

Translation of Article by Dr. W. Demann in Special Reporting from No. 5, Year 1940.

GLASNAUF

The Miscibility of Fuel Oils

By miscibility is meant that property of liquid hydrocarbons which allows them to be mixed in all proportions with one another without the settling out of hard asphalts and free carbon which makes operation with such fuels very difficult. By closer inspection of the facts, the possibility is found of differentiating between relative and absolute miscibility. The latter exists without the danger of sedimentation if the oil is mixed with other whole oils regardless of their composition. This oil used in the blend must itself be free from hard asphalt and free carbon.

The relative miscibility on the other hand defines the case with which other fuel oils can be mixed with the fuel under consideration containing hard asphalt and free carbon. It is opposite from the absolute miscibility which is dependent on the constitution of the added oil.

The miscibility of fuel oils has received very little attention up to now and has not been reported in the literature because the need for such oils was never great as long as large quantities of petroleum residues were always available. With the demand for domestic production of fuel, the relative value of such oils increased as was mentioned in the Mineral Oil Research Council in 1933. From the clear summary of Dr. Miller which emphasizes this point, the domestic supply of various hydrocarbon fuels, as for instance gasoline, Diesel fuels, lube oils and fuel oil, can be obtained not from ore but from many technical processes now on hand. It follows then that the different processes must be inspected for their best application, syntheses, low and high temperature distillation.

Within the framework of the 8-day conference of the Mining Association at Essen, the problem of hard coal will be discussed. Of particular interest are the products from de-gasification of coal, which for many years have been suggested for use as fuel oils. These through various existing processes can contribute largely to the solution of a domestic economic problem. With regard to a suitable conservation of coal, the de-gasification of coal can and must be investigated, if not only to raise the yield of its main product, i.e. coke, but also the yield of fuel oil, seen from the development of the process which aims to raise the yield of light oil. Success has been reached in general by lowering the de-gasification temperature and in so doing producing

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more fuel oil. The quantity of oil so produced to date could go a long way in supplying the demands of domestic fuel oil needs. Economically, the recovery of such oil is important because at present its production cost is low since it is a synthetic rather than a natural oil.

Dr. Müller has shown since 1933 and in other former works that of all the coal carbonization processes, the hard coal carbonization, because of its coke product, is most suitable for solving the fuel oil problem. After the development of this carbonization process came the discovery that the cokes was usable for special purposes, such as the metallurgical and chemical industries. This also increased the yield of fuel oils as a by-product. To this must be added that high temperature coal carbonization produces a tar which can be used directly without further processing because of its valuable properties, i.e. high specific gravity, and low pour point.

In Table 1, are given the average properties of various "hot surface coked" tars. A glance at the data shows that by using hard coal carbonization as opposed to normal high temperature coking as a means of increasing fuel oil output, the total yield of liquid product is 25% greater which also yields 3 to 4 times the yield of fuel oil as compared to coking the same coal. Further, the high temperature coking tar can not be used directly as fuel oil, but must be distilled, whereby 55% of pitch is dropped out. It does not appear practical to distill low temperature carbonization tars and to hydrogenate or use the various cuts therefrom, consequently the low temperature tar should be used directly as fuel oil.

TABLE 1

Properties of a L.T.D. Tar from Ruhr Coal

Viscosity	°Engler	0	20°C	10	-	22
Viscosity	°Engler	0	50°C	2	-	2.8
Specific Gravity		0	20°C	1.06	-	1.03
Pour Point			°C	-10	to	-20 (about)
Content in Asphalts			C	9	-	16.5
Content in Carbon				1.2	-	1.7
Content in B ₂				6.8	-	7.4
Content in Acid Oils				10.0	-	25.0

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Except in special cases it must always be kept in mind for these oils that they must be mutually miscible, because none of the domestic methods now used in their manufacture can meet the demand for them. Hence, it was decided to experiment to see whether and to what extent these fuel oils, all of which have a more or less high hard asphalt content and free carbon content, were mutually miscible and with what other fuel oils they might be mixed if necessary.

This fact led Dr. Miller, in 1934, to have the question of the miscibility of hard coal coking tar with other fuel oils investigated along lines which logically developed the line of thought set forth earlier. The other fuel oils obtained by the de-gasification of hard coal were also to be included within the scope of the tests. These studies, excerpts of which will be discussed below, were also to make some contribution to the general field of hard coal mining, since, they dealt with the solution of a common and significant problem and since, the principles and facts discovered could eventually be applied directly to all hydro-carbon oils or even to all fuel oils.

TABLE 2

Fuel Oil Yields from a Coal with 26% Fluid Content on a Dry Coal Basis

By Low Temperature Distillation	6 % Tar as Fuel Oil
By High Temperature Distillation	3.6% Tar of which,
55 % is Pitch * or 2.08	
45 % is Oil * or 1.72	
	3.80 Tar

* These contain naphthalene and anthracene.

