Viscometric Process for Determining the Miscibility of Hydrocarbon Mixtures, Heating Oil in Particular

By: W. Demann and H.R. Asbach

The question whether different hydrocarbon mixtures are mutually miscible in all mixtures or only within a definite and limited range is, determined by the absence (or presence, as the case may be) of sludging out of hard asphalt or free carbon. Accordingly, a testing of the miscibility must first show definite qualitative or quantitative evidence of sluding out which is formed right after the mixing has been accomplished. Besides this it is necessary especially in the case of hydrocarbons (or oil mixtures) with relatively high boiling points, to establish whether, and to what extent, further sludging out takes place after standing rather a long time - sludging out which, under certain circumstances, is not recognizable immediately after mixing.

In the course of examinations conducted on various mixture systems, results of which were reported on a few years ago[1], (I Demann: Miscibility of Heating Oils. Glückauf 76 (1940) S. 61/68), it was shown that the previously proposed processes for detecting sludging out did not in all cases make possible a definite evidence of immediately formed sludging out. Various tests of the qualitative and quantitative processes that we used even today[2] (Harders: Oil and Coal (1937) S. 1162) probably yield definite and reliable evidence in the case of oil-mixtures of more highly viscous, dark, and opaque heating oils. Also the examination processes proposed for testing for and detecting sludging out formed after rather a long time standing 3 (3 DIN DVM E 3794 Oil and Coal 14 (1938) S.761; DIN DVM E 3793 Oil and Coal 14 (1938) S.761), process in which the mixtures in question were kept standing for a long time and then their flaking out determined mostly by visual observation could usually produce only very unsatisfactory results.

In 1939, a new method was developed which, in said to avoid the disadvantages mentioned above. This was done by supplementing the known examination processes with systematic examinations, which had been carried on over a period of years in the Krupp concern, for determining the miscibility of heating oils. This new method does not pretend to replace in all cases the analysis processes which were previously used for this purpose. Rather, it should fill the gaps which the known processes left open, and should make possible principally the recognition of sludging out in mixture systems with more highly viscous and opaque components. In advance it was required of this new examination process that in all cases an exact, i.e. reproducable ascertainment of sludging out should result, whether, this sludging out take place immediately or after standing for a certain time.

Before describing the process developed by us at the results obtained by its use, it appears suitable to discuss briefly the principles on which it is based.

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TABLE 1

Surface Tension @20°C in dyn/cm Heating Oil "A"	Surface Tension @20°C in dyn/cm of the Added Heating Oil	Surface Tension @20°C in dyn/cm of the Mixture 50:50	REMARKS
34.86	30.20	33.50	-
34.86	32.14	33.50	-
34.86	35.11	34.10	No sludge

The miscibility of heating oils is defined in terms of establishing the absence of the afore-mentioned sludging out upon and after mixing. The sludging out, which is possible when heating oils containing hard asphalt and free carbon are mixed, is dissolved out, according to statements in writings on the subject, chiefly because of the influence of a blending of a lesser surface tension than that of the oils with which they are mixed[4]. (F.J. Hellenstoyn: Chem. Weekbl. 36 (1939) S.362/66). This can cause, it is believed, a disturbing of a previously stable colloidal system, in accordance with individual relationships. This disturbance our knowledge of colloidal chemistry tells us, is due, actually, to an increase of the tension in surface of contact. This change in the surface of contact energy leads, in the final stage, to a coagulation of the dispersed phase (sol.). As was demonstrated by W.L.H. Moll[5] (5 W.L.H. Moll: Collord - Beih. 49 (1939) S. 1/79) through examination of the solubility of highly polymeric substances in different solvents, there occur first tunefaction, conversion into sols, and other reactions, all of which can take place at different rates of speed. Only after these intermediate stages have been passed through does the sludging out begin.

Apart from the exact and reproduceable ascertainment of sludging out which has resulted immediately after mixing, an attempt was to be made, especially in such cases as where sludging out does not occur until some time after mixing, to show in reproduceable fashion the preliminary conditions of the sludging out; and this was to be done as a substitute for the standing trials which are so difficult to carry out. It was obvious to us at the very beginning, that such a measurement - for reasons which will be discussed later - could be only of a qualitative nature. On closer observation, however, this fact does not entail any decrease in the possibilities of evaluation of a measuring process, since - especially in the case of highly viscous mixtures of hydrocarbon oils - one can usually no longer speak (if coagulation sets in) of a more or less clear separation of a solid and liquid phase, i.e. of the possibility of carrying out accurately a quantitative computation.

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Since, as is well known, most heating oils are colloidal systems, it was a matter of determining with particularly suitable processes the sludging out that takes place under given conditions when different oils are mixed and the in-homogenizing produced in the final stages as a result. And since, we are dealing with largely physical occurrences when sludging-out takes place, we expected from the beginning good results from the use of a physical process.

Recent examinations made together with Dr. Forsch (as yet not published) (6, compare also H. Forsch: Technical Information Krupp, Research Reports (Anthracite 11), 6 (1943) s. 57) have shown that coagulation can not be explained simply by a reduction in surface tension. Rather, it was found that in mixtures of hydrocarbon oils in which one component brings the surface tension of the mixture down below that of the other component, there is in some instances no sludging out, while in others there is considerable. The exact proof of this was able to be achieved, as Table 1 shows, by adding different oils with different surface tensions in the same mix ratio each time to a heating oil with hard asphalt content. In each case there occurs a decrease in the surface tension of the mixture to a point below that of the one component. All the added oils must be designated, in the more comprehensive sense, as capillary-active. In one case there was sludging out of hard-asphalt, but in both the others there was none.

