

Analysis of the Deterioration of Mobile Oil accompanied by the Fuel Dilution

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The viscosity changes of mobile oils were investigated by E. H. Kadmer and the various types of time versus viscosity curves obtained from the actual running tests are shown in his report.¹⁾ The writer found some regularity in tendency of the plots of time-viscosity curves and introduced the equation for analyzing the rate of viscosity increase and fuel dilution. The other conditions remaining constant, the viscosity data for the actual running are useful for analyzing the aging of mobile oil by means of the equation proposed by the writer, even when the fuel dilution is accompanied.

I. Introduction

The viscosity of mobile oil generally increases with time due to the oxydation by oxygen in hot air. In the actual internal combustion engines, however, the dilution of mobile oil by fuel oil is more or less always accompanied, and it leads the viscosity data into some perplexity. Due to this perplexity the analysis of the viscosity data has not been attempted up to this paper. The writer has been engaged in the running tests of mobile oils and arranged more than 30 data. As the result, the four types of tendencies of the viscosity curves are found *i. e.*

- 1) Viscosity remains almost constant during the time of the run,
- 2) Viscosity rises monotonously,
- 3) Viscosity goes down nearly exponentially, and
- 4) Viscosity goes down at first and rises after passing the lowest point.

Although a curve shown as *P* in Kadmer's diagram runs irregularly, the datum is due to irregularity in the running conditions and, in the writer's experiment, it was found due to insufficient functioning of ignition plugs, improper supply of fuel due to a defect in the system and so on and so forth. At any rate, the four tendencies mentioned above are sufficient enough to classify the

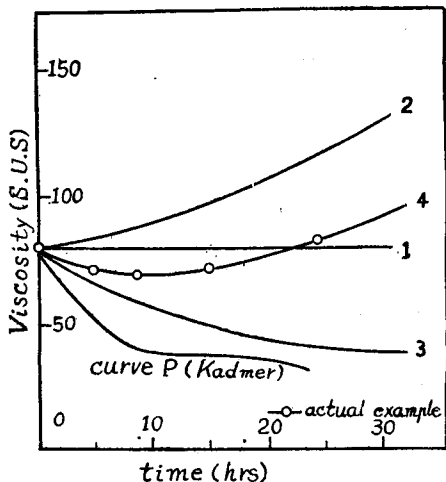


Fig. 1

viscosity data. Those four types are schematically shown in Fig. 1. In Fig. 1, the curve 1 shows the case in which the viscosity increase and the fuel dilution are almost nil. The curve 2 shows the existence of the viscosity increase with the dilution almost none. The curve 3 shows that the viscosity increase is almost nil and a great deal of fuel dilution exists. And the curve 4 shows the remarkable increase in both the viscosity and the fuel dilution.

II. Preliminary experiments and the theoretical treatments

The first problem in the present subject is to derive the rate equation for the viscosity increase when the mobile oil is subjected to oxydation. The second is to derive the rate equation for the fuel dilution. And the third is to select a useful equation for the viscosity formula for binary mixtures from numerous equations which are theoretically or empirically introduced by various authors. For the first problem the viscosity of mobile oil, η_2 , should be given as the function of time only, *i. e.*

$$\eta_2 = f_\eta(t), \dots\dots\dots(1)$$

where f_η means the function which represents the viscosity.

For the fuel dilution we may write the rate of dilution, x , as

$$x = f_x(t), \dots\dots\dots(2)$$

where f_x means the function referring only to the dilution.

For the viscosity of binary mixtures, the resultant viscosity, η , is generally written as follows:

$$\eta = F\{\eta_1, x; \eta_2, (1-x)\} \dots\dots\dots(3)$$

As to the form of the function F , the simplest equation should be chosen so far as there exists sufficient accuracy to analyze the practical data. Inserting eqs. (1) and (2) into eq. (3) the eq. (4) is obtained.

$$\eta = F\{\eta_1, f_x(t); f_\eta(t), f_d(t)\} \dots\dots\dots(4)$$

If the eq. (4) can be derived and x and η_1 are properly eliminated, the rate of viscosity increase can be calculated from the observed values of t and η .