As was stated briefly in the introduction, miscible oils are those which form no precipitates or coagulates when mixed with other oils. These may consist of hard asphalts or asphaltenes and the so-called free carbon. The consensus of various researchers is that they are precipitated, from a colloidal system or organosol that had been stable under certain conditions, under the influence of compounds having less surface tension². According to the circumstances in individual cases, the precipitation is preceded by certain processes

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and changes of condition¹, a discussion of which lies outside the scope of this essay. The final result is an inhomogeneity caused by the precipitates, which can make the use of the oil mixture very troublesome or even completely impossible. Sediment and coke-like deposits can be formed not only in containers used for storage, in pipelines, etc., but also in motors themselves and in burner nozzles and jets so that it seems to become imperative that precipitates of hard asphalts and, although to a lesser degree, or free carbon be avoided.

Among other things the phenomena just mentioned pre-suppose that in the case of one partner to the mixture, instead of pure hydrocarbons, such as exist in refined light fuels, there be present in the unmixed state a normally stable colloidal system. When this is disturbed a more or less rapid flaking out or precipitation of previously highly dispersed hard asphalts and free carbon can occur, which is also known as inhomogenizing.

It will be seen from this that other conditions prevail for fuel oils than for the light fuels consisting practically of pure hydrocarbon groups, such as the benzols and benzines. A mixture of such light fuels is the occasion for a dissolving distribution of differently built-up hydrocarbon groups which are known to be freely soluble in one another. This shows that the question of the miscibility or non-miscibility is more or less important only for oils of the aforementioned type having a medium or higher distillation point, such as those used for Diesel motors and primarily for oil fired boilers.

Hence, in the question of the miscibility of oils that contain hard asphalts and free carbon it can only be a matter of determining what oils they may be mixed with without precipitation occurring. It would be a matter of de-limiting for them the extent of the so-called relative miscibility, in the sense at first described. For reasons that will be gone into later, this depends on the constitution of all the components that happen to be present in the mixture, that is, for each oil there must be not a numerically but a constitutionally conditioned group of other oils with which it is miscible under all conditions without inhomogenizing.

It makes no difference what the absolute amount of hard asphalt and free carbon content may be. Absolute miscibility is impossible for all these oils for the reasons shown above, since even very slight amounts of hard asphalts can cause precipitates. As will be shown, this is more or less the case in all the fuel oils made from de-gasification of hard coals. The same is true for the higher distillation point oils made from the de-gasification of brown coals and oil shales. In Table 3, which makes no pretence at being complete,

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are shown, the according to source and manufacturing method, some representative types of fuel oils made by de-gasification and in part by synthesis of fossil fuels. Along with a difference in their composition one will note what for practical purposes amounts to similar constitution. This is denoted superficially by the relatively high specific gravity, which is about 1, and by the more or less high content of acid (satur) oils, which are not to be found in the case of pure crude fuel oils, and by their more or less high content of hard asphalts and free carbons. Apart from the above-mentioned similarity of constitution, still slighter differences exist, since, the oils made by high temperature de-gasification are purely aromatic, those made by the hydrogenation of hard coals and by hot-surface and gas-bath coking are primarily aromatic-naphthenic, and the brown coal tar oils are less aromatically constituted, as their higher hydrocarbon contents (within the same boiling fractions) reveal.

TABLE 3

* Average Values.

	Vis. 20/	Sp. Gr. 50°C	Sp. Gr. 60°C	Four Point°C	Asphalt- hard %	Free Carbon %	H ₂ %	Acid Oils %
FUEL OILS FROM HARD COAL DISTILLATION								
LTD Coal Tar	16.0	2.4	1.06	- 20 to	14.00	1.50	7.00	16.0
Same deasphalted	3.2	-	1.00	- 30	0.20	-	-	5.0
HTD Tar Oil								
Fuel Oil "A"	2.1	-	1.10	to -11	0.40	-	-	-
Fuel Oil "B"	-	-	1.164	-	8.12	6.37	-	-
Fresh Oil	1.2	-	1.08	- 13	0.18	0.61	6.31	5.0
Inner Oil - Dr. Gergmann	2.0	-	0.977	- 10	0.30	-	9.13	16.0
LTD Coal Tar (Gas Re-cycle)								
Heavy Tar	-	19.26	1.08	+ 6	20.50	4.93	7.95	26.5
Tar Oil	5.25	-	-	- 20	3.65	0.40	6.62	2.0
FUEL OILS FROM LIGNITE DISTILLATION								
Lignite Tar Oil	1.7	-	0.932	- 10	0.45	0.42	11.64	10.8
	2.9	-	0.944	- 15	0.31	0.31	12.25	14.0
	-	1.6	0.977	- 20	2.26	0.22	9.63	17.8
FUEL OILS FROM SHALE DISTILLATION								
Eathonian Shale Oil	9.2	-	1.010	- 19	9.23	-	9.68	29.9
Shale Tar	66.0	8.46	1.005	-	8.42	-	-	-
THROUGH SYNTHESIS ON BASIS OF FUEL OILS FROM COAL								
Fuel Oil "A"	26.0	2.8	1.09	- 20	0.50	-	7.61	-
Hydrogenated Oil "B"	2.11	-	-	-	0.12	-	8.76	6.0
Cracked Residue	100-190	10 - 15	0.97	to +20	6.60	0.30	10.13	-

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TABLE 4

Variation in Hard Asphalt Content in Fuel Oils From Low Temperature Carbonization
of Coal in Storage
(Distilled Oil)

Storage Period Months	Oil #1 ^a	Oil #2 ^a	Oil #3 ^a	Oil #4 ^a
0	0.339	0.432	0.197	0.45
1	0.389	0.670	-	-
2	0.444	-	0.282	-
3	0.499	-	0.449	-
4	0.509	1.189	0.578	-
5	-	1.620	0.746	-
6	-	2.022	-	2.20

In the case of the hard asphalt contents, it must be remembered that for freshly distilled oils these don't represent constants, but increase somewhat dependent on the length of storage time, as Table 4 shows. This does not apply to the oils of this group not treated by distillation, such as hot-surface coke tar, as was shown by several years' storage tests.