The facts established by these as yet unpublished works led to the conclusion that, next to surface tension, the chemical nature and the dio-lectric constants of the oils in the mixture play a considerable part in whatever coagulation takes place. In this connection, the change in dio-lectric constants of the mixture as related to that of the components manifests, if not a complete, at least a less spotty conformity to law (or regularity) than is the case in connection with surface tension. In spite of this, we have not yet been able to get a clear relationship between the change in these physical magnitudes and a sludging-out of an oil mixture which takes place immediately or in a measurable time.

Now it is known from written works that viscosity, especially in colloids, is a very sensitive quantity, in that, minor changes in the conditions of the system, especially structure, change it to a measurable extent7 (7 Wo. Ostwald: Fundamentals of Colloidal Chemistry, Dresden 1912. S. 181; Wo. Ostwald: Kolloid - Z.12 (1913) S.219/22). Therefore it could be supposed that, of all measuring processes, an appropriate viscometric system would soonest offer a possibility of following the change in condition of colloidal systems, such as are probable in heating oil mixtures even before the sludging out or inhomogenization begins. For this purpose the apparatus developed by F. Höppler 8 (8 F. Höppler: Z. Tech. Phys. 14 (1933) S. 165.) proved, after thorough preliminary experiments with different apparatus on the market, to be the best suited of

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all viscosity meters mentioned as having been previously used. It is based on the principle of a ball falling in an inclined tube (pipe). From the time the ball moves, the dynamic and kinematic viscosity of the liquid under examination can be determined by means of the calibration factors. As yet we have not succeeded in attaining an exact mathematical derivation of the occurrences taking place in the Höppler viscosimeter. For a better understanding of the following, we shall now attempt, by using conscious simplifications, to give a derivation for viscosity measurment according to the falling ball process, a derivation which, in spite of the qualifications made above, will suffice to make mathematically understandable at least the occurrences involved in this measuring process in the following formulas:

m	=	Mass of the measuring ball.
s	=	Specific gravity of the measuring ball.
ϱ(rho)	=	Specific gravity of the liquid.
r	=	Radius of the measuring ball.
g	=	Gravity
v	=	Velocity of the measuring ball.
a	=	Measuring way (path)
α	=	Angle of inclination of the pipe.
η	=	Dynamic viscosity.
t	=	Running time of the ball.

When the ball is introduced into the pipe it is effected by the force (k^1)

(1) $$k^1 = m.g. \sin. \alpha$$

This force is opposed to the buoyancy that the ball experiences in the medium, so that the forces (k) actually affecting the measuring ball are re-calculated to:

(2) $$k = \frac{4r^3}{3} \pi (s - \varrho) . g . \sin. \alpha$$

As the measuring ball is moving in a viscous medium, we must take into account the resistance k_w given by the Stokes formula:

(3) $$k_w = 6 \eta . \pi . r . v$$

Thus we get:

(4) $$\frac{4}{3} . r^3 \pi (s-\varrho) . g . \sin. \alpha = 6 \eta . r . v . \pi$$

(5) $$\eta = \frac{2r^2 (s - \varrho) . g . \sin. \alpha}{9v}$$

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In the Höppler viscosimeter the velocity with which the ball sinks between etched markings, i.e. the distance s traveled by the ball in the time unit t, is determined. As the ball moves with constant velocity over the measured distance, we get instead of v the expression:

$$v = \frac{s}{t}$$

If this expression is put in place of v in equation (5) we get:

$$(6) \qquad u = \frac{2r^2 g \cdot \sin \alpha}{9s} \cdot (s-\varrho) \cdot t.$$

The first quotient consists only of constants, namely the radius r of the ball, gravity g, the sine of the angle of inclination and the sinking path s. The last one becomes likewise an apparatus constant by means of the etched-in marks on the measuring pipe. If we replace the expressions:

$$\frac{2r^2 g \cdot \sin \alpha}{9s}$$

By the constant value A, we get the equation:

$$(7) \qquad u = A (\sigma - \varrho) \cdot t.$$

The expression shows that the sinking time of the ball is directly proportional to the dynamic viscosity, multiplied with the apparatus constant A, and the correction for buoyancy ($\sigma - \varrho$). A dimension examination of the above equation leads to the correct dimension value for the dynamic viscosity:

$$(g^{-1} \cdot cm^{-1} \cdot sec.^{-1}).$$

The measuring balls with which the Höppler viscosimeter is equipped undercut each other in the succession in their measuring ranges. In examining a homogeneous system, dynamic viscosities, which agree with each other within error limits are obtained by using two balls which undercut each other in their measuring ranges. It is however, a condition of this measuring that the gliding time of the balls used must at each instance not be less than 30 seconds; otherwise Stokes' Law, which is the basis of this measuring loses its validity (transition from lamiler to turbulent flow). A lamiler measuring of this sort, with two balls undercutting each other in their measuring ranges, we will henceforward, for brevity's sake, call "Kugelschnitt" (Ball cutting).

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There are different ratios when the "Kugelschnitt" is used in the in-homogeneous system within a range which still admits the fundamental possibility of measuring viscosity. In such a system, the measurement, with two balls of differing diameters, the one succeeding the other, gives different gliding times, and differing viscosity values.

