

## Report 9288

THE CONNECTION BETWEEN THE "U.O.P. CHARACTERIZATION FACTOR"  
AND VARIOUS OTHER PROPERTIES OF PETROLEUM FRACTIONS. III

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TranslationN. V. de Bataafsche Petroleum Maatschappij  
Laboratory---AmsterdamPURPOSE AND SUMMARY OF THE EXAMINATION.

In the report No. 9026 it is shown that there is a clear <sup>2332</sup> connection between the "U.O.P. characterization factor" and the aromatic, naphthene and paraffin contents of petroleum fractions of the gas and lubricating oil type. A preliminary comparison (equation) still based on data for the composition of the oils obtained by the application of the ring analysis in accordance with the Sundry Methods Book E 18 has already been worked out in same. Furthermore, starting from the data for individual hydrocarbons, a second comparison was set up which led to somewhat different results than the first mentioned method based on oil data.

In the meantime, however, in connection with the examination for the revision of Method E 18, there have become known more accurate data concerning the composition of the oils; these data have been used in the following in order to impart to the comparison - which expresses the connection between the characterization factor and the composition - a more definite form.

CONCLUSIONS

The revised comparison (equation) for the connection between the characterization factor K and the composition reads

$$K = 0.0869 A + 0.1060 N + 0.1326 P \quad (1)$$

(A, N and P represent herein the percentages of the C-atoms which are contained in the aromatics, naphthene and paraffin structure).

The results obtained from this comparison (equation) were satisfactory; for the 42 oils of different type and molecular weight the values which were computed for the characterization factor by the use of the Equation (1) and the accurate composition figures deviated in the average (with the same reference numbers) only 0.07 from the "true" characterization factor (greatest deviation 0.20).

If one does not have accurate data concerning the composition but only concerning the results of the ring analysis in accordance with Method E 18, it will often be possible to use Comparison (equation) (1) without difficulty, even though the agreement between the K-values computed on basis of E 18 and the true K-values in the case of the 42 kinds of oil which were examined was on an average somewhat less satisfactory (mean deviation 0.10; greatest deviation 0.53).

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On basis of E 18 there were obtained for the non-hydrogenated oils somewhat better results when applying the equation already used for oils in the Report No. 9026, namely:

$$K = 0.0935 A + 0.1010 N + 0.1312 P \quad (2)$$

For hydrogenated oils this comparison (equation), however, gives definitely less satisfactory results than the comparison (1).

Furthermore it appears that the comparison (equation) appearing in the Report No. 9026 on basis of data of individual hydrocarbons, namely:

$$K = 0.0967 A + 0.1094 N + 0.1280 P \quad (3)$$

when applied to petroleum fractions did not satisfy, either when using the composition in accordance with Method E 18 or when using the accurate composition.

For practical purposes one may, independent of the method for determination of the composition, frequently be satisfied with the approximate comparison (equation) obtained by rounding off:

$$K = 0.088 A + 0.106 N + 0.132 P \quad (5)$$

The results are shown completely in Tables I A and I B.

#### INTRODUCTION

In the first Report on the above subject (No. 9026) there was shown among other things that for petroleum fractions there exists a direct connection between the "U.O.P.-characterization factor" and the chemical composition. The characterization factor K can be computed for the non-hydrogenated oils with reasonable accuracy from the aromatic, naphthene and paraffin content with the use of equation:

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$$K = 0.0935 A + 0.1010 N + 0.1312 P$$

(A, N and P represent the percentages of the total number of C-atoms present, which are contained in the aromatics, naphthene and paraffin structure, respectively).

This comparison was of a preliminary character; in connection

with the derivation, use was made of data of oils, the composition of which had been determined with the use of the not very accurate ring analysis method in accordance with the Sundry Methods Book, Method E 18.

In the meantime, in connection with the examination carried out for the revision of the Method E 18, the composition of these oils has been determined in a more accurate manner. The data obtained are now used in order to impart to the comparison concerning the connection between K and the composition a more definite form.