TABLE 5

Surface Tension in Dyno/cm at 20-25°C			
Aliphatic Hydrocarbons		Aromatic Hydrocarbons and Compounds	
Pentane	12.5	Benzol	28
Hexane	17.5	Toluol	29
Petroleum	28.9	Xylol	30
Heptane	18.5	Dec-line	32
Spindle Oil	31.1	Tetraline	34.5
		Anthracene Oil	40 (at 40°C)
		Cresol	34
		Pyridine	35.5
		Aniline	42
		Quinoline	45

As may be seen from Table 5, it is well known that the aromatic hydro-carbons have higher surface tensions than the aliphatic hydrocarbons having about the same boiling point and that again in both groups those having a higher

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boiling point have higher surface tensions than those having a lower boiling point, that is, than the lower molecular hydrocarbon oils. Since, all the asphalt containing fuel oils made by the degasification of coal, which are characterized by their high specific gravity and higher boiling point, almost exclusively contain higher boiling aromatics, it may be concluded that they represent organosols in which, in part, various amounts of hard asphalts and free carbon are dispersed with high boiling aromatic hydrocarbons. Keeping mind the works in this field published by Mallison, Hellensteyn and others¹, it was hence to be expected that fuel oils of this group, which for the sake of simplicity were usually called degasification fuel oils, would be mutually miscible in any proportion and without precipitation.

In order to check the question which thus needed to be answered next: with what other fuel oils the coke tar made by hot-surface coking of hard coals was miscible, this coke tar was next mixed with the various oils listed in Table 3 in varying proportions and under a multitude of different conditions. This was supposed to show whether the relative miscibility, which could logically be assumed, of coke tar and all the other fuel oils having the constitutional properties common to this group, actually existed, or whether it would have to be determined experimentally for each individual case. This question was all the more important since a practical evaluation of the experiments might make it possible within certain limits to avoid a time consuming and precarious empiricism. It is not necessary to mention here the analytical and experimental methods used in proving and recognizing miscibility.

It will suffice to say here that the miscibility within this group of degasification fuel oils has been clearly proven on the basis of extensive experiments made both by us and by others in order to verify this point of view.

Table 6, shows, for example, some of the mixtures used by us in time tests extending over several months. It should be pointed out especially that, as was to be expected, there is no precipitation of asphalts even if one adds to a highly aromatic but very asphalt-y oil, one that is constitutionally similar or related that contains only negligible amounts of hard asphalts, such as, for example, a coke tar that has been de-asphalted by some special process or a low asphalt synthetic oil. The same may be said for fuel oils having a higher boiling point made by the degasification of brown coal or of oil shale.

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TABLE 6

<u>Miscibility of Fuel Oils from Low Temperature Distillation of Fossil Fuels</u>	
Low Temperature Tar & High Temperature Tar Fuel Oil "A"	1:1, 1:5, 1:10
Low Temperature Tar & High Temperature Tar Fuel Oil "B"	1:1, 1:5, 1:10
Low Temperature Tar & De-asphaltized Low Temperature Tar	1:1, 1:5, 1:10
Low Temperature Tar & Tar from Gas Circulation Distillation	1:1, 1:5, 1:10
Low Temperature Tar & Estonian Shale Oil	1:1, 1:5, 1:10
Low Temperature Tar & Fuel Oil "A" from Synthesis	1:1, 1:5, 1:10

It may be said in summary that all the fuel oils made from de-gasification of hard coals, brown coals, and oil shales, as well as various one made synthetically from a coal base are mutually miscible in any proportion. Our experiments might have been considered completed at this point, except for a description of the research methods used, since, we had met the problem of recognizing and delimiting the so-called relative miscibility of hard coal coke tar and all the fuel oils made by de-gasification of hard coal. The results also had a practical value, since, according to our findings all the de-gasification fuel oils might be mixed in any proportion without disastrous results for the user. In other words, it was no longer necessary to adjust certain tanks or oil burners to some special fuel oil, which might only occur in limited quantities or in certain regions, while other layouts were being adjusted to another fuel oil of this group which happened to be made by some other method.

Incidentally, as far as the miscibility of various domestic fuel oils made by from the de-gasification of fossil fuels is concerned, Dr. Miller's earlier suggestion that the method of meeting domestic oil needs be built up of not one but many methods has proved sound and practicable. Even a quantitatively very small production of fuel oils can be mixed or precipitated out inside this group without the slightest disadvantage. Hence, there was also the possibility of freely using hard coal coke tar as a cheap fuel oil in order to ease the domestic fuel oil demand.