A section view of the pipe and ball of the Höppler viscosimeter shows that the fluid to be measured flows past the ball through a sickle-shaped circular gap. The size of this gap is dependent upon the ratio of the pipe diameter to the ball's diameter - in inverse proportion; i.e. the greater the diameter of the ball, the smaller the sickle-shaped circular gap. If the liquid passing through this gap is homogeneous, then we will get for the running time of two measuring balls values which, according to the calibration of the device, provide equal (within error limits) viscosities when put into equation (7). If, on the other hand, the medium flowing through the gap is not homogeneous, then these in-homogeneities will make themselves more plainly perceptible with a smaller gap (and larger ball) than with a larger gap consequently with the larger ball a greater increase of the running time t_1 occurs than with the small one, which, calculated according to formula (7) leads to a greater viscosity increase for the larger ball. In borderline cases the larger ball can even stop in the pipe because of in-homogeneities of the system to be measured, so that its running time $t_1 = \infty$ (infinity); whereas, the smaller ball in the same system still yeilds a measurable running time. From these representations it is evident that the sensistivity of the process depends upon the difference in radius of the measuring balls used. In increases with the increasing radius - difference - but we must not overlook the fact that the smaller ball must never be allowed to exhibit a running time of less than 30 seconds.

As we have already remarked, the viscosity of a colloid exhibits positive magnitudes at the slightest change in the conditions of the system. Now, if one wishes to draw inferences based upon available variations in the "Kugelschnitt" as to the degree of homogeneity or in-homogeneity of the liquid under examination, the following points of view will be indicative. Above all, the oil or oil mixture to be measured must be free or nearly free from gritty impurities, as these even though foreign to the system can be mistaken for an in-homogeneity which really does not exist in the sense of an in-homogeniety which will mean sludging-out of hard asphalt or free carbon. To eliminate these sources of error, all oils to be examined must first undergo filtration through glass grits. Furthermore, an in-homogeneity can be caused by a too high water-content of the components of the mixture. However, since in judging miscibility we are not so much concerned with recognizing a condition of in-homogeneity in the general sense, but rather with a condition of in-homogeneity due to sludging-out, it will be advantageous, as exhaustive tests have shown, to reduce the water content of the oils below 1 %.

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Besides the afore-mentioned influences - foreign bodies and water content - affecting the viscosity variations in the "Kugelschnitt", we must also take into consideration the following points. Every apparatus shows a definite accuracy of measurement, and in the Hoppler viscosimeter this is of the order of ± 0,5 % (when working conditions are maintained). This accuracy is applicable to normal measurement that is done with a ball. Using the "Kugelschnitt" we found that the error limit rises to ± 1 %. Variations in the "Kugelschnitt" of this order of magnitude fall within the error range of the apparatus and cannot be clearly blamed on an inhomogeneity at the oil being examined. Furthermore, we must remember that technical heating oils, (and it is with the determination of their miscibility that we are now principally dealing) do not necessarily represent homogeneous systems in the strictest interpretation of the concept. Many of these oils are in manufacture loaded with foreign bodies which are present in such finely divided form that they cannot be removed even by filtering before making the tests.

Besides these foreign matters, in-homogeneities may be caused by finely distributed paraffine flakes, and hence, also by highly dispersed droplets of water. In this latter case the water content may even be below 1 %. The measureable in-homogeneities thus caused, may be disregarded for all practical purposes in any consideration of the miscibility of fuel oils. In order to eliminate them from any evaluation, we found in the course of our experiments that the permissible limit of variation in spherical section (Kugelschnitt) should be fixed at 2 %. All systems that show variations within this value can, as thorough tests have shown, be considered homogeneous for technical purposes. If the variation in the spherical section amounts to more than 2 %, this is a clear indication of the presence of an inhomogenization that may not be disregarded in evaluating the miscibility.

The degree of the variations of the viscosity values determined with both balls in the case of spherical section shows, as was proved in countless experimental series, a qualitative, accurately reproduceable measure of the degree of inhomogeneity of the mixture concerned. The phenomenon just described gives us a ready means of determining the beginning and the progress of an inhomogenization of mixtures of two or more fuel oils. It should be noted here, that the same phenomenon is to be observed when the turbidity zone is reached, for example, in benzine and aniline and similar systems.

It is useful in characterizing the miscibility or non-miscibility of fuel oils to determine the beginning of the in-homogenization dependent upon a change of the mixture proportion occurring at the same time intervals. We will discuss this test system again later.

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It is, moreover, clear that it is possible by measuring the viscosity of a definite mixture proportion of two or more fuel oils to determine whether a homogeneous or in-homogeneous mixture be present. In the case of mutually non-miscible fuel oils it is not only possible to determine the in-homogenization preceding sludging, but also sludging dependent upon the proportions of the mixture. A beginning of in-homogenization tells us that with this mixture proportion sludging will occur after considerable storage periods. In the most usual cases it suffices for this purposes if flaws in the mixture of 20:20 parts are selected. Keeping in mind also the viscosity-mixture relationship of Ubbelohde and Walther, the following should be noted:

In the viscosity temperature measuring table of Ubbelohde and Walther there is also contained a section for computing the mixing or mixture viscosity of two oils. In the use of this the "figured" viscosities of all mixtures are given by joining in a straight line the viscosities of the initial components over the parameter of the mixture ratio. If one enters in this network of coordinates the discovered viscosity values of the individual mixtures, this results:

The viscosity values of a homogeneous, i.e. miscible system of two components either lie on the above mentioned theoretical straight line or generally slightly under it, which last, in our opinion, can be explained by a mutual solution of crystalloid parts, such as, parafines and similar substances.