1. Determination of $f_\eta(t)$.

It can be considered that the viscosity increase of mobile oil is caused by the air oxydation. Therefore, the viscosity data can be obtained by observing the viscosity changes in the ordinary apparatus used for the oxydation test of mineral oil. A flask, 150 cc capacity, with three openings was used for the convenience of measuring viscosity. The top opening was used for the intake of air and the one of the two side openings was used for the outlet of exhaust air, and the other was for the thermometer dip and sampling of the probe. The oxydation test was made at the temperature of $200 \pm 1^\circ\text{C}$ by passing the air under atmospheric pressure at the rate of 20 l/hr for 100 cc of the mobile oil. An example of the result of the test on a certain commercial SAE-20 mobile oil is shown in Table 1.

Table 1.

Time (hrs)	Viscosity 210 F. S. U. S.	A
0	43.0	—
2	45.0	0.50
5	53.2	0.41
7	55.9	0.26
10	62.6	0.19
12	70.0	0.19
14	78.0	0.18
16	87.2	0.17
17	96.2	0.18

The plot of the data in Table 1 runs parabolically when expressed by curves. So the function f_η is put tentatively as:

$$\eta_2 = A't^2 + B't + \eta_0, \dots\dots\dots(5)$$

where η_0 is the viscosity when t is zero, and A' and B' are constants. The result of the calculation showed that B' is smaller compared with A' , therefore, eq. (5) can be approximately rewritten as:

$$\eta_2 = At^2 + \eta_0. \dots\dots\dots(5)'$$

The figures in the third column of Table 1 are the values of A calculated from eq. (5)'. The values of A is constant beneath the 10 hour line. The reason for the greater values of A in the upper part of the table may be attributable to the evaporation of the light fraction or the rapid oxydation of the unstable fraction in the mobile oil. The empirical equation (5)' is considered to be useful for the present purpose and it is also applicable in the case of saturated or unsaturated fatty oil.

2. Determination of $f_m(t)$.

As to the rate of the fuel dilution, the actual data can be referred to in the usual dilution test. The writer made a running test by using an engine with a carburettor having a fuel nozzle which was so released as to allow excess gasoline to flow into the intake manifold of the engine. As the result of feeding oil to the standard level every day, the dilution curve runs in a zigzag course. The change of the degree of dilution is plotted in Fig. 2. Plotting the mid point of these discontinuous two points, the curve becomes an exponential function of time in a fairly good approximation. That is,

$$x = a(1 - e^{-kt}), \quad \dots\dots\dots(6)$$

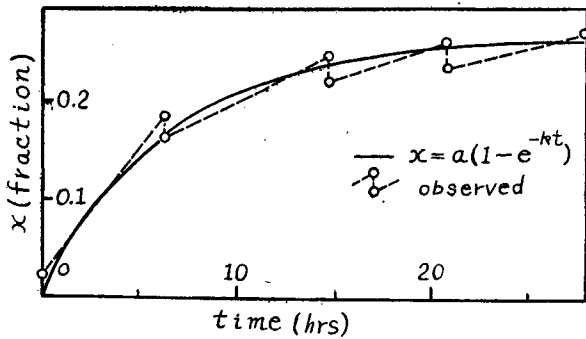


Fig. 2.

where a is the equilibrium dilution (expressed in fraction) which converges to 1 when all the mobile oil is replaced by the fuel, and k is the rate constant of the fuel dilution. The dotted line in Fig. 2 is the value calculated by eq. (6), where $a = 0.25$ and $k = 0.2$ (fraction/hrs). The degree of

its approximation may be considered close enough for the purpose of following the average dilution rate.

3. Determination of $F\{\eta_1, x; \eta_2, (1-x)\}$.

The viscosity equation for binary mixtures is originally given by J. Kendall as,

$$\log \eta = x \log \eta_1 + (1-x) \log \eta_2 \quad \dots\dots\dots(7)$$

But this equation is not sufficient in the case of the mixtures of mobile oil and fuel oil. For example, the viscosity of binary mixtures of a heavy oil (vacuum distillation residue) and lighting oil was measured as shown in Table 2.