In this connection it seemed promising to compare the properties of the mixtures possible within this group of fuel oils with the properties of the various components that happened to be used. Thus, we were able to determine that the measuring values of the various components of the

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mixture were considerably improved by the mixing, i.e. for example, that the viscosity, the pour point, and the freedom from settlement night, in part, be better than would normally have been expected from the proportions used and the computed data for the resulting mixture.

TABLE 7

VISCOSITY OF FUEL OIL BLENDS				
BLENDS		VISCOSITY		DIFFERENCE BETWEEN Calculated and Observed Viscosities % @ 20°C
Low Temp.	Tar Oil %	Calculated OR @ 20°C	Observed OR @ 20°C	
100	0	-	17.23	0.00
90	10	15.64	10.82	4.82
80	20	14.66	6.71	7.95
70	30	12.47	4.60	7.87
60	40	10.89	3.34	7.55
50	50	9.30	2.60	6.70
40	60	7.72	2.13	5.59
30	70	6.13	1.84	4.29
20	80	4.55	1.63	2.92
10	90	2.96	1.49	1.47
0	100	-	1.28	0.00

TABLE 8

VISCOSITY OF FUEL OIL BLENDS				
BLENDS		VISCOSITY		DIFFERENCE BETWEEN Calculated and Observed OR @ 20°C
Synthetic Fuel Oil %	Tar Oil %	Calculated OR @ 20°C	Observed OR @ 20°C	
100	0	-	31.49	0.00
90	10	23.46	12.70	15.76
80	20	25.44	8.05	17.39
70	30	22.39	4.68	17.91
60	40	19.26	3.12	16.24
50	50	16.33	2.20	14.13
40	60	13.30	1.78	11.52
30	70	10.27	1.55	8.72
20	80	7.24	1.44	5.80
10	90	4.21	1.39	2.82
0	100	-	1.17	0.00

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Thus, for example, it is shown that the viscosities of the mixtures are frequently much lower than what would have been expected from the viscosities of the components and the proportions in which they were mixed. This, of course, may be traced back to the fact that the viscosities of mixtures cannot be computed additively from those of their components. Instead, according to the viscosity-mixture-relationship set up by Ubbelohde and Walther, they result from the viscosities of the mixture components when one lays them out graphically over 0 to 100 on a double logarithmic coordinate system. Then the viscosities of all the mixtures are supposed to lie, according to this system, in a straight line connecting both points and, compared to the arithmetical system, show a progressively greater reduction or lowering of the viscosity of the various mixtures. Naturally, the prerequisite remains that there be no precipitation. Tables 7 and 8 and the graph Figure 1 show the viscosities of various mixture series and the over proportional reduction of the mixture viscosities thus determined.

It is significant, however, that in many cases the viscosities of the mixtures are still lower than the relationship set up by Ubbelohde and Walther shows, as may be seen from Figure 2.

It may be due to this phenomenon, which in our opinion comes from a mutual dissolving of crystalloid and micro-crystalline oil components, that by mixing different oils their sediment contents and pour points may be so over proportionally improved.

TABLE 9

IMPROVEMENT OF POUR POINT OF OILS THROUGH BLENDING					
Blend	Four Point °C	Blend	Four Point °C	Blend	Four Point °C
Oil "A"	+ 4	Oil "A ₂ "	- 8	Oil "A ₃ "	- 12
Oil "B"	- 28	Oil "B"	- 28	Oil "B"	- 28
Oil "C"	- 2	Oil "C"	- 2	Oil "C"	- 2
Blend		Blend		Blend	
1:1:1	- 12	1:1:1	- 20	1:1:1	- 24
	- 9(coke)		- 13(coke)		- 14(coke)

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It would take too long to evaluate here all the phenomena of the same basic process which our experiments turned up. It will suffice to mention that hot surface coke tar can not only improve the sediment content of some higher-boiling high temperature tar oils, which is conditioned by the giving off of raw anthracene, but can actually eliminate it. As Table 10 shows, only relatively slight admixtures are necessary. No wonder that this phenomenon becomes more apparent mainly when the mixtures concerned are cooled to lower temperatures. It should also be mentioned that the high temperature tar oil used in these experiments was an oil that had previously been suitably saturated with raw anthracene so as to more clearly bring out the various relationships being studied, while it is commonly known that the higher boiling fuel oils made from the high temperature distillation of tars are usually freed, by some suitable method, of their raw anthracenes and suchlike. The same fact was proved elsewhere in actual practice, as a result of our experiments. In the operation of certain oil burning boilers during the cold season, hot surface coke tar was added to high temperature tar oils in order to avoid the giving off of raw anthracene, etc. which otherwise sometimes occurred at lower temperatures.