#### CARRYING OUT OF THE EXAMINATION

##### 1. The oils used, their characterization factors and their compositions.

The data which were used for the revision of the above mentioned connection between K and the composition all refer to the oils mentioned in Table II of the Report No. 9026, namely, to the oils to which reference has already been had in the data contained in the temporary comparison appearing in the Report No. 9026. All the products mentioned in Table II of the said report have been used except the four net hydrogenated Miri-fractions and the hydrogenated B VII oils, the accurate composition of which cannot yet be determined for the present. The oils used cover a wide field both with respect to type and composition and with respect to their boiling point.

It is clear that the values for  $K_{kpt}$ , which have been mentioned in Report No. 0926 for these oils, can be taken over in this connection without any difficulty ( $K_{kpt}$  is the K-value which, in accordance with the definition of the characterization factor, is computed directly from the average or mean boiling point and the specific gravity of the oils).

The improved determination of the "ring" composition requires some explanation. The aromatics-containing oil, the composition of which had to be determined, were completely hydrogenated for this purpose, which means that the aromatics present were converted in the corresponding saturated ring systems. The part of the C-atoms which was contained in the products after hydrogenation in the naphthene ring structure could be derived from the main molecular formula of the saturated oils; the latter was computed from the results of the accurate determination of the molecular weight and the H- and C-content of these products. In order to state these results in percentages of the total number of C-atoms present, some assumptions had to be made concerning the type of the naphthene rings present (See for particulars Report No. 9228 which discusses the revised ring analysis methods for saturated oils). 2355

In order to determine the number of C-atoms which was present prior to the hydrogenation in the aromatics structures, there was determined, in addition to the said molecular formula after hydrogenation, also the formula prior to hydrogenation (by accurate determination of

the molecular weight and the H- and C-content prior to the hydrogenation). The increase which the number of H-atoms shows in the formula on account of the hydrogenation (when the number of C-atoms remain equal) is equal to the number of C-atoms in the aromatics structure in the original oil.

This ("accurate") method for the determination of the com- 2336  
position of the oils will be discussed in greater detail in the report which is now being prepared concerning the ring analysis method for oils containing aromatics. For the results of the determinations, reference may be had to Table I (the figures for the aromatics, naphthene and paraffin content are mentioned in connection with the computation to be made in this connection in tenths of 1 per cent which, however, does not mean that this accuracy is obtained completely).

2. The computation of the formula for the connection between K and the composition.

When revising the formula for the connection between K and the composition, we started, the same as in Report No. 9026, in principle, from the general equation

$$K = x A + y N + z P.$$

In this connection it is therefore assumed that each one of the percentages C in aromatics (and naphthene and paraffin respectively) structure supplies the same contribution to the value of K, independent of other structure influences or of the molecular weight; this contribution is for the C-atoms in the aromatics structure x, for those in the naphthene structure y and for those in the paraffin structure z.

In Report No. 9026 we based ourselves exclusively on the data for non-hydrogenated oils. In connection with the obtaining of the equation, the available data for the hydrogenated oils were not used. For each one of the non-hydrogenated oils the experimentally determined values for K, A, N and P were entered in the general equation; in order to obtain from the thus produced large number of equations, which are partly practically identical in part, the desired number of 3, these equations were separated into three groups in accordance with their agreement with each other. For each one of the groups, by the addition of all equations of the group in question, there was obtained an average equation; in this manner there were obtained three equations from which the three unknown x, y and z could be arrived at without great difficulty. In this manner there was obtained a formula for the connection between K and the composition which, for oils containing aromatics, appear to be sufficiently satisfactory. For the hydrogenation oils it appeared, however, that the agreement was much less satisfactory.

