naphthalene in the middle oil.

For example in the mixture 40% anthracene oil - 2 to 60% middle oil - 2, almost 13.6% naphthalene and 4.40% anthracene residue are kept in solution. Further attempts to evaluate the mutual optimum solubilities of naphthalene on anthracene oil - 2 of raw anthracene on middle oil - 2 meet with fundamental difficulties. These are caused by the fact the above made assumptions can not be proven exact, namely that with mixtures of anthracene oil - 2 less than 50%, that only naphthalene crystalizes out (see Table 2). As was shown in Figure 1a,

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the evaluation of the optimum solution of naphthalene in anthracene oil - 2 and also of raw anthracene in middle oil - 2 is shown in Figure 2a. Here the values are seen to be 25% of naphthalene at a mixture of anthracene oil/middle oil of 80:20, and 34% of raw naphthalene at a ratio of 40:60.

Since the value of the calculated optimum solution can be influenced by the difference in the content of sediment in both components, a third experiment was run on oils both having equal amounts of sediment. The quantity was 15% 0°C. The results of the test are assembled in Table 3. As with Table 1, the calculated and observed values are separated, so that the differences can be found. As would be expected and as later clarified, the small amounts of sediment found in the compared anthracene oil - 3 and middle oil - 3 as compared to the calculated values, are also less in the mixture. This is the result, despite the fact that it can not be exactly proven. Within the zone of the mixture, no further sedimentation occurs.

The difference between the observed and calculated quantities of sediment again gives the quantities of raw naphthalene and anthracene residues that have gone into solution.

This oil was arbitrarily taken for the experiment. At a mixture of 30% middle oil, the total raw anthracene held in the anthracene oil - 3, that is 10.5%, was kept in solution. Conversely, with 30% anthracene oil - 3 to 70% middle oil - 3, gives the same result. The effect of middle oil - 3 on the raw anthracene is greater than the effect of anthracene oil - 3 on naphthalene. A mixture of 20% middle oil - 3 only holds 1.5% anthracene residue, while the quantity of naphthalene residue at the inverse ratio mixture is 4.17%. These results are tabulated in Figure 3 which gives an overall picture of the mixtures. The naphthalene content of the mixture is defurred by line AA, while the anthracene content is fixed by line BB. The total residue is represented by line AB. The area within lines AEC and BAC shows the material held in solution in the oil mixtures - naphthalene and anthracene, while the material not in solution is shown in the shaded areas AED and BAC. That within the area EEF indicates the total material held in solution. It shows that either side of the 50:50 mixture are almost identical. It follows that the mutual solubilities of the components containing equal quantities of sediment which crystallize out at 0°C is practically the same.

In Figure 3A, the experiment of expressing the solubility of middle oil - 3 on anthracene residue and vice versa based on 100 parts of the oil and anthracene itself. The curve shows that the optimum mixtures are 20:80 to 80:20. The curve further shows that the solubility of middle oil - 3 is greater in the anthracene residue than is the anthracene oil - 3 on the naphthalene. This is probably due to the anthracene oil content in middle oil - 3.

Experiments on the Mutual Solubilities of Tar Oils (Cont'd).

From Figure 3, it is evident that the mutual solubilities of both components is by far not yet exhausted. Far from exhaustion of solubility one soon sees the point where all blending ratios tend to drop sediment.

The 4th experiment was made with a middle oil - 4 and anthracene oil - 4 each containing 25% rather than 15% of raw naphthalene and anthracene residue. These results are given in Table 4 and Figure 4.

As is evident, with 0.15% (?) anthracene only a mixture of 50:50 is free from residue. Further, a rise in middle oil percentage over anthracene oil, shows that the solubility of middle oil - 4 for anthracene is less than the same quantity of anthracene oil for naphthalene. As a result of experiment 4, the solubility powers of the oils is still sufficient to hold their residues in solution and that, further, the solubility of both oils is equal for their respective residues.