In Table 2 the deviation of the calculated values from the observed values are always negative and not allowable even in the case in which the fraction may be at its probable magnitude. Therefore, it necessitates to use another equation which, though it may not be so theoretical, is sufficiently convenient for the practical analysis. Although such empirical formulae as were derived by J.S. Gourlay²⁾, E. P. Irany³⁾ and others are fairly precise for the viscosity of binary mixtures, they are not so convenient for the present purpose owing to

the uneasiness of the numerical calculation. For this reason the writer used the viscosity formula proposed by T. Ishikawa⁴⁾ which is convenient for the numerical treatment notwithstanding the obscurity in its theoretical meaning. Ishikawa's formula for the viscosity of binary mixture is written as follows:

$$\eta = \eta_1 + \frac{\eta_2 - \eta_1}{Kx/(1-x) + 1}, \dots\dots\dots(8)$$

where

- x : fraction of the liquid whose viscosity is η_1 ,
- η : viscosity of the mixed liquid,
- η_1, η_2 : viscosity of each component liquids, respectively,
- K : constant determined by the experiment.

Rewriting eq. (8), K is evaluated as,

$$K = (1-x)(\eta_2 - \eta) / x(\eta - \eta_1). \dots\dots\dots(9)$$

Table 2.

Heavy oil	Light oil	Viscosity observed	(cSt. at 50°C) calculated	K
1.0	0.0	807.0	—	—
0.9	0.1	622.4	475.8	2.8
0.8	0.2	454.8	280.5	3.1
0.7	0.3	278.5	165.3	3.5
0.6	0.4	177.7	99.45	3.5
0.5	0.5	116.3	57.45	3.4
0.4	0.6	52.63	33.87	3.4
0.3	0.7	25.28	19.96	3.1
0.2	0.8	13.47	11.77	3.0
0.1	0.9	6.75	6.94	3.1
0.0	1.0	4.09	—	—

Using eq. (9), the values of K for the blended viscosity data are shown, as an example, in the last column of Table 2. In the range where x is from 0 to 0.3 the constancy of K is sufficient, and actually the greatest value of x for the purpose of the present analysis is not greater than 0.3. So the eq. (8) was used for the further calculation. Inserting eqs. (5)' and (6) into eq. (8), the equation that gives the viscosity of the mobile oil in the working state at the time t is written as,

$$\eta = \eta_1 + \frac{At^2 + \eta_0 - \eta_1}{K \frac{\alpha(1 - \exp(-kt))}{1 - \alpha(1 - \exp(-kt))} + 1}. \dots\dots\dots(10)$$

With the arbitrary three sets of observed values of η versus t , eq. (10) may be solved as to A , a and k . Comparing the values of A , the severeness of the running conditions and the relative quality of mobile oil can be estimated. From the values of a and k , the working conditions of the fuel supplying system can be noted. In eq. (10) putting $A \approx 0$ and $a \approx 0$, $\eta = \eta_0$ is derived immediately. This corresponds to the curve 1 in Fig. 1. When $A \neq 0$ and $a \approx 0$ hold, eq. (10) becomes eq. (5)' and this corresponds to the curve 2. When $A \approx 0$ and $a \neq 0$ hold, eq. (10) becomes

$$\eta = \eta_1 + \frac{\eta_0 - \eta_1}{K \frac{a(1 - \exp(-kt))}{1 - a(1 - \exp(-kt))} + 1}, \dots\dots\dots(11)$$

and this corresponds to the curve 3. All the cases in Fig. 1 are contained in eq. (10) and the generality of the equation derived by the writer is verified by this results.