At any rate, when the spherical section is used, as long as no in-homogenization or sludging occurs while the measurement is being made, any variation of the measured viscosities with both balls over the previously stated range of 2 % could not be determined (The pre-requisite is absolutely constant temperature during the test)

In the case of the in-homogeneous systems the relationships are fundamentally different. Within a mixture series of two components there occurs a rise of the measured viscosity over the mixture-viscosity-curve of Ubbelohde and Walther just before the mixture gap is reached, i.e. just at the start of the area of in-homogeneity. At the same time it can happen that with the same mixture proportion a variation of over 2 % cannot be determined, in the viscosities measured with both balls using the spherical section. This suggests that just before sludging a swelling (tumefaction) or even a solvat formation occurs, which recent research shows often runs parallel with a corresponding change of the specific gravity. Since, this phenomenon is to be regarded as a forerunner of an in-homogenization in the sense of a progressive increase of the asphalt precipitating component in the mixture system concerned, our research shows the possibility of replacing bothersome storage tests by viscosity measurements in such cases. For in all cases in which the measured viscosity exceeds the mixture-viscosity-curve of Ubbelohde and Walther, it is a question of mixtures which will later become in-homogeneous, even if no serious variations can be determined by spherical sections immediately after the mixing.

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After this area is passed, which can only be shown for higher viscous mixture systems, the so-called mixture-gap occurs, i.e. the area of actual inhomogenization. From here on the spherical section shows a variation of the viscosities measured with two balls of over 2 %. Furthermore, the temporal progress of sludging can often be recognized by the fact that when the measurement is repeated after a certain length of time, it is no longer possible to reproduce the viscosity values previously achieved with a certain definite ball. In this case a rise or drop in viscosity values may be determined if the time element is allowed to go on, but the variation of the values arrived at with consecutive balls generally, but not in order of magnitude, remains constant, this suggests that in the first case one is dealing with the expression of a speed of sedimentation for the sludging that differes according to the existing conditions. The more rapidly this rises, the more or the faster the viscosity drop. The dropping of the measured viscosity, as related to the corresponding points of the mixture-viscosity-curve of Ubbelohde and Walther, is in this case much greater than in the case of miscible systems in which a mutual solution of previously crystalloid or microcrystalloid parts is present. In this connection it must be observed - and, as previously said, this limits the applicability of this method - that after final and complete sedimentation of all the sludged parts, the spherical section can no longer show variations of over 2 %. Under these circumstances, the measurement yields values which one would also get in the ideal case after the sludged out consitutents were removed, as by filtering. These relationships, which it was possible to show in many tests, occur principally in low-viscous, non-miscible systems, in which the sedimentation - speed of the sludged parts can be so great that they precipitate out on the bottom or on the surface of the mixtures in the shortest time (during the test).

In the second case, i.e. where the viscosity rises when the measurement is repeated after a time and which is supposed to occur in only the case of higher-viscous oils, we think there exists a precipitation process which goes on at a measurable speed of reaction. If followed further this reaches a maximum amount and then, depending on the magnitude of the sedimentation speed, it either stops at this value or approaches a minimum determined by the length of time involved. Under certain circumstances the reaction speed at 20°C can be so small that any sludging of hard asphalts or free carbon in measureable amounts occurs only after many hours. In such cases, directly after the mixture to be tested has been mixed, the spherical section will agree within the permissible limits, or will only show such slight variations that one might assume the system to be miscible. In order not to be exposed to such a deception, it has proven advantageous to increase the reaction speed of the precipitation reaction that may occur by raising the test temperature. Thorough measurements have shown, that at 50°C the sludging of hard asphalts or free carbon occurs in each case so rapidly, ie. the reaction speed becomes so great, that the spherical sections vary from one another within the corresponding limits or framework.

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At this point we should mention a special case which can occur especially in the case of fuel oils containing paraffine. With such oils it was noted that at a test temperature of 20° without the admixture of any other mixture component, serious variations up to 9 % can occur in the spherical section. If the same fuel oil is tested at 50° without any other treatement, the variations in spherical section fall below 2 %, i.e. they move within certain known, definite limits. This is a typical in-homogenization caused by paraffine sludging, which are dissolved again at higher temperatures. If any precipitation of asphalts or of free carbon occurs, then, as was said above, with any raising of the test temperature the variations in the spherical section would either remain constant or become still larger. With such fuel oils one may speak of a removable in-homogenization, in which case the sludging of asphalts or free carbon must conversely be spoken of as non-removable in-homogenity.

It was possible to prove by many experiments the conformity to certain laws and the facts that were developed in part from the results set forth in the various publications in the field. Some typical cases were chosen from the multiplicity of results at hand, in which, as will be shown below, all the phenomena are evident that lie within the limits of the discussion.

After having now discussed the theoretical bases of the new research method, we are going to discuss the experimental features of the method based on some mixture systems that have been so selected from the results at hand as to serve as useful examples for most cases occurring in general practice.

TABLE 2

Fuel Oil	Hard Asphalt Content %	Specific Gravity @ 50°C	Viscosity in Cp @ 50°C Small Sphere	Viscosity in Cp @ 50°C Large Sphere	Δ Cp in %
A	6.84	0.964	1,479.40	1,492.30	0.87
B	0.56	1.009	15.65	15.81	1.01
C	13.99	1.016	13.32	13.48	0.18
D	0.00	0.832	2.39	2.41	0.82
E	9.46	0.972	231.17	233.81	1.12
F	0.49	0.851	4.92	4.96	0.81
G	8.24	0.957	77.56	78.28	0.92
H	0.47	0.956	7.20	7.31	1.42

Table 2 shows, the oil components to be used in the mixture series herein described with their most important analyses.