TABLE 10

IMPROVEMENT IN SOLID CONTENT OF HIGH TEMPERATURE DISTILLED TAR OILS BY BLENDING					
BLEND		Four Point °C	SOLID CONTENT %		
Tar Oil	Low Temp Tar		+ 8°C 3-Hr Cooling	0°C 3-Hr Cooling	+4°C 2-Hr Cooling
100	0	- 13	-	-	-
93	67	- 25	-	-	-
0	100	- 29	-	-	-
-	-	-	+15°C 60Hr Cooling	+8°C 20Hr Cooling	+4°C 45Hr Cooling
100	0	-	-	0.947	Completely Solid
83	17	-	-	0.910	About 4.5%
50	50	-	-	0.918	About 1.5%
0	100	-	-	-	-

In summary it may be said that a mixture of this universally mutually miscible group of mainly aromatic fuel oils not only serves to compensate for their relative scarcity in view of the total fuel oil demand, but is also of advantage in the adjustment or improvement of the measuring values of the various mixtures. It also makes possible the influencing of certain measuring values at will. The relative miscibility which may be observed within this group is not accidental, having to be re-checked from time to time, but is fundamental, since it is based on the similar constitution of these oils. It may be taken as a practical evaluation of the results of our experiments, that a considerable part of these mainly aromatic fuel oils are no longer delivered to the

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never unmixed, but mixed together.

Nevertheless, the relationships are quite different in the case of fuel oils made from natural crudes. (Erdölheisole - which can also possibly mean mineral oil here assumed to mean as shown). As will be seen by a glance at the crude fuel oils shown in Table 11, and in contrast to the fuel oils made from de-gasification of coal or those made synthetically from a coal base, it is a question here of oils having great differences in composition and constitution. This may be explained by the different structure of the crude oils and by the different methods used in the preparation of fuel oils from them.

TABLE 11

	VISCOSITY		PETROLEUM FUEL OILS				
	CP/20°C	CP/50°C	Sp. Gr. @20°C	Four Point Car- bon	Free Benz	Asphalt cont %	H ₂ S Acid Oils %
Aruba Oil	-	15.83	0.990	-	-	11.73	-
Venezuela Dies. O.	2.10	-	0.886	-	-	7.80	13.39
Venezuela Oil	-	48.51	0.976	-	-	7.60	-
Angola Raw Oil	-	29.18	0.958	-	-	4.50	11.71
DAPAG Fuel Oil	2.20	1.40	0.869	-29	2.06	0.40	13.21
EBARO Oil	2.30 to 5.35	-	0.924	-16	0.07	0.28	11.27
Glenoil	-	-	-	-20	-	9.40	11.09
PACUHA Special Oil	-	-	0.894	-	-	-	11.50
Rhenania Oil	4300	19000	0.925	11	-	7.25	10.97

Even among swamp oils it is possible to differentiate according to constitution: paraffine base, asphalt base, and mixed base oils. On the other hand, fuel oils can be derived from natural crudes either as the residue remaining after distillation under normal pressures or vacuum, or as the result of the cracking process used to get a maximum light oil output. For all these reasons the various fuel oils made from natural crudes can show a wide divergence not only in their composition, but especially in their constitution.

TABLE 12

BLENDS OF ETHYLENE FUEL OILS

BLEND

HARD ASPHALT DEPOSIT %

Aruba Fuel Oil	• 400 % Gas Oil	11.73
Venezuela Oil "C"	• 400 % Gas Oil	1.60
Angola Crude	• 400 % Gas Oil	1.25

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TABLE 13

BLENDS OF PETROLEUM FUEL OILS		DEPOSIT BASED ON % GLXK OR PHENANOL
GLXK	PHENANOL	
Glaxoil with	400 % NAPAG Fuel Oil	About 6.0
Phenanalia Oil with	400 % NAPAG Fuel Oil	About 4.0

From the experiments conducted with degasification fuel oils it would seem that the difference in the constitution of the fuel oils made from natural crudes would be expressed in a different miscibility or non-miscibility from that of the first named group. This conclusion, which was based on our earlier experiments, was fully and completely borne out by means of suitable miscibility experiments, as opposed to the view point often expressed earlier. That the fuel oils made from natural crudes were perfectly mutually miscible. So, as Table 12, shown, it was found that precipitations up to almost 12 % occurred from various asphalt-containing fuel oils made from natural crudes when mixed with four times the same amount of a gas-oil frequently used as fuel oil. Table 13 shows that the same results were attained in a second mixture series of different crude fuel oils.

TABLE 14

MISCIBILITY OF A HIGHLY ASPHALTIC PETROLEUM FUEL OIL WITH A FUEL OIL FROM DISTILLING REFINERIES		NO DEPOSITS FOUND
BLENDS		
L.T.D. Tar and Phenanalia Oil		1:1, 1:5, 1:10
De-asphaltized Tar and Phenanalia Oil		1:1, 1:5, 1:10
L.T.D. Tar and Glaxoil		1:1, 1:5, 1:10
De-asphaltized Tar and Glaxoil		1:1, 1:5, 1:10

On the other hand, as Table 14, shows, it is possible to mix the crude fuel oils having high asphalt content, and which are also all characterized by a higher specific gravity, with one another as well as with the degasification fuel oils. But it must be pointed out that for these fuel oils the scope of their relative miscibility must always be tested from case to case in what are often very tedious experiments, something which is no longer necessary in the case of the degasification fuel oils. Moreover, some of these oils are peculiar in

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that they often react quite differently. For instance, they may experience some precipitation themselves as well as producing it in other oils. This fact, which at first seems contradictory, was first proved after we used a new method developed in cooperation with Asbach, about which more will be written later. It will suffice to mention that by this method one can prove in a very short time whether any inhomogenization of an oil mixture is just beginning or has already begun.