The optimum ratio of blend for middle oil - 4 and for anthracene oil - 4 is 10:90 for both (Figure 4a). The shifting of the results of the above experiment explains the higher content of residue in both components.

By the orders of the Reich Commissioner for Oil, the acid oils from all middle oils had to be removed. This brought up the question of how much influence these acid oils had on the solutions investigated. To solve this problem, middle oil - 3 was treated with NaOH, which completely removed the acid oils. This was blended with anthracene oil - 5 which in composition differed but slightly from anthracene oil - 3. These results are given in Table 5, and Figures 5 and 5a. It is evident that the phenol free middle oil - 5 is definitely less soluble than middle oil - 3. A 20% blend of phenol rich middle oil - 3 will hold 10.5% anthracene in solution, while the same ratio of phenol free oil will only hold 2.9% anthracene in solution. The graph also shows that solubility ratios of both oils when compared with experiment 3 are almost identical, for the areas ABC and ABC are almost equally big.

The Figure 5a which shows data from Table 5. The optimum ratio for both components is 30:70.

Table 6, shows a blending test of an anthracene oil - 6 and a fuel oil whose residue was cooled and to which 15% anthracene and naphthalene were added. The experiments and cooling procedure followed that used in the previous experiments 3 through 5. The solubility of both oils, as would be expected, is less than with middle oil - 3 and anthracene oil - 3. In all blends, residue is present. Only at a ratio of 40% anthracene oil 60% heavy oil 1, does the

naphtholene remain in solution, while only half of the anthracene remains on. The solubility of heavy oil 1 for anthracene is definitely less than anthracene oil for naphthalene. With the blend 30% heavy oil and 70% anthracene il, no anthracene remains in solution, while in the reverse ratio 80% or 57% naphthalene remains in solution. Figure 6, indicates the small influence of heavy oil 1 on the solubility of the residue in each mixture as compared to the middle oil. The curve makes it evident that at all ratios larger quantities of anthracene and naphthalene remain not in solution. The largest quantity of anthracene residue which will remain in solution with the heavy oil 1 is 3.2%, while the largest amount that anthracene oil will hold of naphthalene residue is 8.5%. The optimum solution of heavy oil - 1 in anthracene residue is at 50:50 and for the reverse at 40:60.

If the naphthalene is removed from the heavy oil, the solubility improves. Table 7 and Figure 7 show the result of blends of a naphthalene free heavy oil - 2 with anthracene oil.

As is to be expected, the solubility of heavy oil - 2 is opposed heavy oil - 1 is not inconsiderably raised, reaches somewhat the solubility of middle oil - 3 and remains below the phenol free middle oil 5. This result shows that the mutual solubility of the oil considerably relaxes the requirements of the boiling range. The heavy oil is furthermore better above to keep large quantities of anthracene residue in solution but less than a middle oil as used in experiments 1, 3 and 5.

In conclusion, these experiments prove that mixtures of middle oils and anthracene oils can hold varying amounts of crystallizeable oils in solution whereby it is not necessary to remove the residues from one of the other of the components. It is more important that the components keep this material. The most favorable solutions occur when using equal quantity of residues in both middle oil and anthracene oil. The largest quantity of naphthalene and anthracene residues which the oils under consideration of the above uses is about 15 to 20%. The best solubility of the middle oil for anthracene oil is between 20 and 30%, and that of the anthracene oil for naphthalene 30%. The solubility of the middle oil is greatest when it contains acid oils. Lower solubility for anthracene residues are the higher boiling heavy oil. The solubility of the heavy oil can be improved by removing potential residues therein. The results of this experiment should be carried out further on larger scale.

