J Forensic Sci, Sept. 2002, Vol. 47, No. 5
Paper ID JFS2001374_475
Available online at: www.astm.org

TECHNICAL NOTE

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Boiling Point Measurement of a Small Amount of Brake Fluid by Thermocouple and Its Application

ABSTRACT: This study describes a new method for measuring the boiling point of a small amount of brake fluid using a thermocouple and a pear shaped flask. The boiling point of brake fluid was directly measured with an accuracy that was within approximately 3 C of that determined by the Japanese Industrial Standards method, even though the sample volume was only a few milliliters. The method was applied to measure the boiling points of brake fluid samples from automobiles. It was clear that the boiling points of brake fluid from some automobiles dropped to approximately 140 C from about 230 C, and that one of the samples from the wheel cylinder was approximately 45 C lower than brake fluid from the reserve tank. It is essential to take samples from the wheel cylinder, as this is most easily subjected to heating.

KEYWORDS: forensic science, criminalistics, automobile accident investigation, brake system trouble, brake fluid, boiling point

Hydraulic brake systems are used in passenger cars, cargo-carrying vehicles, etc. Braking force, caused by depressing the brake pedal, is transmitted to the piston of the master cylinder and converted into brake-fluid pressure. The brake-fluid pressure is then transmitted through the brake pipes and hoses to the wheel cylinders and disk brake units that are installed on each wheel, and the brake linings and pads are pushed against their respective brake drums and disk rotors.

Among the many different types of automobile accidents, some accidents are caused by failures in these hydraulic brake systems. In order to clarify the causes of these accidents, we have conducted forensic examinations and inspections on every part and element in these braking systems. In these forensic investigations, boiling point measurements of brake fluids are performed.

Brake fluids possess hygroscopicity since their main ingredient is diethylene glycol ether. Therefore, one of the characteristics of a brake fluid is that its boiling point drops sharply when a small amount of moisture is absorbed. When a brake fluid with a low boiling point is used in brake equipment and the brakes are operated with a high degree of frequency, the temperature of the brake fluid rises, vapor bubbles form in the pipes and hoses, and, ultimately, conditions that can lead to a vapor lock can easily develop.

For this reason, when an accident has been caused by the braking system failure, it is necessary to measure the boiling point of the brake fluid in order to investigate whether the cause of the accident was due to the low boiling point of the brake fluid or to driver error and so on.

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Received 2 Nov. 2001; and in revised form 26 Feb. 2002; accepted 22 March 2002; published 31 July 2002.

A standard method to measure the boiling point of a brake fluid is prescribed in JIS (Japanese Industrial Standards) K 2233 (1). According to this standard, the volume of brake fluid that is required to perform a measurement must not be less than 60 mL. When a traffic accident occurs, however, it is often the case that the prescribed volume of material cannot be obtained. In these instances, the indirect measurement of the boiling point of a minimum amount of 7 to 8 mL of brake fluid by means of a relative-permittivity method has been suggested by Hara et al. (2,3). However, depending on the automobile that has been involved in the accident, it sometimes happens that only a very small volume of brake fluid can be collected. In addition, from the standpoint of measurement errors, there is the problem of not being able to determine the boiling point directly due to the analytical curve method.

This paper introduces a new measuring method to determine the boiling point of break fluid that uses pear shape flasks as containers and performed temperature measurements by means of thermocouple. This new method was applied to obtain actual measurements of the boiling points of vehicular brake fluids.

Materials

The tests conformed to JIS K 2233 (BF-3) as well as to the Federal Motor Vehicle Safety Standard (FMVV No. 116) and used a non-ferrous oil-based brake fluid for automotive use (Toyota 2500H) that has passed the BF-3 requirement that is equivalent to DOT 3. As shown in Table 1, the specifications for the properties of this brake fluid require a boiling point of not less than 205°C. Furthermore, in order to assure that an identical brake fluid was used in each test, the brake fluid was dispensed from the same 18-liter-capacity container and used in all of the tests. Finally, BF-4 brake fluid was used in some of the tests for purposes of comparison.