Inasmuch as it was obvious that efforts should be made to give to the definite equation a character which could be applied as generally as possible, the revision which was now made was based on the data of the non-hydrogenated and the hydrogenated oils together. In the first place there

was calculated, with the assistance of the available data for K and the accurate composition of the hydrogenated products, the contribution to K/per cent C in the naphthene and paraffin structure; in other words the values of y and z in the general formula which, in the case of the saturated oils (A - O), has taken the form of

$$K = y N + z P.$$

In connection with the computation of y and z the method of the smallest squares was used. For this purpose there were available for us the data of the 9 oils of Table I B (See also Fig. 1). 2337

By entering the values found for y and z and of the K-, A-, N- and P- results for the non-hydrogenated oils of Table I A in the general equation mentioned on page 3, it was possible to obtain for each one of these oils the value of x. The mean of these individual values for the contribution to K/per cent C in the aromatics structure was accepted as the definite value for x. (It was logical in this connection to apply to the oils with higher aromatics content a greater weight than to the oils with low aromatics figures; as a matter of fact, however, this resulted in practically the same value for x as the common mean with equal weight for all oils).

It is clear that this revised computation method could also be applied when using the composition in accordance with E 18; for the sake of completeness this was done.

### RESULTS

For the connection between the accurate composition and K, the following equation was found in the manner described above:

$$K = 0.0369 A + 0.1060 N + 0.1326 P \quad (1)$$

In comparison we mention here once more the equation obtained in Report No. 9026 for non-hydrogenated oils for the connection between the ring composition in accordance with Method E 18 and K:

$$K = 0.0935 A + 0.1010 N + 0.1312 P \quad (2)$$

In Report No. 9026 there is moreover shown another equation on basis of data for some individual hydrocarbons; we are reproducing same here:

$$K = 0.0967 A + 0.1094 N + 0.1280 P \quad (3)$$

The equation (comparison) for the connection between the ring composition in accordance with E 18 and K obtained in accordance with the amended computation method, in connection with which the hydrogenated as well as the non-hydrogenated oils were used, reads:

$$K = 0.0832 A + 0.1051 N + 0.1518 P \quad (4)$$

For judging of the usefulness and for the mutual comparison of these formulas, they were now applied in reverse for the computation of K from the composition of the oils (used for the obtaining of same) in Tables I A and I B. The values computed in this manner for K have always been compared with the true K ( $K_{kpt}$ ). 2338

First of all K is in this manner computed with the definite equation (1) and the accurate composition ( $K_{1-n}$ , see Columns 6 and 7 in Tables I A and I B). Altogether the agreement between  $K_{1-n}$  and  $K_{kpt}$  is very satisfactory. This applies both for the non-hydrogenated and for the hydrogenated oils. Deviations of  $>0.1$  appear rarely; the average deviation in the case of equal reference numbers is 0.07 while the greatest deviation is 0.20.

Much less favorable are the results if K is computed with the equation (3) based on the individual hydrocarbons and the accurate composition ( $K_{5-n}$ , see columns 8 and 9 in Tables I A and I B). The differences amount in many cases to more than 0.1 - 0.2 (mean 0.16; greatest deviation 0.40). The equation (1) based on the oil data, therefore, is more satisfactory than the equation (3) based on the data of the individual hydrocarbons. Similar results we also find in Report No. 9026 when using the composition in accordance with the E 18 method.

Considering that the data of the accurate composition in practical operation will give rise to difficulties, while the data in accordance with the method E 18 can be applied, there were furthermore carried out various computations applying the composition E 18.

In the first place in Tables I A and I B, Columns 10 and 11, there were copied the values which are computed in the Report No. 9026 for K with the equation (2) appearing in same and the composition in accordance with the E 18 method ( $K_{2-E 18}$ ). For the non-hydrogenated oils it appears that the combination of the equation (2) with the composition in accordance with E-18, is on an average not inferior to the combination of Equation (1) with the accurate composition. However, the situation is less favorable for the hydrogenated oils in connection with which  $K_{1-n}$  clearly deserves preference over  $K_{2-E 18}$ . 2339

However, it would be most attractive if equation (1), in addition to the accurate composition could also be combined without great difficulty with the composition in accordance with E 18. The results of the composition of K with equation (1) and E 18 composition ( $K_{1-E 18}$ ) is shown in Columns 12 - 13 of Tables I A and I B. The difference  $K_{kpt} - K_{1-E 18}$  is, on an average, 0.10 the greatest deviation being 0.33. On an average  $K_{1-E 18}$  is somewhat inferior to  $K_{1-n}$  although  $K_{1-E 18}$  gives in many cases very satisfactory results. The most disagreeable factors are the deviations encountered in connection with the first two Penna- and Bilik fractions.