TABLE 1

Distillation			Percent						
	°C	%							
Residue Free Middle Oil - 1 (26.1 % acid oil)	180 240 250	0 80 90	70	60	50	40	30	20	10
Anthracene Oil - 1 with 6 % residue	220 300 360	0 25 75	30	40	50	60	70	80	90
Observed Residue								0.6	2.5
Calculated Residue			1.8	2.4	3.0	3.6	4.2	4.8	5.4
Remaining in Solution			1.8	2.4	3.0	3.6	4.2	4.2	0.9

Distillation			Percent										
	°C	°F											
Middle Oil -2 with 22.7% Naphthalene	180	2	100	90	80	70	60	50	40	30	20	10	0
	250	95											
Anthracene Oil-2 with 11% Anthracene	253	0	0	10	20	30	40	50	60	70	80	90	100
	360	81											
Observed Residue													
Naphthalene			22.7	19.8	15.6	9.3	9.02	-	-	-	-	-	-
Anthracene			-	-	-	-	-	-	0.7	1.8	3.9	10.7	11.0
Calculated Residue													
Naphthalene			22.7	20.43	18.16	15.89	13.69	11.35	9.08	6.81	4.54	2.27	-
Anthracene			-	1.10	2.20	3.30	4.40	5.50	6.60	7.70	8.80	9.90	11.0
	SUM		22.7	21.53	20.36	19.19	18.02	16.85	15.68	14.51	13.34	12.17	11.0
Remaining in Solution													
Naphthalene			-	0.63	2.56	6.59	13.60	11.35	9.80	6.81	4.56	2.27	-
Anthracene			-	1.10	2.20	3.30	4.40	5.50	5.90	5.90	4.70	-	-
	SUM		-	1.73	4.76	9.89	18.00	16.85	15.70	12.71	9.26	2.27	-

TABLE 3

Distillation	°C	%	Percent										
Middle Oil -3* with 15% Naphthalene	180	2	100	90	80	70	60	50	40	30	20	10	0
	250	95											
Anthracene Oil -3 with 15% Anthracene	215	0	0	10	20	30	40	50	60	70	80	90	100
	360	80											
Observed Residue													
Naphthalene			15.0	10.83	4.17	-	-	-	-	-	-	-	-
Raw Anthracene			-	-	-	-	-	-	-	-	1.5	10.8	15.0
	SUM		15.0	10.83	4.17	-	-	-	-	-	1.5	10.8	15.0
Calculated Residue													
Naphthalene			15.0	13.5	12.0	10.5	6.0	7.5	6.0	4.5	3.0	1.5	-
Raw Anthracene			-	1.5	3.0	4.5	9.0	7.5	9.0	10.5	12.0	13.5	15.0
	SUM		15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Remaining in Solution													
Naphthalene			-	2.67	7.83	10.50	9.0	7.5	6.0	4.5	3.0	1.5	-
Raw Anthracene			-	1.50	3.00	4.50	6.0	7.5	9.0	10.5	10.5	2.7	-
	SUM		-	4.17	10.83	15.00	15.00	15.0	15.0	15.0	13.5	4.2	-

* This oil contains 26 % acid oils.

TABLE 4

Distillation			Percent										
	°C	%											
Middle Oil -4* with 25% Naphthalene	180	0											
	240	80	100	90	80	70	60	50	40	30	20	10	0
Anthracene Oil -4 with 25% Anthracene Residue	300	0											
	360	88	0	10	20	30	40	50	60	70	80	90	100
Observed Residue													
Naphthalene			25.0	18.15	14.03	10.45	5.14	-	-	-	-	-	-
Anthracene			-	-	-	-	-	0.19	2.23	8.08	11.93	19.98	25.00
	SUM		25.0	18.15	14.03	10.45	5.14	0.19	2.23	8.08	11.93	19.98	25.00
Calculated Residue													
Naphthalene			25.0	22.5	20.0	17.5	15.0	12.5	10.0	7.5	5.0	2.5	-
Anthracene			-	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0
	SUM		25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Remaining in Solution													
Naphthalene			-	4.35	7.38	8.50	10.48	15.50	17.0	7.50	5.00	2.50	-
Anthracene			-	2.50	3.59	6.55	9.38	12.31	12.77	9.42	8.70	5.02	-
	SUM		-	6.85	10.97	15.05	19.86	24.81	22.77	16.92	13.70	7.52	-

* This oil contains 26% acid oil.

