The Cloud Point Test for Low Temperature Lubricant Oil and Some Remarks on the Clouding of Liquid

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The Cloud Point Test for Low Temperature Lubricant Oil and Some Remarks on the Clouding of Liquid*

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Synopsis

An apparatus was constructed with which the cloud point of the low temperature lubricant oil was measured by the photo-electrical method. This method had superiority over the former one in the following respects: (1) very high sensitivity (2) obtaining perfect equilibrium value of turbidity at every temperature, (3) estimating the amount of clouding materials and (4) obtaining the data for further improvement of the oil.

The lubricant oil made from fish oil was tested by this method and its quality was improved by low temperature filtration. The problem of the induction period of the clouding was discussed. It was found that the velocity of clouding was proportional to the reciprocal of the viscosity of medium oil.

I. Introduction

The method of cloud point test for the low temperature lubricant oil now used is very imperfect either from the practical or from the theoretical standpoint. Owing to the large viscosity of the sample, much precaution must be taken for the establishment of equilibrium in the course of experiments. Especially in the turbidiy test, even a slight difference in thermal history or in cooling rate will result in a large difference in the appearance of clouding.(1)

The sample contained in a test tube was cooled in an alcohol-dry ice bath by the usual method. The observation of cloudness was made by taking it out from the bath at a definite time interval in the course of cooling. The observation, however, becomes soon difficult because of the frosting on the outer surface of the test tube. Besides, in this method, the temperature of the sample is measured with a mercury thermometer immersed in the bottom of the test tube, and accordingly, the exact temperature of the sample is hardly known due to the poor thermal conductivity of the sample in the course of cooling or heating. It is obvious that by such a method the equilibrium value cannot be obtained at any. To improve the quality of oil, equilibrium values at all temperatures are necessary. As mentioned above, it takes a very long time to establish the sufficient equilibrium in the sample. A low temperature thermostat which is controlled precisely and maintained at a desired temperature for a long time, is necessary. To obtain relative values of the cloud point, however, it will be sufficient to test at a constant cooling rate. The usual method now used is imperfect even for this purpose.

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(1) We noted especially these precaution in the previous papers concerning the glassy state of supercooled iso-butanol: E. Kanda, A. Ôtsubo and T. Haseda, Sci. Rep. RITU. A, 2 (1950) 9; 16.

II. Apparatus and procedure

1. The turbidity test

We devised a new method for detecting the cloud point by measuring photo-electrically the intensity of transmission light through the oil at various temperatures, taking much precaution against the temperature equilibrium for the abovementioned reason. The arrangement of the apparatus is shown in Fig. 1. Light source f is an usual 200 W. tungsten lamp. The light passes vertically through the sample b and is received by the photo-tube. Amplifying this weak photo-current,(2) even a slight clouding in the sample could be detected. The cryostat is a specially made Dewar vessel. Sample is introduced into b through a and protected from moisture by a calcium chloride tube. The volume of the container b is about 30 cc and c is the alcohol bath. The spiral-tube d leads liquid nitorogen for cooling, and e is a stirrer. The temperature of the sample is measured by a thermocouple at the top of the container and can be controlled within the fluctuation of ±0.1°C during the measurement by regulating both the current of the heater g and the flow of liquid nitrogen through the tube d. The microammeter current is adjusted to 100 μA when the sample is perfectly transparent at first. As the clouding grows, the current decreases propotionally to the turbidity. But the clouding can scarcely be observed with naked eyes, till it falls to 90 μA.