Compared with the results in accordance with  $K_2 - E 18$ ,  $K_1 - E 18$  is somewhat inferior to the non-hydrogenated oils; however, it is considerably better for the hydrogenated oils.

Finally there follows in Columns 14 and 15 of Tables I A and I B the comparison between  $K_{kpt}$  and the K values, computed with the E 18 composition and the equation (4) ( $K_4 - E 18$ ), revised on basis of the E 18 composition. As could be expected on basis of the change in the derivation,  $K_4 - E 18$  was clearly more satisfactory for the hydrogenated oils than  $K_2 - E 18$  (and approximately equal to  $K_{1-n}$ ). For the non-hydrogenated oils, however,  $K_4 - E 18$  is in the average clearly inferior with respect to  $K_2 - E 18$ .  $K_4 - E 18$  in connection with these products, also does not offer any decided advantage over  $K_1 - E 18$ .

Altogether, therefore, in connection with the use of accurate data for the composition, the equation (1) should undoubtedly be given the preference. Also when using the composition in accordance with Method E 18 it will be possible in most cases to apply the said equation without any difficulty. Somewhat more accurate results may be sometimes expected when using the E 18 compositions for the non-hydrogenated oils when applying equation (2); for hydrogenated oils, however, equation (1) is frequently better than equation (2).

In view of the fluctuations which occur in the coefficients  $x$ ,  $y$  and  $z$  calculated in different manners, one is inclined to round same off to three decimals instead of four decimals as is done in equations (1) to (4). Also the carrying out of the computations is made more simple in this way.

Also taking into consideration the compositions in accordance with the method E 18, we arrive, when rounding off the coefficients in equation (1), at the equation:

$$K = 0.086 A + 0.106 N + 0.152 P \quad (5) \quad 2340$$

Same supplies, both when applying the accurate compositions as well as the composition figures in accordance with E 18, results for K, which, in by far the greatest number of cases, are accurate to an extent of about  $\pm 0.1$ . (The differences between  $K_{kpt}$  and  $K_{5-n}$ , respectively  $K_{5-E 18}$ , can be directly explained by the columns showing the differences for  $K_{1-n}$  and  $K_1 - E 18$  in Tables I A and I B, by adding of  $\pm 0.04$  to  $\pm 0.06$ .)

For practical purposes one can therefore be satisfied in general with the use of these approximate simple equations independently of the method of determination of the composition.

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Initials

TABLE I B - HYDROGENATED OILS

- a. Accurate composition. 2541
3. % C in the naphthene structure.
4. % C in the paraffin structure.
5.  $K_{kpt}$  from  $K_{kpt}$  and ..... (one word illegible).
6.  $K_{1-n}$  in accordance with equation (1) with accurate composition.
7. Difference - Columns  $\Delta$  5 - 6.
8.  $K_{3-n}$  in accordance with equation (3) with accurate composition.
9. Difference - Columns  $\Delta$  3 - 8.
10.  $K_2$  - E 18 in accordance with equation (2) with old composition from E 18 (x).
11. Difference - Columns  $\Delta$  5 - 10.
12.  $K_1$  - E 18 in accordance with equation (1) with old composition from E 18 (x).
13. Difference - Columns  $\Delta$  5 - 12.
14.  $K_4$  - E 18 in accordance with equation (4) with old composition from E 18 (x).
15. Difference - Columns  $\Delta$  5 - 14.

(x) Based on the preliminary determinations for H K (with molecular weights determined by the cryoscopic methods.)



TABEL I 8 : GEWYNDENDE OLIEB.