TABLE 5

Distillation	°C	%	Percent										
Phenol Free Middle Oil with 15% Naphthalene	190	0											
	260	90	100	90	80	70	60	50	40	30	20	10	0
Anthracene Oil with 15% Anthracene	270	0											
	360	85	0	10	20	30	40	50	60	70	80	90	100
Observed Residue													
Naphthalene			15.0	13.5	8.7	2.28	-	-	-	-	-	-	-
Anthracene			-	-	-	-	-	-	-	2.3	9.1	13.5	15.0
Calculated Residue													
Naphthalene			15.0	13.5	12.0	10.5	9.0	7.5	6.0	4.5	3.0	1.5	0
Anthracene			0	1.5	3.0	4.5	6.0	7.5	9.0	10.5	12.0	13.5	15.0
	SUM		15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Remaining in Solution													
Naphthalene			-	-	3.3	8.22	9.0	7.5	6.0	4.5	3.0	1.5	-
Anthracene			-	1.5	3.0	4.50	6.0	7.5	9.0	8.2	2.9	-	-
	SUM		-	1.5	6.3	12.72	15.0	15.0	15.0	12.7	5.9	1.5	-

TABLE 6

Distillation			Percent										
	°C	%											
	232	0											
	300	90	100	99	80	70	60	50	40	30	20	10	0
	273	0											
	360	88	0	10	20	30	40	50	60	70	80	90	100
Observed Residue													
Naphthalene													
Anthracene													
	SUM		15.0	13.88	9.88	5.74	3.73	6.80	10.53	14.19	14.60	2.85	15.0
Calculated Residue													
Naphthalene			15.0	13.5	12.0	10.5	9.0	7.5	6.0	4.5	3.0	1.5	0
Anthracene			0	1.5	3.0	4.5	6.0	7.5	9.0	10.5	12.0	13.5	15.00
	SUM		15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0
Remaining in Solution													
Naphthalene													
Anthracene													
	SUM		-	1.12	5.12	9.26	11.27	8.20	4.47	0.81	0.60	-	-

TABLE 7

Distillation	°C	%	Percent										
Residue Free Fuel Oil	240 300	0 90	100	90	80	70	60	50	40	30	20	10	0
Anthracene oil with 15% Anthracene			0	10	20	30	40	50	60	70	80	90	100
Observed Residue Anthracene			-	-	-	-	-	-	1.28	4.20	7.96	13.50	15.0
Calculated Residue Anthracene			-	1.5	3.0	4.5	6.0	7.5	9.0	10.5	12.0	13.5	15.0
Remaining in Solution Anthracene			-	1.5	3.0	4.5	6.0	7.5	7.72	6.3	4.04	-	-

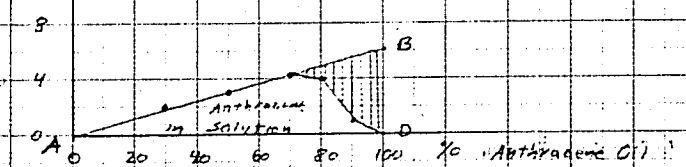
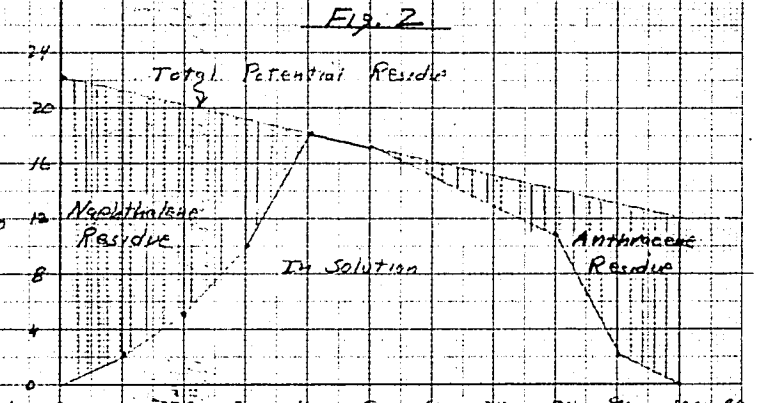