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In the first test series to be discussed we have a mixture of fuel oil A with fuel oil B. The viscosity of each of these oils as well as that of their mixtures 80:20, 50:50, 20:80 at 20° was determined in the Höppler viscosimeter and a spherical section was made at each viscosity measurement. Columns 4 and 5 of Table 3 shows the values arrived at. The final column of each table shows the percentual variations Cp between the viscosity values measured with two balls.

TABLE 3

Wt. % Fuel Oil "A"	Wt. % Fuel Oil "B"	Sp. Gravity @ 20°C	Viscosity in Cp @ 20°C Small Sphere	Viscosity in Cp @ 20°C Large Sphere	Cp in %
100	0	0.983	32,685.56	33,026.00	1.03
80	20	0.989	4,409.70	4,449.38	0.89
50	50	0.998	372.92	374.60	0.45
20	80	1.009	71.28	71.73	0.63
0	100	1.013	27.26	27.39	0.47

Figure 1 shows graphically the values found in the log-log system according to Ubbelhode and Walther, in which the ordinate shows the viscosities in centipoises and the abscissa shows the composition of the mixture in weight percentages. The connecting line of the viscosity from 100 weight percent A and 100 weight percent B (dotted line) represents the theoretical mixture-viscosity-curve of both oils.

The viscosity values from the measurement made with the larger ball are shown as crosses, those from the measurements made with the smaller ball are shown as circles.

As Table 3 shows, the variations in the case of the spherical section, i.e. the Cp values of all mixtures, vary less than 2 %. This is also shown graphically where the viscosity values of both balls coincide. Furthermore, all the mixture viscosities lie on the theoretical viscosity curve. The graphical coincidence of the spherical sections and their magnitude of less than 2 % show, as was said earlier, thatthis is a case of two freely mutually miscible oils, which represent a "homogeneous" system, in any mixture proportion, that is free from sludging of hard asphalt or free carbon. Storage tests made on the same mixtures yielded the same results.

Figures 2 and 3 show two further examples of the curve of freely mutually miscible systems. Here it is a matter of a mixture of fuel oils B and D or E with B. In Tables 4 and 5 the viscosity values for both balls and the accompanying percentual variations Cp are shown.

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TABLE 4

Wt. % Fuel Oil "B"	Wt. % Fuel Oil "D"	Sp. Gravity @ 50°C	Viscosity in Cp @ 50 ° C Small Sphere	Viscosity in Cp @ 50°C Large Sphere	Δ Cp in %
100	0	1.009	15.65	15.81	1.01
90	10	0.999	11.48	11.61	1.11
70	30	0.951	6.84	6.90	0.86
50	50	0.915	4.60	4.65	1.08
30	70	0.883	3.31	3.35	1.19
10	90	0.851	2.48	2.50	0.80
0	100	0.832	2.39	2.41	0.82

As may be seen from Figures 2 and 3, in the graphical representation the viscosities measured with two balls, i.e. the spherical sections, coincide. The corresponding Tables of figures in no case show a Δ Cp of over 2 %. This finding indicates what for practical purposes is complete homogeneity of all mixture relationships or proportions that might occur. But what differentiates these curves from the one in Figure 2, is the fact that this time there is no agreement of the theoretical

TABLE 5

Wt. % Fuel Oil "B"	Wt. % Fuel Oil "D"	Sp. Gravity @ 50°C	Viscosity in Cp @ 50°C Small Sphere	Viscosity in Cp @ 50°C Large Sphere	Δ Cp in %
100	0	0.972	231.17	233.81	1.12
90	10	0.976	158.76	160.12	1.34
70	30	0.982	84.42	85.85	1.60
50	50	0.990	45.37	45.88	1.11
30	70	0.998	28.83	28.91	0.28
10	90	1.003	18.90	19.09	0.99
0	100	1.009	15.65	15.81	1.01

with the measured viscosities, but that the latter in all cases lie beneath the Ubbelohde and Walther curves. This, in itself slight drop of the measured viscosities below these that were theoretically required can, we think, be explained by a mutual dissolution of crystalloid and microcrystalline oil constituent parts. This in no way affects the homogeneity of the mixture, since, as may be seen from the curves and the tables, the spherical sections show no variations of more than 2 %. Comparative tests on all the mixtures thus far used showed, after a storage time of 6 months, no more precipitate than would occur with pure mixture components.

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TABLE 6

Wt. % Fuel Oil "C"	Wt. % Fuel Oil "D"	Specific Gravity @ 20° C	Viscosity in Cp @ 20°C Small Sphere	Viscosity in Cp @ 20°C Large Sphere	Cp in %
100	0	1.036	82.03	81.65	1.01
95	5	1.031	65.22	66.07	1.28
90	10	1.018	56.76	57.23	0.82
85	15	1.006	46.48	46.57	0.19
80	20	0.997	38.22	38.42	0.52
75	25	0.987	32.96	33.21	0.72
70	30	0.976	28.01	28.13	0.36
65	35	0.951	18.06	18.24	0.99
60	40	0.940	14.38	15.22	5.52
55-I	45	0.933	10.72	15.24	29.66
55-II	45	0.933	15.98	32.59	50.96
0	100	0.858	4.73	4.73	0.00

Since Figures 1 to 3 show examples of absolutely miscible systems, Figures 4 to 8 all show mixture-viscosity-curves of systems which are not freely mutually miscible.

