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A rapid infrared method for measuring hydroxyl value in industrial fatty oils

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Abstract

A rapid infrared method has been developed to measure with precision the hydroxyl value in industrial lubricating oils containing different fatty materials, *e.g.* octyl, lauryl and cetyl alcohols or hydroxyl stearic acid. The results showed a good correlation between hydroxyl value and infrared absorbance at two wave numbers, 1100-1000 and 3500-3300 cm^{-1}.

Key words: –OH content, hydroxyl value, industrial oils, infrared absorbance.

1. Introduction

Fatty alcohols and acids are incorporated into most of the industrial oils to increase their lubrication efficiency. To measure the –OH content in these oils, either for quality control purpose or to check the performance level, the method of the American Society for Testing and Materials (ASTM-D 1957/74 method)[1] is usually applied. In spite of the fact that this method covers the determination of hydroxyl value (mg. KOH/g. sample) for wide range of fatty alcohols, mono, di-glycerides, hydroxy stearic acid, and derivatives of the products, etc., and is used on a routine basis in most analytical laboratories, it is tedious, needs a lot of chemicals, and standard solutions and is time-consuming. Infrared spectroscopy, on the other hand, offers a convenient tool. It has been used intensively[2-4] for the analysis of different lubricating oils (either as motor or industrial oils) and their additives and also to check the rate of their deterioration.

In this paper, the use of infrared spectroscopy to measure the –OH content in different industrial fatty oils has been investigated either on qualitative or quantitative basis and the results compared with that of the ASTM method[1], with the aim of finding a correlation between the two techniques.

2. Experimental

A double beam infrared spectrophotometer (Perkin Elmer Model 598) capable of comparing difference in absorption of test samples against a standard mineral base oil as reference (Table I) was used. Cells of 0.1 mm path length were employed.

Table I
Specifications of straight base oil used as reference

Property	Test method	Value
Density @ 20°C	IP 160/68	0.8680
Kinematic viscosity	IP 71/80	
@ 40°C		31.45 Cst.
@ 100°C		5.36 Cst.
Acidity	IP 1/74	0.07 mg. KOH/g
Pour point	IP 15/67	— 15°C
Flash point	IP 34/80	
Closed		202°C
Open		220°C

To cover various industrial oil formulations (test samples) from different fatty alcohols (*e.g.* octyl alcohol, lauryl alcohol, cetyl alcohol) and hydroxy stearic acid were added to the base oil in graded concentrations (1,2, ... 10% wt). About forty blends were formulated and studied (Table II).

Table II
Hydroxyl content in added fatty compounds (% wt)

Fatty alcohol (% wt.) in base oil blends	—OH content g. mole.		
	Octyl alcohol	Lauryl alcohol	Cetyl alcohol
1	0.131	0.091	0.07
2	0.262	0.183	0.14
3	0.392	0.274	0.21
4	0.523	0.366	0.28
5	0.654	0.457	0.35
6	0.785	0.548	0.42
7	0.915	0.639	0.49
8	1.046	0.731	0.56
9	1.177	0.823	0.63
10	1.308	0.914	0.70

Infrared absorbance maxima at the wave number range as listed below were selected to carry the measurements and thereby the absorbance (log I_o/I) was used to correlate the —OH content of the fatty alcohols (Table III).

1100 - 1000 cm^{-1} for the C-O Stretching vibration
1725 - 1705 cm^{-1} for the C = O group, in case of blends containing fatty acids.
3500 - 3300 cm^{-1} for the O-H stretching vibration.

Table III
Ranking —OH content against absorbance for tested samples

—OH content, g. mole.	Absorbance @ 1100-1000 cm^{-1}	Absorbance @ 3500-3300 cm^{-1}	Hydroxyl value ASTM method, mg. KOH/g. sample
0.07	0.047	0.018	6.4
0.091	0.063	0.017	8.34
0.131	0.069	0.029	11.98
0.14	0.072	0.046	12.82
0.183	0.116	0.021	16.76
0.21	0.099	0.062	19.24
0.262	0.179	0.062	23.99
0.274	0.170	0.087	24.94
0.28	0.148	0.088	25.65
0.35	0.203	0.0125	30.06
0.366	0.238	0.154	33.57
0.392	0.235	0.092	35.95
0.42	0.252	0.171	38.47
0.457	0.279	0.185	41.85
0.49	0.294	0.234	44.88
0.523	0.328	0.159	47.90
0.548	0.324	0.271	50.20
0.56	0.339	0.301	51.29
0.63	0.399	0.372	57.71
0.639	0.392	0.318	58.50
0.654	0.417	0.250	59.91
0.7	0.459	0.456	64.12
0.731	0.451	0.371	66.90
0.785	0.556	0.342	71.96
0.823	0.500	0.414	75.40
0.914	0.560	0.460	83.65
0.915	0.629	0.429	83.80
1.046	0.830	0.577	95.81