Fig. 1



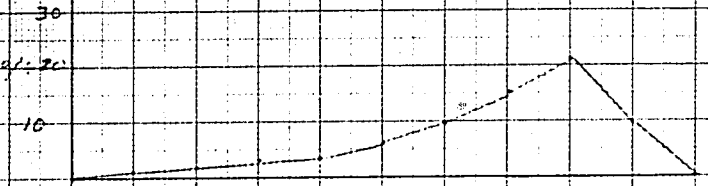


Fig. 1a

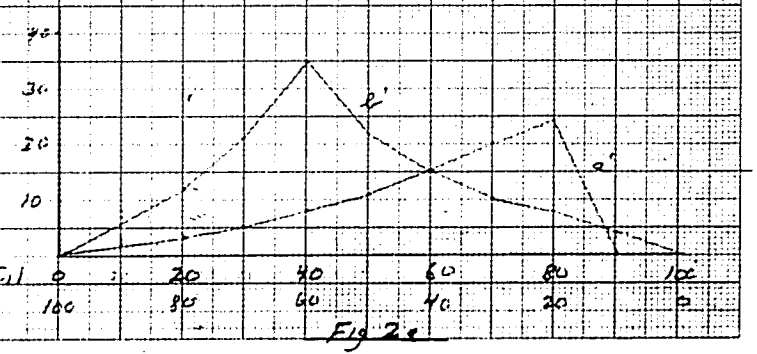


Fig. 2a

Fig 3

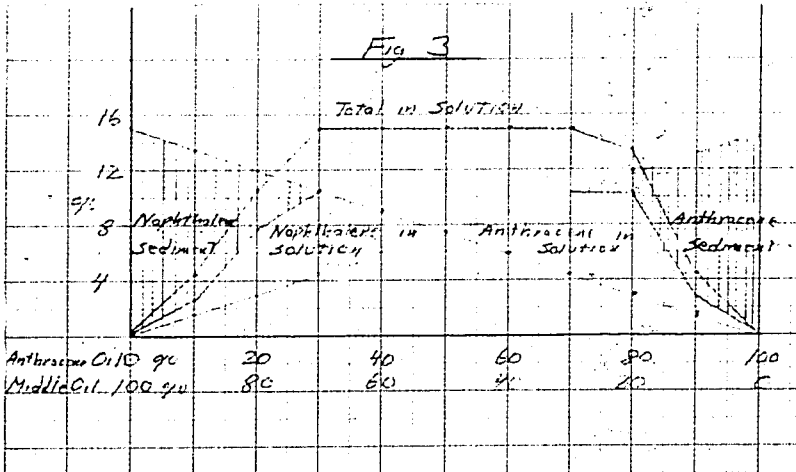


Fig 4

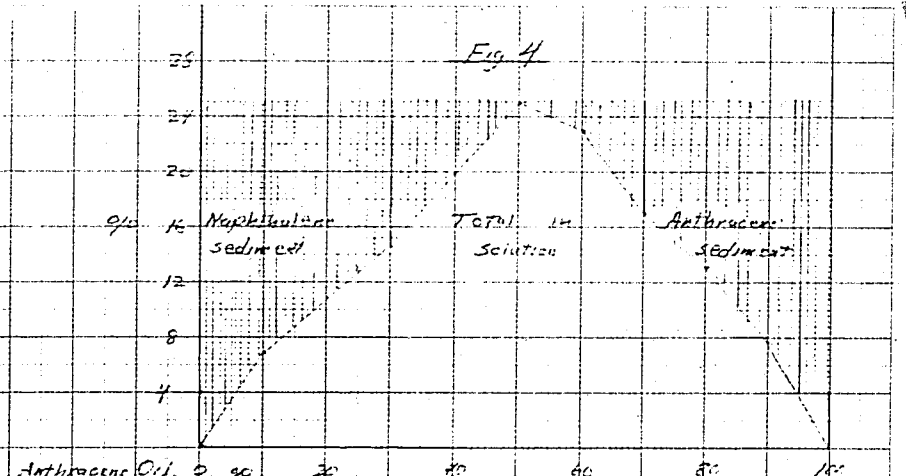