The pair of fuel oil C with fuel oil D shown in Figure 4 remains homogeneous up to a mixture proportion of 70 C to 30 D. The spherical sections of the individual mixture proportions, i.e. the Δ Cp values, all lie below the permissible limit of 2 %, as Table 6 shows. Moreover, the spherical sections coincide on the graph. When the above mentioned proportion is exceeded, the measured viscosity drops below the theoretical viscosity, while the spherical sections still show coincident values. If the fuel oil component D is further increased to 40 percent of weight, then a variation of the viscosity values measured by the two balls occurs, which amounts to 5.52 %. If the D component is still further increased, i.e. to a mixture proportion of 55 C to 45 D, the variations in the spherical become quite considerable and are inconstant in point of time. Table 6 shows that at this point in the mixture series, and with the larger ball, differences up to about 17 Cp resulted, i.e. based on the theoretical viscosity of about 18 Cp, a variation of 94.4 %. From the proportion 60 C to 40 D the mixture gap of this system begins and hence, the sludging of hard asphalts. It is useless to run the curve beyond the proportion of 55 C to 45 D, apart from the fact that in such a range no exact measurement of viscosity is longer possible, because any measurement of viscosity in this range of in-homogenesity would yield no results that could be evaluated for practical application.

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TABLE 7

Wt. % Fuel Oil "C"	Wt. % Fuel Oil	Specific Gravity @ 50° C	Viscosity in Cp @ 50° C Small Sphere	Viscosity in Cp @ 50° C Large Sphere	Δ Cp in %
100	0	1.016	13.32	13.48	1.18
95	5	1.009	12.22	12.37	1.21
90	10	0.999	10.90	11.08	1.62
85	15	0.988	9.61	9.71	1.02
80	20	0.979	8.65	8.76	1.25
75	25	0.966	7.72	7.91	2.40
70	30	0.957	7.30	8.01	8.86
70	30	0.957	7.36	8.63	15.19
65	35	0.931	5.42	5.45	0.92
60	40	0.922	5.10	5.11	0.20
55	45	0.913	5.30	5.36	1.12
0	100	0.832	2.39	2.41	0.82

If, as said above, with a proportion of 55 C to 45 D the viscosity measurement was made again a little later, Table 6 shows, that the smaller ball, in contrast to the first measurement of 10.72 Cp, now has a value of 15.98 Cp. The proportions were about the same for the larger ball also where 15.24 Cp was found with the first test, and 32.59 with the second. It seemed as if this might be or give evidence of a sludging process operating with a measurable reaction speed. If this supposition was correct, as was said above, using a higher temperature would cause an acceleration of the sludging reaction. So the temperature was raised from the 20° of the first test to 50°. The measuring values attained are shown in Table 7 and the curve is shown graphically in Figure 5. It will be seen that by increasing the temperature the mixture gap is moved to the right, i.e. while a mixture of 80 fuel oil C with 20 fuel oil D at 20° is to be considered practically homogeneous, nevertheless at 50° in the same series there begins at this point a tumefaction or solvat formation. According to Figure 5, the start of the actual sludging of hard asphalts begins with the proportion of 75 C to 25 D, which may be clearly seen by the variation of the spherical section of over 2 %. As the asphalt precipitating component D is progressively added, the variations in spherical section become greater, reaching a maximum at a mixture proportion of 70 C to 30 D of 15.19 %. When this proportion is exceeded, Table 7 shows that the spherical sections vary under 2 % again and thus coincide on the graph. This fact is surprising in itself. But it may be explained by the fact that raising the temperature accelerates the reaction speed of the sludging process. This is expressed by the shifting transposition of the mixture gap in the direction of a smaller part of the fuel oil component D, i.e. from the proportion 60 C to 40 D at 20° to the proportion 75 C to 25 D at 50°. Moreover, by raising the measuring temperature the sedimentation speed of the sludging is so increased that sludge appears on the bottom of the viscosimeter even during the test. The mixture which then

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remains standing over the sludge has thus practically become homogeneous again. Since, during the test the balls only run through the space over the sedimented sludge, i.e. since, they only sink through a homogeneous medium, the spherical sections in this case must again yield values of less than 2 %. This the recession of the Cp values beneath the permissible limit in the case of the proportions of 65 C to 35 D 60 C to 40 D, and finally 55 C to 45 D, have a natural explanation. Figure 6 and Table 8 show the results of measurements of a mixture series of fuel oil C with fuel oil F. The graph, upon superficial observation, resembles Figure 2, and in fact the measured viscosities here also lie below those that are theoretically required. But, the difference between the theoretical and the measured viscosity is much greater.