I	3	4	5	6	7	8	9	10	11	12	13	14	15
Tegelen	II	70-3	20-9	21-39	0-00	11-49	2-0-10	11-16	+ 0-23	11-35	- 0-14	11-44	- 0-08
	V	60-0	30-0	11-45	+ 0-01	11-54	- 0-05	11-19	+ 0-27	11-36	- 0-10	11-47	- 0-21
	VIII	04-1	30-0	11-55	- 0-01	11-61	- 0-07	11-22	+ 0-32	11-33	- 0-04	11-33	+ 0-04
Pegels	II	30-0	70-3	20-32	- 0-20	22-37	+ 0-05	12-33	- 0-01	12-37	- 0-25	22-49	- 0-17
	VI	30-7	70-3	20-65	+ 0-20	22-25	+ 0-40	12-30	+ 0-35	22-34	+ 0-11	22-46	+ 0-20
Smeermidde	II	30-0	47-3	11-02	- 0-04	11-02	0-00	11-7	+ 0-20	11-06	- 0-14	11-07	- 0-08
	VI	40-0	50-4	20-02	+ 0-05	11-50	+ 0-12	11-57	+ 0-35	11-09	+ 0-04	11-09	+ 0-12
Olie	II	30-0	60-0	20-25	- 0-07	12-15	+ 0-11	12-20	+ 0-05	12-44	- 0-20	12-35	- 0-08
	IV	30-1	60-0	12-31	+ 0-09	12-07	+ 0-24	12-09	+ 0-22	12-36	- 0-05	12-27	+ 0-04

b) gebaseerd op voorlopige bepalingen van NK (met cryoscopische met. gestichtes).

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## TABLE I A - NON-HYDROGENATED OILS

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- a. Computation of the characterization factor K with the comparisons.
  1. Revised comparison.
  2. Preliminary comparison from Report 9026.
  3. Comparison based on the data for individual hydrocarbons.
  4. Comparison on basis of E 18 compositions revised method of computations.
  5. Table I-A non-hydrogenated oils.
  6. Column Number.
  7. Description.
  8. Accurate composition.
  9. % C in aromatic structure.
  10. % C in naphthene structure.
  11. % C in paraffin structure.
  12.  $K_{kpt}$  (illegible)
  13.  $K_{1-n}$  in accordance with (1) with accurate composition.
  14. Difference - Columns  $\Delta$  5-6.
  15.  $K_{3-n}$  in accordance with (3) with accurate composition.
  16. Difference - Columns  $\Delta$  5-8.
  17.  $K_2 - E 18$  in accordance with (2) with old composition from E 18 (x).
  18. Difference - Columns  $\Delta$  5-10.
  19.  $K_1 - E 18$  in accordance with (1) with old composition from E 18 (x).
  20. Difference - Columns  $\Delta$  5-12.
  21.  $K_4 - E 18$  in accordance with (4) with old composition from E 18 (x).
  22. Difference - Columns  $\Delta$  5-14.
  23. (x) Based on preliminary ascertainments of HK (with determination of the molecular weight by the cryoscopic method.

Translation submitted by the Standard Oil Development Company's  
Film Study Group.

BEDEKING VAN DEN CHARACT. ATOM FACTOR K MET DE VERWELJINGEN A

- (1) K = 0,0889 A + 0,1069 N + 0,1128 P (herziene verrijfing)
- (2) K = 0,0855 A + 0,1039 N + 0,1112 P (voorloopige verrijfing uit rpl. 9028)
- (3) K = 0,0967 A + 0,1094 N + 0,1280 P (verrijfing gebaseerd op gegevens voor individuele koolwaterstoffen)
- (4) K = 0,0832 A + 0,1061 N + 0,1119 P (verrijfing op basis E 10-aanstellingen; herziene berekeningsmethode)

TABEL I A : NIET-GEWONEN OLIE.

Kolom No.	Product No.	Omschrijving	2		3	4	5	6	7	8	9	10	11	12	13	14	15	
			K C in aromaat etc.	Naukeurige aanstelling K C in naphthoor. etc.														
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e) gebaseerd op voorloopige bepalingen van NK (met cryoscopische methode)

FIG. 1.

2845

CONNECTION BETWEEN THE CHARACTERIZATION FACTOR  
AND THE ACCURATE RING COMPOSITION OF COMPLETELY  
HYDROGENATED OILS.

VERBAND TUSSENEN DE CHARACTERISATION FACTOR EN  
DE NAUWKEURIGE RINGSAMENSTELLING VAN VOLLEDIG  
GEHYDREERDE OLIËN