Fig 3a

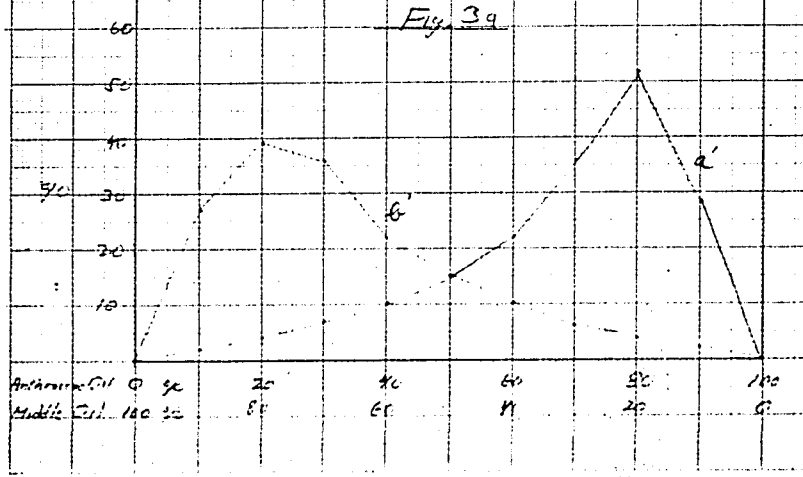


Fig 4a

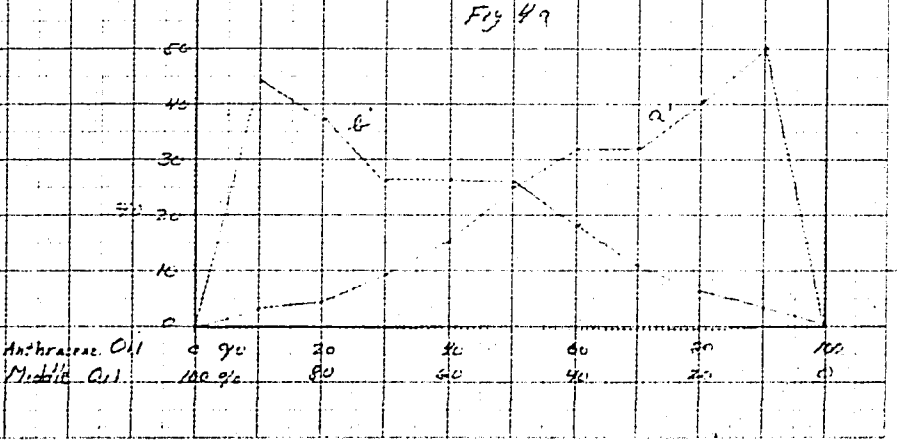
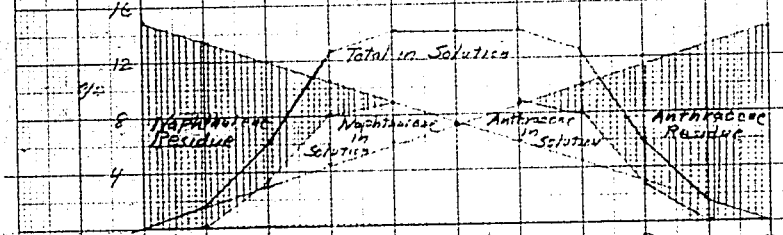
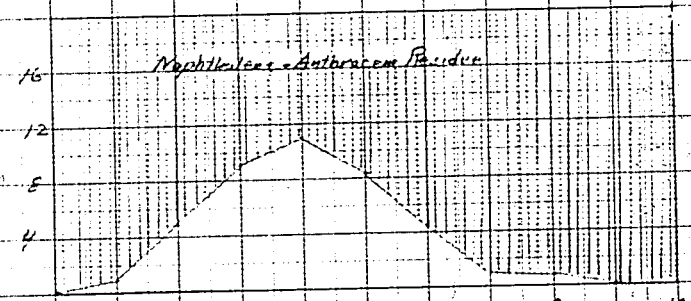