III. Treatment of the actual analysis and an example

1. Calculation of A , k and a .

In the equation (10), unknown quantities are A , k and a , and besides these it is necessary that the constant K is known by the preliminary experiment or other method of estimation. As to the quantity of K a description will be made afterwards. In the present case unknown quantities are assumed to be the following three quantities only. Assuming $\eta_1, t_1; \eta_2, t_2; \eta_3, t_3$ to be the three sets of observed data, the simultaneous algebraic equations (12) are written out immediately from eq. (10)

$$\left. \begin{aligned} \eta_1 &= \eta_f + \frac{At_1^2 + \eta_0 - \eta_f}{K \frac{a(1 - \exp(-kt_1))}{1 - a(1 - \exp(-kt_1))} + 1}, \\ \eta_2 &= \eta_f + \frac{At_2^2 + \eta_0 - \eta_f}{K \frac{a(1 - \exp(-kt_2))}{1 - a(1 - \exp(-kt_2))} + 1}, \\ \eta_3 &= \eta_f + \frac{At_3^2 + \eta_0 - \eta_f}{K \frac{a(1 - \exp(-kt_3))}{1 - a(1 - \exp(-kt_3))} + 1}, \end{aligned} \right\} \dots\dots\dots(12)$$

where η_f means the viscosity of the fuel oil. Eliminating A by use of the former two equations in eqs. (12), a quadratic equation for the unknown quantity a , which contains k in the constant term, *i. e.*,

$$Ua^2 + Va + W = 0, \dots\dots\dots(13)$$

where

$$U = 3t_1^2(\eta_2 - \eta_f) \alpha(1 - \beta) - 3t_2^2(\eta_1 - \eta_f) \beta(1 - \alpha) + \{t_2^2\eta_1 - t_1^2\eta_2 - \eta_0(t_2^2 - t_1^2)\} \alpha\beta,$$

$$V = 3t_2^2(\eta_1 - \eta_f)(1 - \alpha) - 3t_1^2(\eta_2 - \eta_f)(1 - \beta) - \{t_2^2\eta_1 - t_1^2\eta_2 - \eta_0(t_2^2 - t_1^2)\} (\alpha + \beta),$$

$$W = t_2^2\eta_1 - t_1^2\eta_2 - \eta_0(t_2^2 - t_1^2).$$

and

$$\alpha = 1 - \exp(-kt_1), \quad \beta = 1 - \exp(-kt_2). \quad \dots\dots\dots(14)$$

When α is eliminated from the two sets of equations of the eq. (13) type, a complicated logarithmic equation is developed. It is a convenient method to solve eq. (13) by treating k as a parameter and find the intercept of two sets of $k \sim \alpha$ curves.

As to the value of K a study was made of the various kinds of mixtures in which the viscosity ratios of component oils were in the range between 10 and 200, and it was found that the values of K varied only from 2.9 to 3.1. Consequently, the value 3.0 can be approximately assumed for K taking the average of them without essential error even when the preliminary experiments are not made.

2. An example.

An example for the actual running test is shown here. A caterpillared car weighing about 8 tons and equipped with the air-cooled diesel engine of the direct injection type, was used. The running test was made under nearly constant conditions for about 30 hours and the samples were taken at about every 5 hours. The viscosities of the samples were measured with the glass viscosimeter of Ubbelohde type. And

the viscosity values were reduced to Saybolt Universal Second by use of the A. S. T. M. reduction table. The viscosity of the fuel oil (light oil) was 2.5 cSt. at 210°C and the value of

Table 3.

k	a_1	a_2	$a_1 - a_2$
0.40	5.676 $\cdot 10^{-3}$	5.614 $\cdot 10^{-3}$	0.062 $\cdot 10^{-3}$
0.44	5.618	5.613	0.005
0.442	5.616	5.613	0.003
0.444	5.614	5.613	0.001
0.450	5.607	5.613	-0.006

K was supposed to be 3.0. The three sets of observed values used for the calculation are given below.

<i>t</i> (hrs)	9.0	16.0	28.0
η (cSt)	14.0	16.0	17.0

The values of a calculated from the left two data, a_1 , and that from the right two data, a_2 , are shown in Table 3.