From the point of view of the aim of our efforts it was most valuable to learn that similar experiences had been had in the operation of oil fired boilers where for special reasons fuel oils made from natural crudes were mainly burned. The fact which our experiments proved, that in contrast to the group of the so-called degassification fuel oils the natural crude fuel oils generally show no relative mutual miscibility, must be re-emphasized all the more since the plans to increase domestic fuel oil production on the assumption that the natural crude fuel oils were freely mutually miscible, were often made on the further assumption that the degassification fuel oils were also miscible with all the natural crude fuel oils. The results of our experiments have helped bring people to realize that this point of view is not exactly in line with the facts. Our belief was further strengthened by the fact that the proved relative miscibility of hard coal coke tar and the other primarily aromatic oils made it possible to clear up the question of their practical application.

Before considering the question of absolute miscibility, it is necessary to consider briefly the principal reasons for precipitation from mutually non-miscible fuel oil mixtures. It is striking that precipitation does not occur in all the proportions in which mutually non-miscible oils are mixed. Rather, such oil systems are miscible within a range that changes from case to case. Precipitation only occurs at certain mixing proportions, which may be called mixture-gaps, as the expression of a process which may vary in length.

TABLE 15

DEPOSITION OF FREE CARBON BY THE ADDITION OF BENZOL					
Low Temp. Distilled Tar		L.T.D. Tar from Gas Re-cycle		Fuel Oil 22°	
Ratio of Oil To Benzol	Ratio of Oil Deposited Free Carbon	Ratio of Oil To Benzol	Ratio of Oil Deposited Free Carbon	Ratio of Oil To Benzol	Ratio of Oil Deposited Free Carbon
1:3	1.15 %	1:3	3.8	1:3	5.2 %
1:5	1.28 %	1:5	3.1	1:5	5.7 %
1:10	1.20 %	1:10	4.3	1:10	5.9 %
1:20	1.26 %	1:20	4.4	1:20	6.3 %

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"ZUSAMMENFASSUNG"

The Miscibility of Fuel Oils

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In so far as one of the mixture components contains so called free carbon in addition to the hard asphalts, this free carbon may generally be precipitated out by adding oils of a higher surface tension, than is necessary for the precipitation of hard asphalts under the same conditions. For example, in the case of coke tars the addition of larger amounts of kerosol having a surface tension of 28 dyn/cm would suffice for this purpose. (Table 15). The same thing will work for all oils that contain free carbon. Naturally, it must be pointed out that for practical reasons such an admixture can never be considered.

Since a sufficient admixture of oil with lower surface tension is necessary for the precipitation of hard asphalts, the free carbon contained in the oils is also precipitated out. This is also true for those frequent instances where the hard asphalts are only partially precipitated. It should be noted that these relationships were carefully checked in a special piece of work carried on jointly with Dr. Forsch in a study of pitch extracts, which will be treated elsewhere later.

We checked this precipitation process years ago for various non-miscible systems, by determining the mixture-gaps as accurately as the then available methods permitted. For example, we found that for a coke-tar/diesel oil system no precipitation occurred up to an admixture of about 40 parts diesel oil to 60 parts coke tar. Then, after a range in which there were suspended asphalt precipitations whose sedimentation speed was very slight, there followed a range of precipitations. These were precipitations whose sedimentation speed was sufficient for them to be deposited on the bottom or on the walls inside the observation period used. As Figure 3 shows, and as might be expected, the precipitations, with reference to the weight of the mixture (usually about 100 cm³), increase with a greater admixture of the precipitant, only to drop again. Figure 4, reveals that the drop in precipitations in g, or in percentages of the mixture is only apparent. If one bases it in percentages on the asphalt content oil, there is an almost uninterrupted increase with the admixture of the precipitant. Not until the end, that is, at a mixture content of almost 100% of oils causing precipitation does the precipitation of hard asphalts fall off because of difficulties in observing it or in measuring it quantitatively. This is actually caused by such a fine distribution of the precipitates occurring at this stage that an area of dispersion seemed to follow the preceding range of precipitation. We were able to make the same sort of observations for other systems also. These facts may also be explained by the various results set forth in the writings mentioned earlier.

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Hence, it will be seen that an absolute mixture can occur only in the case of fuel oil partners that are completely free of hard asphalt and free carbon. Naturally, it would be an almost ideal situation if, considering economic and operational questions, it were possible to have sufficient quantities of just such oils for fuel oil uses everywhere. But it should be remembered that absolutely miscible, that is, completely asphalt-free oils, in so far as they are mainly aromatically constituted, have a tremendous advantage over the absolutely miscible aliphatic oils. This actually lies in the fact that, as said before, the aromatic oils have a considerably higher surface tension than the aliphatic oils of the same boiling point. This would have the practical effect that when any other oil was added to absolutely asphalt-free aromatic oils, the latter would suffer an asphalt precipitation, and that they also, in contrast to the aliphatic oils, could cause asphalt precipitation from other oils, a fact that must be gone into more carefully.

We next tried to prevent precipitation occurring when oils were mixed that would normally cause precipitation, by adding suitable substances. All sorts of compounds were tested and it was found that only certain bodies were effective. Nevertheless, in many cases the admixtures had to be so large that any practical application seemed impossible because of the high price and the small amounts available.