3. Results and discussion

3.1. Testing of industrial test oils containing fatty alcohols

The infrared spectrum of both the base oils and the test samples, where the two spectra were run separately against air as reference, are nearly identical with the exception of very small difference in the absorption at 1100-1000 and 3500-3300 cm^{-1}. Such results, therefore, are neither suitable for identification nor for quantitative purposes. However, the spectrum of the test sample by using the standard base oil as a reference indicates that absorption bands due to the base oil are cancelled and those due to R-OH group (pertaining to the fatty compounds) appear clearly. The absorbance maxima at 1100-1000 and 3500-3300 cm^{-1} are then calculated (vide pages 73-74) and represented graphically against the fatty alcohol concentration (fig. 1-3).

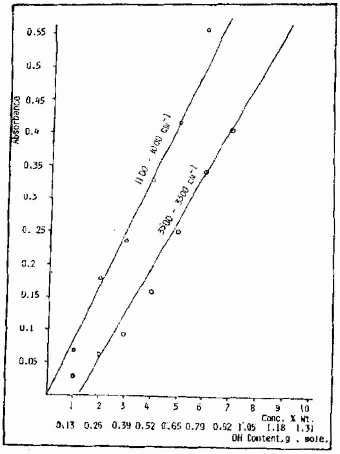

FIG. 1. Octyl alcohol concentration and −OH contents against absorbance at 3500-3300 (Correlation coefficient = 0.96) and 1100-1000 cm^{-1} (correlation coefficient = 0.96)

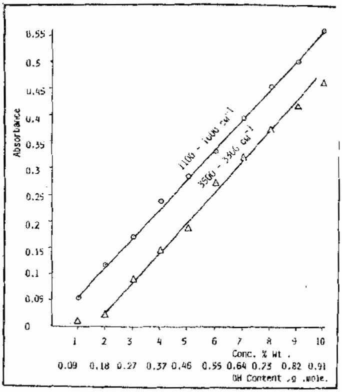

FIG. 2. Lauryl alcohol concentration and −OH contents against absorbance at 3500-3000 (correlation coefficient = 1) and 1100-1000 cm^{-1} (correlation coefficient = 1).

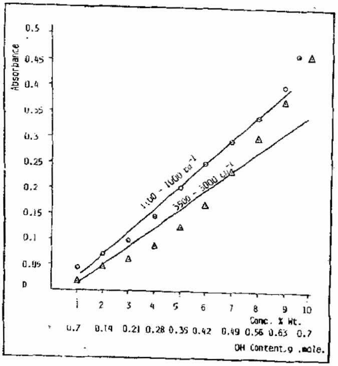

FIG. 3. Cetyl alcohol concentration and −OH contents against absorbance at 1100-1000 (correlation coefficient = 1) and 3500-3000 cm^{-1} (correlation coefficient = 0.97).

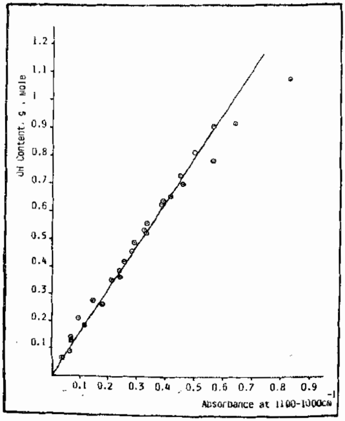

FIG. 4. Correlation between absorbance at 1100-1000 cm^{-1} and −OH content, g. mole.

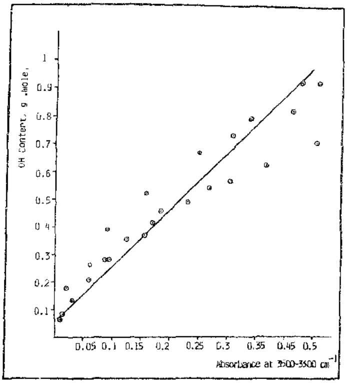

FIG. 5. Correlation between absorbance at 3500-3000 cm^{-1} and –OH content g. mole.