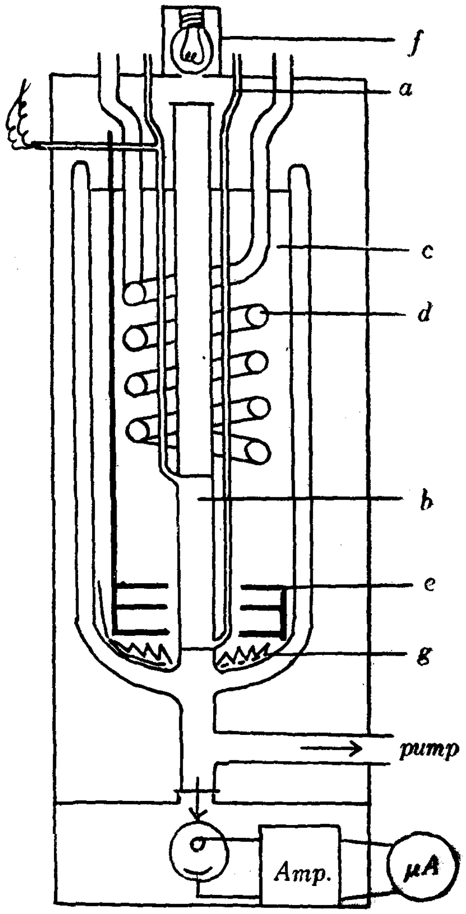

Fig. 1

2. The low temperature filtration

We tried the filtration at low temperatures for the refinement of the quality of oil. The scheme is shown in Fig. 2. Whole part of A is immersed in a cryostat which is kept at the desired temperature during filtration. a is a glass filter. Part b is filled with particles of silicagel. The filtration was made by the suction from c. It took so long time that it was hoped to find out the optimum mesh of the glass filter and the proper amount of silicagel. Thus, the filtration was performed at −25°C and −43°C using the ordinary glass filter for chemical analysis.

III. Experimental results

1. The cloud point test and low temperature filtration

Low temperature lubricant oil made from fish oil was thoroughly tested with our

(2) Markus & Zeluff. Handb. Ind. Electronic Circuits, (1948), p 204.

apparatus. A typical result is shown in Fig. 3, in which readings of micro-ammeter taken from photo-cell are plotted for each temperature. Curve a is the result of a roughly purified sample measured at the cooling rate in usual method. The large hysteresis shows that, if the measurement is carried out at the perfect equilibrium, the cloud point will appear at about 0°C. By the usual method, the cloud point of the same sample proved to be about −20°C. If the sample is required not to become cloudy below −25°C, it must be filtrated at −25°C. Curve b is of such a sample. The dotted lines indicate cooling or warming curve, and the solid line represents perfect equilibrium values which were obtained by keeping the sample long enough at each constant temperature. This indicates sharp clouding at −25°C, followed by ones near −30°C and −40°C, reaching the final value of 70 μA below −45°C. This increasing of clouding suggests the step-like precipitation.

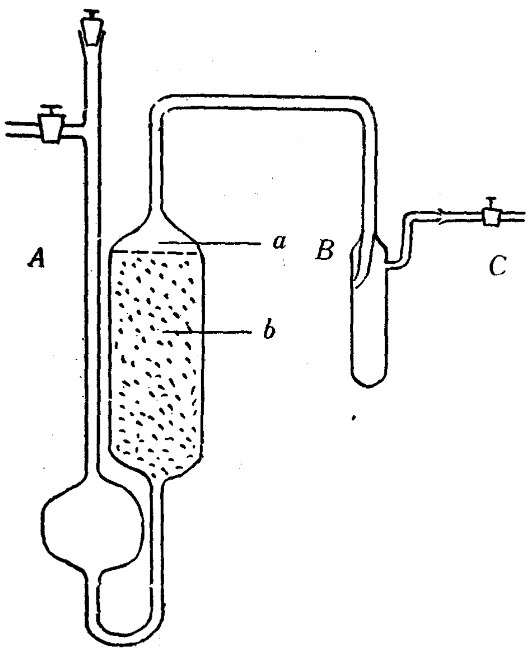

Fig. 2

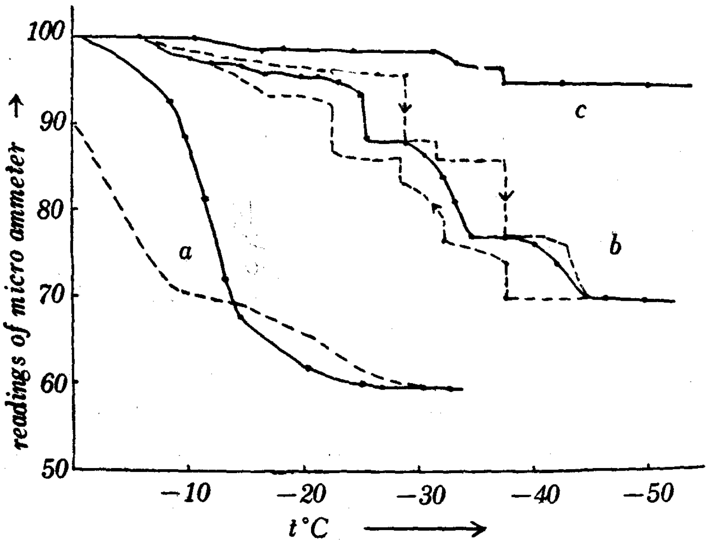

Fig. 3

These facts indicate that this sample contains three species of impurities. The sample was filtrated once more at −34°C and its results are shown in curve C. As mentioned above, visual clouding corresponds to the reading of 90 μA. Any cloud point of this new sample could not be observable till −60°C and, when tested by the former method, it could not be found down to or below −80°C.

The final reading of micro-ammeter of curve a was 60 μA below −25°C, that of curve d was 70 μA below −45°C and that of curve c was 95 μA below −34°C. These readings indicate the amount of impurities. Thus, a rough estimation of the amount of clouding impurities could be made, which could not be obtained by the former method.