In the case of those materials it is either the high surface tension or the ability to emulsify freshly precipitated hard asphalts that is useful. The second possibility has been thoroughly tested by experiments which Dr. Borchers made some years ago. At first we proceeded from the idea of keeping the precipitated hard asphalts suspended like an emulsion similar to (Fliegskohle) by the proper admixtures. It was never possible to find a completely satisfactory solution, whether, because the emulsion was not sufficiently stable, whether, its viscosity increased too much, or because the required admixtures were too costly.

Many other possibilities were also tested out in this connection, but the admixtures, which had to be made to asphalt containing oils in those cases where great amounts of asphalt precipitating materials had to be used, were so large that the practical application of this method, which cannot be discussed here, was made very difficult or too expensive.

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The Miscibility of Fuel Oils

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At any rate, these experiments showed that for economic reasons it is impossible to prevent precipitation from asphalt containing oils for all mixture proportions, particularly in those cases where large amounts of asphalt precipitants must be used. On the other hand it is possible, and even sometimes economical, to reduce the unpleasant operational effects of precipitation for certain numerically stable non-miscible mixtures. This may be considered economical when only small amounts of asphalt-precipitants are involved. Nevertheless and in spite of the fact that our experiments in this direction were halted because of the uneconomical prospects, we would be grateful if they were continued somewhere else, since, a suitable admixture could actually give fuel oils a miscibility that would automatically preclude any precipitation when oils of lower surface tensions were added. Thus one would have freed oneself from pure empiricism in this field.

TABLE 16

THE PRODUCTION OF ABSOLUTELY MISCIBLE OILS FROM HARD COAL TAR (L.T.D.) THROUGH COLD PROCESSING

	Unprocessed	Processed
Viscosity Engler @ 20°C	15.5	1.7
Sp. Gravity @ 20°C	1.047	0.986
Four Point °C	-13	-32
Hard Asphalt Content %	16.56	0.12
Yield in Asphalt Free Oil by Cold Processing %	-	76.5
Yield in Asphalt Free Oil by Distillation %	-	65.0 (About)

After the conclusion of these experiments, which at any rate showed the fundamental possibility of preventing asphalt precipitation, we tried to reach the same goal by another route. In this we could go back to the results of earlier experiments in the making of so-called tar-gas oils from hard coal tars and hard coal tar oils by treating them with mainly medium-middle-boiling aliphatic oils, about which Dr. Hoehris¹ reported earlier. For the reasons mentioned earlier, we proceeded here from hot surface coke tar, and succeeded in getting a fuel oil that was as good as asphalt-free. We were also able to determine that essentially higher production of asphalt-free oils was possible by this method than by using distillation methods. Table 16 shows the data on raw coke tar and the absolutely miscible fuel oil made by de-asphaltizing. Similar experiments were made with gas-bath coke tars, in which somewhat higher asphalt contents were found in the final oils. A thorough test of the asphalt-free oils made by de-asphaltizing, based on the new short test method described above, proved the absolute miscibility of these oils. On the basis of their aromatic constitution, just as in the case of the fuel oils made synthetically from coal, they have the big advantage over the corresponding aliphatic oils that because of their high

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surface tension they cause no precipitation of asphalt in other oils. Furthermore, when they are added to a non-miscible system of two oils, such as coke tar-Diesel oil, they make it possible to shift the mixture gap of this system to higher to higher admixtures of Diesel oil. Thus, it is seen that these oils are extremely effective as solvents - not actually, but at least as far as results are concerned, since, these are not genuine solutions. It should be mentioned that this property, which is common to all asphalt-free and low asphalt aromatic oils, has up to now never been expressed in any corresponding evaluation of these oils. On the other hand this shows that, contrary to the opinion so often expressed earlier, the aromatic fuel oils have many advantages over the aliphatic fuel oils.

Considering the possibilities of using hard coal coke tar, it was especially important to prove that absolutely asphalt-free fuel oils could be manufactured from this coke tar at prices that were, for all practical purposes, the same as those for synthetic oils. There is, to be sure, a certain unavoidable reduction in quantity.