TABLE 8

Wt. % Fuel Oil "C"	Wt. % Fuel Oil "F"	Specific Gravity @ 50°C	Viscosity in Cp @ 50°C Small Sphere	Viscosity in Cp @ 50°C Large Sphere	Cp in %
100	0	1.016	13.32	13.48	1.18
90	10	0.975	8.51	8.81	3.46
70	30	0.946	7.39	7.67	3.65
50	50	0.907	6.32	6.86	7.87
30	70	0.884	5.61	6.25	10.24
10	90	0.862	5.15	5.72	9.96
0	100	0.851	4.92	4.96	0.81

Furthermore, even at a ratio of 90 C to 10 F, the spherical sections begin to show slight differences, which then become greater as the admixture of fuel oil F components increases. According to the examples thus far, a variation of the spherical section of more than the permissible limit of 2 % is always the result of inhomogenisation just beginning, which, however, in this case, i.e. in a proportion where the viscosities measured with both balls lie below the theoretical curve, has not yet led to the final stages of sludging. In these mixtures one is not yet able to detect any sludging with the naked eye. The coagulation of precipitated materials only becomes visible at a proportion of 70 C to 30 F. The system shown in Ill. 6, thus, represents a typical example of a series in which no sludging may be detected with the naked eye up to a certain mixture proportion, here 70 C to 30 F. As thorough storage tests on such systems showed, sludging does, nevertheless, occur at the proportions named and after considerable periods of storage. The speed of coagulation or of sedimentation in such systems is very slight in comparison with that shown in Figure 4, and the recognition of sludging or any decision as to the miscibility of such oils must take a great deal of time with the present methods, if it is possible at all. Figure 7 (Table 9) shows the path of a mixture curve of fuel oil B with fuel oil D. Here, a measurable zone of tumefaction precedes the mixture gap, which begins at a mixture ratio of about 30 B to 70 D.

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Viscosity measurements made some time later on this same mixture proportion showed that, as was suspected, the progressing coagulation caused an increase in the viscosity values measured some time later. Hence, here also the coagulation of asphalt substances occurred with measureable velocity speed.

Similar relationships exist, as shown in Figure 7, for the pair of fuel oil G with fuel oil C, shown in Figure 8 and Table 10. As may be seen, the mixture gap for this system is at the proportion of 10 G to 90 C. From 30 percent of weight of fuel oil G on up, all other mixture proportions are homogeneous and completely free from sludging.

TABLE 9

Wt. % Fuel Oil "G"	Wt. % Fuel Oil "D"	Specific Gravity @ 50° C	Viscosity in Cp @ 50° C Small Sphere	Viscosity in Cp @ 50°C Large Sphere	Cp in %
100	0	0.956	7.20	7.31	1.48
90	10	0.944	6.26	6.34	1.25
70	30	0.918	4.70	4.75	1.05
50	50	0.892	3.55	3.63	2.20
30	70	0.868	2.84	3.05	6.88
30	70	0.868	3.14	3.65	13.97
30	70	0.868	3.18	3.80	16.31
10	90	0.847	2.53	2.61	3.06
0	100	0.832	2.39	2.41	0.82

TABLE 10

Wt. % Fuel Oil "G"	Wt. % Fuel Oil "C"	Specific Gravity @ 50° C	Viscosity in Cp @ 50°C Small Sphere	Viscosity in Cp @ 50°C Large Sphere	Cp in %
100	0	0.957	77.56	78.28	0.92
90	10	0.969	61.21	61.54	0.54
70	30	0.973	30.84	31.12	0.89
50	50	0.995	23.76	23.93	0.71
30	70	1.001	20.43	20.49	0.29
10	90	1.009	15.55	16.98	8.42
0	0	1.016	13.32	13.48	1.18

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By W. Ehmann and H.R. Asbach

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SUMMARY

The present essay discusses a method for determining the miscibility of fuel oils. It is based on a measurement of viscosity in the Hoppler viscosimeter, in which the viscosity measurement is not made with the usual one, but with two balls which correspond (überschneiden) in their measuring areas. The variations thus discovered between the viscosity values determined by the balls of different diameter are connected with the degree of in-homogenity of the oil mixture being studied. From countless examples it can be shown that not only the beginning but also the final stages of a coagulation may be recognized. Compared to other methods in use to date, this method has the advantage, that although it is only qualitative, it is more sensitive and it saves a tremendous amount of time.

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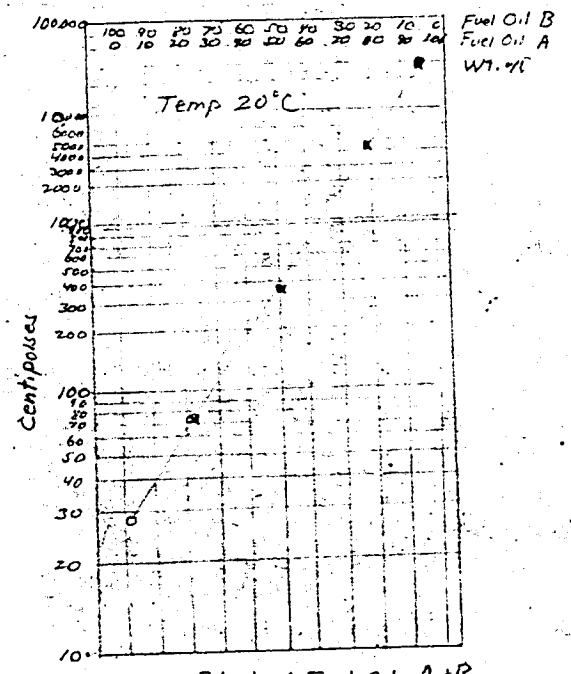