From the plot of the data in Table 3, $k = 0.444$ and $a = 0.00561$ are known. Inserting these values into each equation of eqs. (12), the values of A become $5.074 \cdot 10^{-3}$, $5.085 \cdot 10^{-3}$ and $5.084 \cdot 10^{-3}$ respectively, and their relative accuracy is sufficient. Inserting the mean value of those constants into eq. (10) the following numerical relation is obtained :

$$\eta = 2.5 + \frac{5.08t^2 \cdot 10^{-3} + 13.1}{\frac{0.1684(1 - \exp(-0.444t))}{1 - 5.613 \cdot 10^{-2}(1 - \exp(-0.444t))} + 1} \dots\dots\dots(15)$$

Table 4.

<i>t</i> (hours)	viscosity (S. U. S.)	
	calculated	observed
0	80.1	80.1
5.0	73.5	73.2
9.0	73.9	73.8
16.0	76.6	77.0
23.5	81.6	81.6
28.0	85.7	85.7

Eq. (15) gives the viscosity variation of the mobile oil under the present running conditions. The comparison of the calculated values from eq. (15) and the observed values are shown in Table 4.

The agreement of the calculated values and the observed values is sufficient for the practical utility.

IV. General consideration

The example shown in the preceding section gave a satisfactory result for our method of analysis. The problem of what these calculated values mean in the actual running conditions comes next.

As to the magnitude of A , there are the testing standards of the lubricating oils in which the viscosity ratio is defined as the standard of anti-oxydation property. But, the modification of eq. (5)' gives the following relation.

$$A = \frac{\eta_1 - \eta_0}{t^2} \dots\dots\dots(16)$$

When A is calculated by use of eq. (16) for oils of Saybolt 80,100, and 120" whose viscosity ratios before and after the oxydation test (12 hours) are 1.5, 2.0, and 2.5 respectively, the values of A are as shown in Table 5.

Comparing each values of A on the same line in Table 5, it is found that A does not agree when the viscosity varies. They have a rising tendency with the

Table 5.

η/η_0	80"	100"	120"
1.5	0.278	0.347	0.417
2.0	0.556	0.694	0.833
2.5	0.833	1.04	1.25

increase of viscosity in magnitude, and this means that the stability of the heavy oils is to be found smaller than that of the light oils for the same viscosity ratio.

This is an essential mistake in the definition of the testing standard and should be corrected accordingly. As a personal proposal, the writer considers it appropriate to determine the values of the viscosity ratio to correspond to the same value of A .

The mobile oil used for the present running test had the following characteristics.

viscosity (210°F)	80.1 S. U. S.
viscosity index	81
acid value	0.3 mg KOH/gm
flash point	174.0°C
Conradson carbon	0.5%
viscosity ratio (210°F)	2.3 (B. A. M. method)
carbon increase	0.7%

Comparing the magnitude of A in the running condition with that in the usual oxydation test, the former is far smaller by $0.005/0.723 = 1/144.6$ than the latter. This means that the overall oxydizing conditions in the actual running state is far more mild than that of the usual oxydation test, and the greater part of the so-called waste mobile oil usually remains unchanged.

As to the magnitude of a and k , the value 0.0056 for a is very small one as the ultimate amount of fuel dilution, and the overall condition of the combustion system may be considered sufficient for the running in this case. For the value $k = 0.444$, the quantity $\exp(-kt)$ becomes the order of 0.1 five hours after the beginning of the running, which means that the decrease of viscosity in the mobile oil reaches the stationary state before the time. When the value of a is great and that of k is small as in the case of the running condition for a gasoline engine in the cold season, $a = 0.3$ and $k = 0.05$, a dangerous condition for the lubrication may occur in some ten hours of running.

V. Conclusion

1. A theoretical treatment for the analysis of the aging of mobile oil in the running state was made.
2. An example of analysis of the actual result was shown, and the characteristics of the constants in the equation were discussed numerically.
3. A suggestion concerning the definition of oxydation test was made on the base of the results of the preliminary experiments for the rate of viscosity increase.

Literatures

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