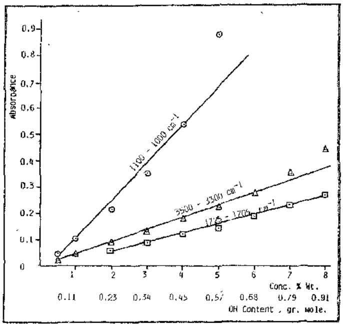

FIG. 6. Hydroxy acid concentration and –OH contents against absorbance at 3500-3000, 1100-1000 and 1725-1705 cm^{-1}.

These results support the direct relationship between the –OH content for different tested fatty compounds and absorbance. It is also clear that absorbance at the same concentration of the fatty alcohol in oil is increasing from blends with octyl alcohol to those with lauryl alcohol and cetyl alcohols. Such difference is due to the decrease of –OH content in the total per cent of fatty compound in oil by the increase of molecular weight of the fatty alcohol.

Generalization of results: In order to generalize the results of absorbance against the –OH content for tested oil samples these are listed in the ascending ranking of the –OH content (Table III) and represented graphically against absorbance (figs. 4 and 5). These two figures also support clearly the direct relationship between the –OH content against their absorbance especially at 1100-1000 cm^{-1} band. Hence by employing the following regression correlation equations the –OH content can be calculated.

$$-\text{OH content, g. mole} = 0.06 + 1.38\,(A_1) \qquad R_1 = 0.99 \tag{1}$$
(fig. 4)

$$-\text{OH content, g. mole} = 0.18 + 1.38\,(A_2) \qquad R_2 = 0.96 \tag{2}$$
(fig. 5)

where

(A_1) : Absorbance at 1100-1000 cm^{-1} maxima.
R_1 : Correlation coefficient corresponding to (A_1).
(A_2) : Absorbance at 3500-3300 cm^{-1} maxima.
R_2 : Correlation coefficient corresponding to (A_2).

Based on these results, it is preferable to use the absorbance data at 1100-1000 cm^{-1} band maxima.

3.2 Testing of industrial oils containing hydroxyl stearic acid

Following procedure as outlined above, determination of the —OH content in different industrial fatty oil blends containing stearic acid (Table IV, fig. 6) is arrived at by the mathematical relationship:

$$-OH \text{ content g.mole} = 0.07 + 0.62\,(A_3) \qquad R_3 = 0.97 \tag{3}$$

$$-OH \text{ content g. mole} = 0.06 + 2.05\,(A_4) \qquad R_4 = 0.99 \tag{4}$$

where

(A_3) : Absorbance at 1100-1000 cm^{-1} maxima.
R_3 : Correlation coefficient corresponding to (A_3).
(A_4) : Absorbance at 3500-3300 cm^{-1} maxima.
R_4 : Correlation coefficient corresponding to (A_4).

Similarly the absorbance at 1725-1705 cm^{-1} due to C = O also (fig. 6) gives a linear plot with the change in hydroxy stearic acid content. Hence, the —C = O content can be calculated by using the following equation:

$$-C = O \text{ content g. mole} = 0.02 + 2.77\,(A_5) \qquad R_5 = 0.99 \tag{5}$$

where

(A_5) : Absorbance at 1725-1705 cm^{-1} maxima.
R_5 : Correlation coefficient corresponding to (A_5).

3.3. Precision limits

To calculate the precision limits of the method, spectrum for one of the tested samples is repeated several times under the same measurement conditions. Results obtained are substituted in the standard deviation equation, the tolerance of the method are found to be ±0.10% of the mean result either for absorbance at 1100-1000 cm^{-1} or at 3500-3300 cm^{-1}.

Therefore, it seems that the precision limits for the present infrared method are quite satisfactory.

3.4. Correlation between hydroxyl value by ASTM method and infrared absorbance method

Results obtained from the present infrared method agree well with those of the ASTM Standard method[1] (Tables III and V & fig. 9). Figure 7 represents the relation between infrared absorbance for tested samples at 1100-1000 and 3500-3300 cm^{-1} bands against their hydroxyl value measured by the ASTM method. Therefore, it is possible to derive the following mathematical equations:

Table IV
Infrared absorbance for hydroxy stearic acid sample against —OH content and hydroxyl value by ASTM method[1]