2. The rate of clouding

It will be interesting to note the rate of clouding at each step in curve b. In Fig. 4, the readings of micro-ammeter are plotted for the time during which the sample was kept constant at each indicated temperature. At −26°C and −28°C at which the clouding was first observed, the induction period of clouding was very long, and unless sufficient care was taken, the cloud point might easily be missed. At the subsequent steps near −33°C and −40°C, no induction was observed. When the clouding was allowed to delay down to a lower temperature by a large cooling rate the induction period became very long at the lower temperature at which the clouding occurred. From these facts, it may be considered that the precipitation at the first step needs a long induction period and that if there exists any precipitant, even if of different species, the precipitation will take place easily without any induction. We can also see in Fig. 4 that the higher the temperature is, the larger the inclination of the curve or the rate of clouding becomes.

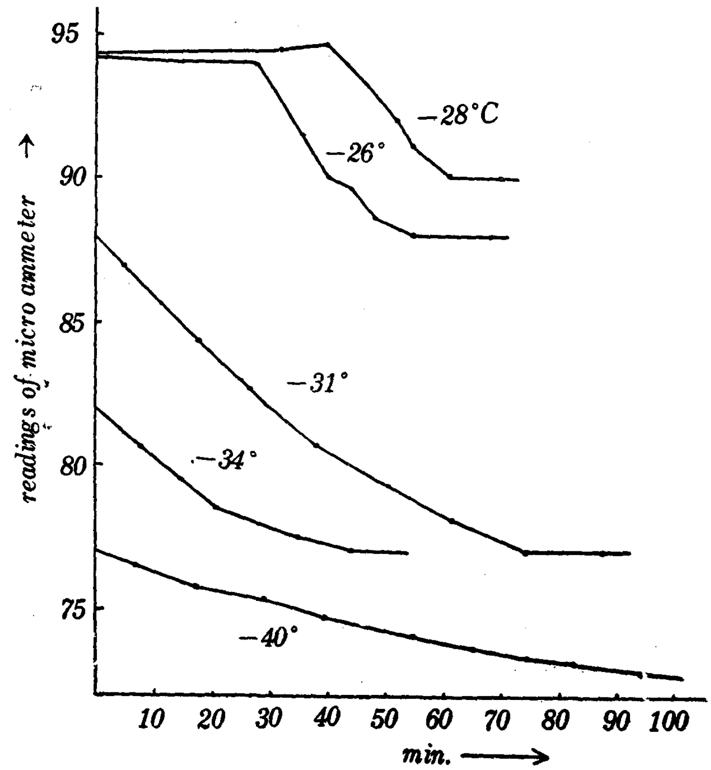

Fig 4

From the initial inclinations of curves in Fig. 4, the rate of clouding at each temperature can be calculated. In Table 1, the rate at each of three steps and the viscosities at the corresponding temperatures measured with the specially made viscosimeter of Ostwald type are shown.

Table 1.

t°C	rate k μA/min	η poise	$k\ \eta$
−28	0.27	15.1	4.05
−31	0.20	21.0	4.20
−40	0.059	70.2	4.08

The fact that $k\eta$ is almost constant at each temperature is very interesting. Being related to these problems, the linear velocity of crystallization of supercooled glycerol was measured by Volmer and Marder.(3) Using these data, Richards obtained the relation(4) that the velocity was proportional to the reciprocal of the viscosity of glycerol. In general, light scattering is proportional to the number of scattering particles and is dependent of the size of particle. It is difficult to tell if one of these causes is predominant or both of them are simultaneously contributing in our case. The constancy of $k\eta$, however, seemes to suggest that the rate of the clouding is proportional to the reciprocal of the viscosity of the medium oil.

(3) Volmer and Marder. Zeits. Phys. Chem. A **154** (1937), 97.
(4) Richards. Jour. Chem. Phys. **4** (1936), 449.

Summary

New method for the cloud point test has the following advantages; (1) very high sensitivity, (2) obtaining perfect equilibrium value of turbidity at every temperature, (3) estimating the amount of clouding materials and (4) obtaining the data for further improvement of the oil.

The low temperature lubricant oil tested by this method showed the clouding in three steps, suggesting the three species of impurities. The rough estimate was made about the amount of these impurities and applying the low temperature filtration at the proper temperature, the oil of better quality was obtained, which showed no clouding by the former testing method.

The long induction period at the first step of clouding and no induction at the successive steps suggested that the induction was necessary only for the formation of the nuclei of precipitation. It was found that the rate of clouding was proportional to the reciprocal of the viscosity of the medium oil.

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