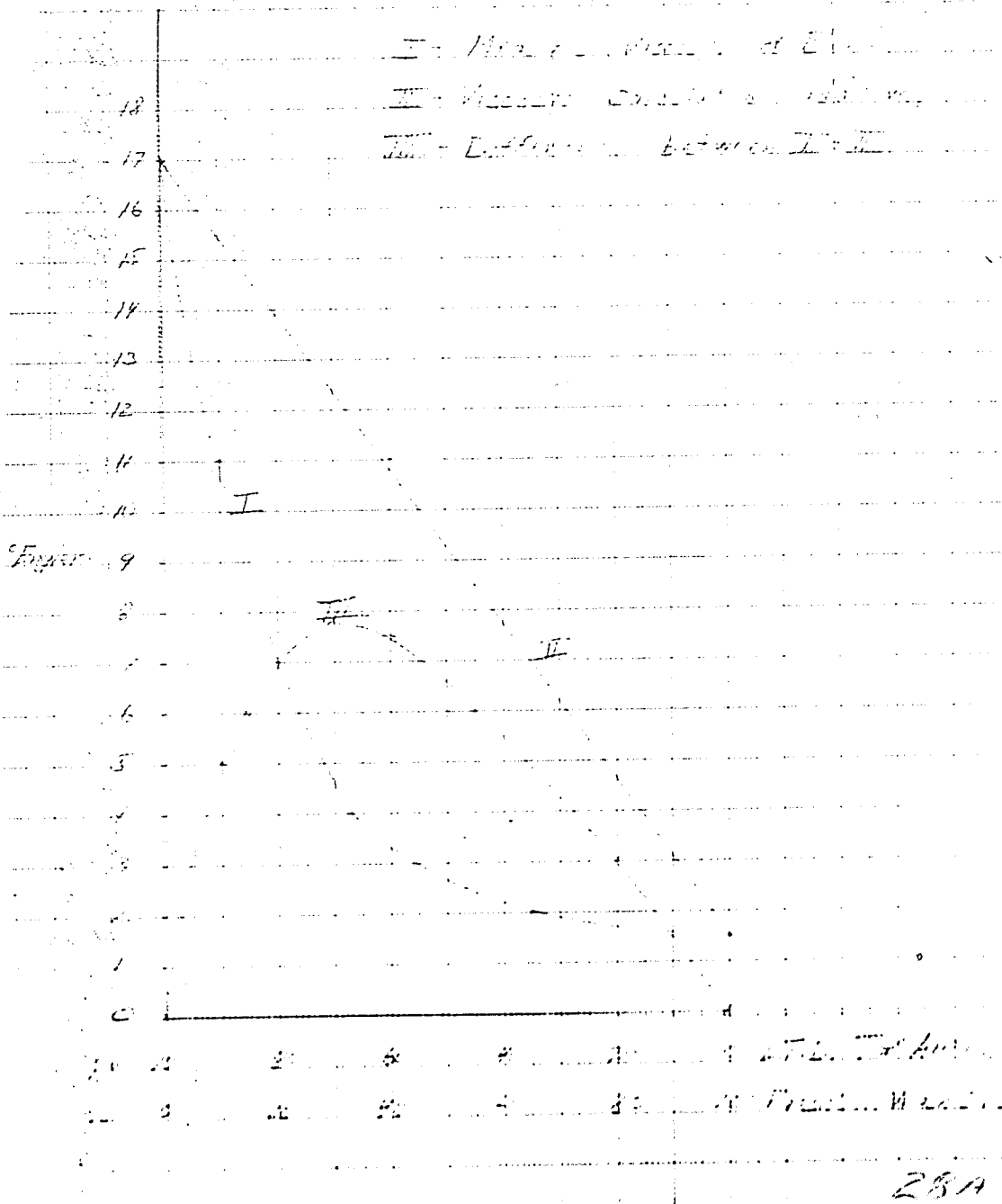
It may be said in summary that all the primarily aromatically constituted oils are mutually miscible in any proportion, without differences in the amount of asphalt content making any serious difference. This miscibility is not accidental but fundamental, and does not need to be reaffirmed for domestic oils. In contrast to the relationships existing for the petroleum fuel oils, it is advisable to mix the fuel oils that are primarily aromatically constituted with one another, as has already been done in part. Such mixing also achieves an additional improvement of their measuring values. These procedures make it possible to place additional amounts of fuel oils at the disposal of domestic users at reasonable prices and at the same time to protect the underground coal reserves. In the hard coal sector, and within the limits of the possible use of low temperature coals, it is the coking of hard coal that is chiefly capable of increasing the production output of fuel oil.

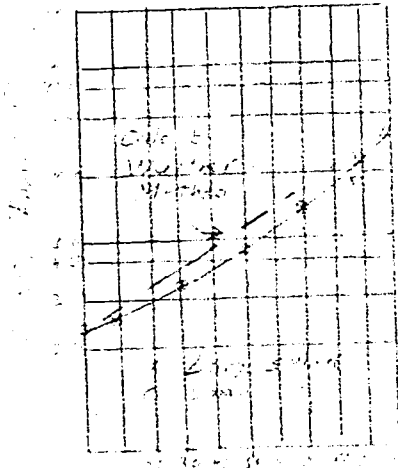
The miscibility of the primarily aromatic asphalt-containing fuel oils with aliphatic fuel oils may be accomplished by adding certain substances that will cause a re-dissolving of sludge, although in many cases these substances are not available or would be uneconomical to use. There is, moreover, the possibility of de-asphalting asphalt-containing aromatic oils by some suitable method, whereby one would have universal oils which have the advantage over the asphalt-free aliphatic oils of being solvents.

I cannot conclude my remarks without thanking Dr. Müller for his active support in the cooperative effort herein reported, nor without thanking my colleagues Dr. Borchers, Asbach, Dr. Stinendorfer and Dr. Porsch for their zealous cooperation.

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Fig 1 - Influence of Various Bacteria Upon the
 Cell walls of *Staph. aureus* in the B.P.





2. The graph shows the relationship between frequency and wavelength. The frequency increases from 1000 Hz to 10000 Hz, and the wavelength decreases from 30 cm to 3 cm. This indicates an inverse relationship between frequency and wavelength.