Hydroxy stearic acid (% wt.)	—OH content g. mole	(C = 0) content g. mole	Absorbance @ 1100-1000 cm^{-1}	Absorbance @ 3500-3300 cm^{-1}	Absorbance @ 1725-1705 cm^{-1}	Hydroxyl value mg. KOH/g. sample ASTM method[1]
0.5	0.056	0.047	0.042	0.018	0.018	2.6
1	0.114	0.093	0.106	0.046	0.037	5.72
2	0.226	0.187	0.216	0.088	0.061	11.15
3	0.340	0.28	0.347	0.125	0.087	16.57
4	0.454	0.378	0.548	0.180	0.123	21.39
5	0.566	0.467	0.875	0.225	0.147	26.90
6	0.680	0.56	1.775	0.279	0.189	32.14
7	0.794	0.653	—	0.355	0.235	37.37
8	0.906	0.746	—	0.446	0.273	42.49
9	1.02	0.84	—	—	—	48.72
10	1.134	0.933	—	—	—	53.94

Table V
Correlation between hydroxyl values as measured by both ASTM and infrared methods

Sample No.	Hydroxyl value, (mg KOH/g) measured by ASTM method[1]	Hydroxyl value (mg KOH/g) calculated from IR method according to absorbance @	
		1100-1000 cm^{-1}	3500-3300 cm^{-1}
1	11.9	12.42	19.05
2	24.9	25.55	26.68
3	25.6	26.82	27.94
4	51.2	50.63	53.22
5	75.4	74.4	69.7
6	83.8	82.3	78.5

$$\text{Hydroxyl value} = 5.23 + 126.7\,(A_1) \qquad R_6 = 0.99 \tag{6}$$

$$= 15.3 + 126.38\,(A_2) \qquad R_7 = 0.93 \tag{7}$$

where (A_1) and (A_2) are absorbances at maxima of bands 1100-1000, 3500-3300 cm^{-1} respectively, and R_6, R_7 are corresponding correlation coefficients.

Further, representation of hydroxyl value (mg. KOH/g. sample) by ASTM method against the —OH content (g. mole) (fig. 8) can be expressed by the following mathematical equation:

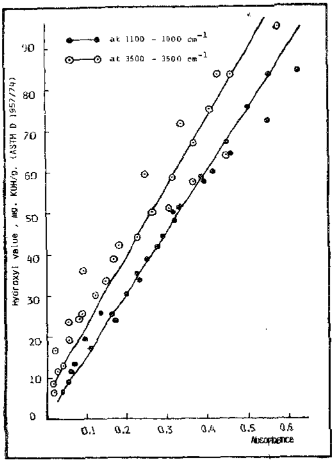

Fig. 7. Correlation between absorbance at 1100-1000 and 3500-3300 cm^{-1} and hydroxyl value[1].

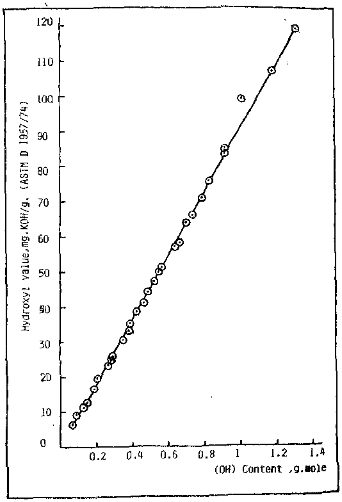

Fig. 8. Hydroxyl value[1] against –OH content.

$$\text{Hydroxyl value (mg. KOH/g. sample)} = -0.15 + 91.74\ (\text{–OH})\ \text{content (g. mole)} \quad (8)$$

$$R_8 \simeq 1$$

where R_8 is corresponding correlation coefficient.

4. Conclusion

Infrared spectrum can be used to measure hydroxyl value and –OH content for a wide range of industrial fatty oil blends containing different fatty alcohols or hydroxy fatty acids. Correlation between results obtained from this method and those by ASTM method[1] are satisfactory and can be expressed in simple mathematical relations. The method, in general, is precise, simple and can be used for a fast routine analysis.

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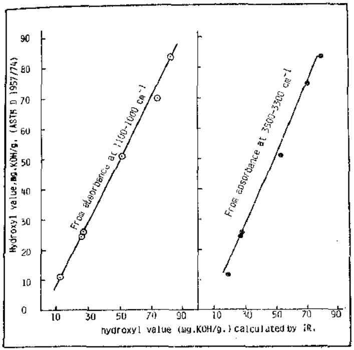

FIG. 9. Hydroxyl value[1] against infrared methods.

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