Fig. 1, Blend of Fuel Oils A+B

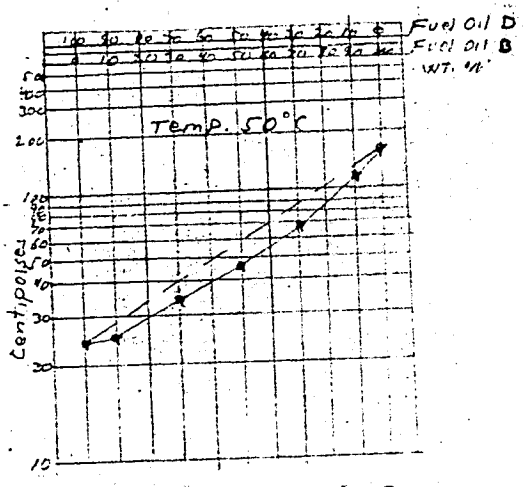

Fig. 2 - Blend of Fuel Oils B+D

Note: In all Curves X = Large Sphere
C = Small "

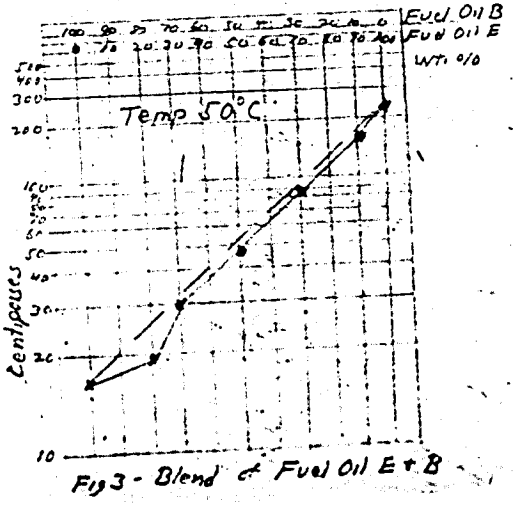

Fig 3 - Blend of Fuel Oil E + B

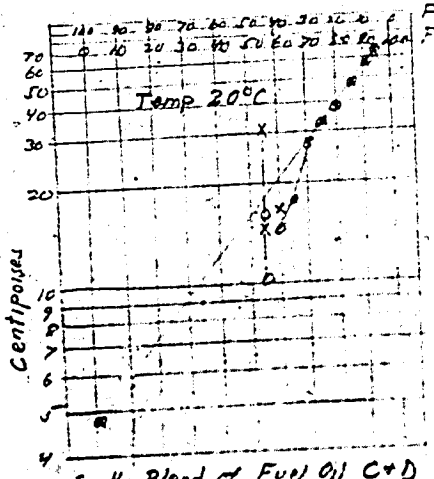

Fig. 4 - Blend of Fuel Oil C+D

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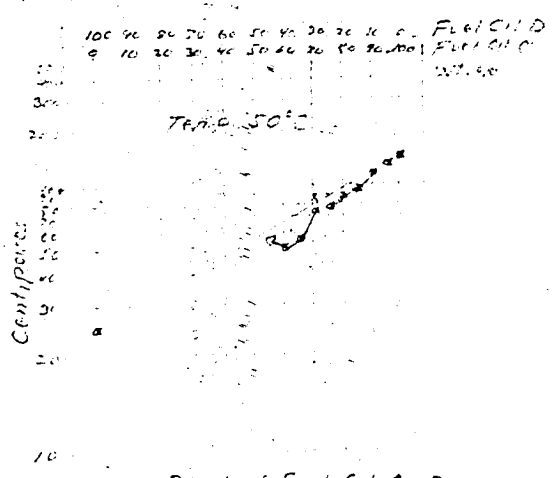

Fig 5 - Blend of Fuel Oil C+D

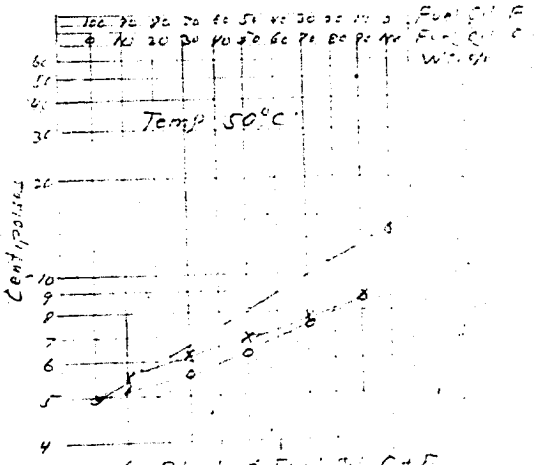

Fig. 6 - Blend of Fuel Oil C+F

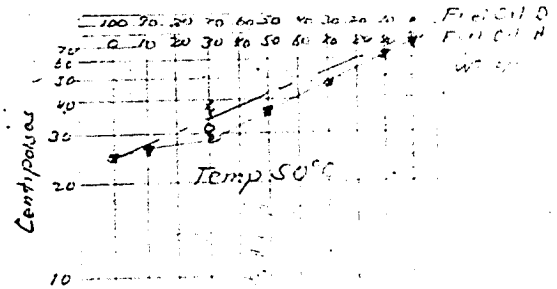

Fig. 7 - Blend of Fuel Oil H+C

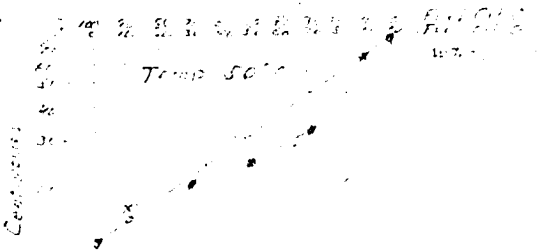

Fig 8 - [illegible]

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