Fig. 5



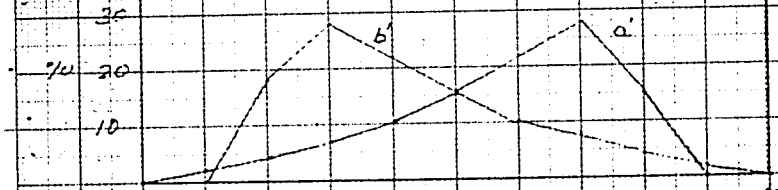
Anthracene Oil 0 % 20 40 60 80 100
Middle Oil 100 % 80 60 40 20 0
with 0.2 % Naph.

Fig. 6



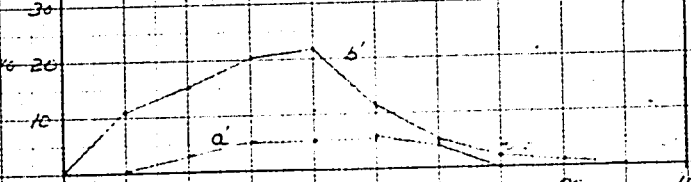
Anthracene Oil 0 % 20 40 60 80 100
Feed Oil 100 % 80 60 40 20 0

Fig. 5a



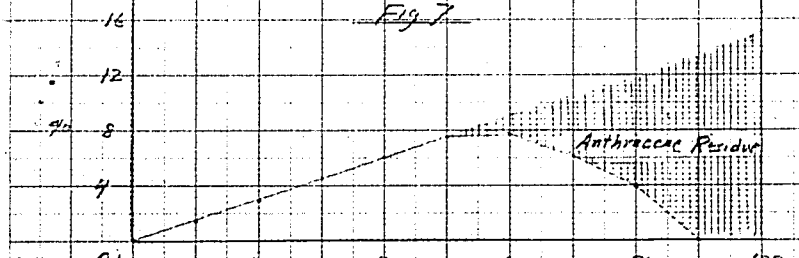
Anthracene Oil 0 % 20 40 60 80 100
Middle Oil 100 % 80 60 40 20 0

Fig. 6a



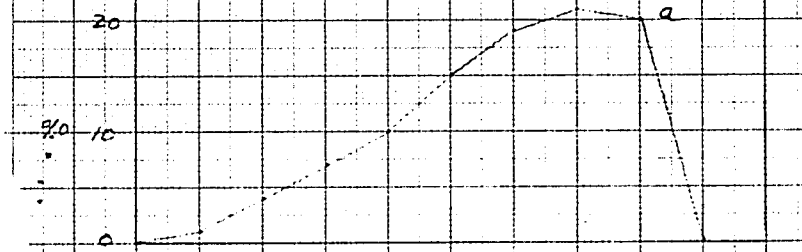
Anthracene Oil 0 % 20 40 60 80 100
Feed Oil 100 % 80 60 40 20 0

Fig 7



Anthracene Oil	0 %	20	40	60	80	100
Fuel Oil	100 %	80	60	40	20	0

Fig 7a



Anthracene Oil	0	%	20	40	60	80	100
Fuel Oil	100	%	80	60	40	20	0