TABLE 1—*Specifications of brake fluid.*

Item \ Class	Specification	
	BF-3	BF-4
Balanced reflux boiling point (°C)	205 min	230 min
Wet boiling point (°C)	140 min	155 min
Kinematics viscosity mm^2/s (−40°C)	1500 max	1800 max
PH value	7.0 to 11.5	

Methods

Measurements of Brake-fluid Boiling Points

The Measurements of the brake-fluid boiling points were performed by using a container that is specified by JIS K 2233 and the method outlined below that conforms to the corresponding measuring method.

- The thermometer shall be inserted from the side tube, sealed up tightly with thick rubber tube and fixed so that its lower end is about 6.5 mm high from the center of flask bottom.
- 60 mL of sample and 3 pieces of boiling chips shall be put into the round bottom flask.
- The sample shall be heated for 10 ± 2 min so as to effect a reflux of 1 to 5 drops per second. Next, the heating shall be regulated to keep the balance reflux speed of 1 to 2 drops per second for 5 ± 2 min. While this condition is further maintained for 2 min, the temperature shall be read to the nearest 0.5°C every 30 s 4 times, and the average value shall be taken as the measured temperature.

Although the standard mentioned above specifies that approximately 2 mm size of well-dried and clean carborundum is to be used as the boiling chip, glass boiling chips that are generally used in chemical experiments were used in these tests. And a mantle heater with a slidak transformer for controlled and input voltage was used for heating.

Measurement by Means of Thermocouple

The balanced-reflux method was used to measure the boiling points in order to confirm the amount of error in the indications between the thermometer and the thermocouples at the same time that the measurements were performed.

The special-made flask used in this test had a diameter of approximately 60 mm, a round bottom, and three necks. The measurements of the boiling points of the brake fluid were carried out while a pre-calibrated thermometer was inserted in the side neck and a thermocouple was installed in the other side neck. A water-cooled condenser was installed in the middle neck.

And 0.3 mm-diameter copper and constantan (C. C.) wires and 0.65 mm-diameter chromel and alumel (C. A.) wires were used for the thermocouple materials. No protective tube was used on the hot junction of the thermocouple. Instead, the thermocouple wires were passed through an insulator tube and fastened in position when the hot junction had been exposed by approximately 3 mm and so that the junction was just in light contact with the spherical section of the thermometer. The cold-junction side of the thermocouple was maintained at 0°C inside a thermos bottle containing ice water.

Additionally, a digital voltmeter which was capable of providing minimum readings in μV units was used to measure the thermo-electromotive force from the thermocouple and a voltage-time pen recorder was used to record and monitor the thermo-electromotive force.

Reflux Speed

JIS K 2233 specifies, "Heating shall be regulated so that a balanced reflux speed of two drops per second is maintained." In other words, it is prescribed that heating shall be performed with the interval between each drop being maintained at 0.5 to 1.0 s. We therefore investigated the influence on the boiling point of the heat that was input to the brake fluid by using pear shape flask with three necks and round bottom. In this test, a slidak transformer was used to regulate the voltage to change the heating conditions, and the interval of the drops was measured in a balanced reflux state and when the thermometer indication was approximately constant.

Measurement of a Small Amount of Brake Fluid

We confirmed the minimum amount of brake fluid necessary for the measurement of boiling points and investigated the relationship between the volume of the sample and the boiling point. The brake-fluid boiling points were measured by using special-made pear shape flasks with two neck and capacities of either 30 mL or 50 mL as containers, and a thermocouple to perform the temperature measurements. An illustration of the test equipment is shown in Fig. 1.

Measurements of Boiling Points of Brake Fluids that Contain Water

Since brake fluids are hygroscopic and their boiling points drop when water is absorbed, vapor locks become more likely to occur as more water is absorbed. We added distilled water to the brake fluid and investigated the relationship between the percentage of water in the brake fluid and the boiling point. After the prescribed amount of distilled water was added to the brake fluid, a magnetic-stirrer was used to stir the brake fluid and the water thoroughly for a period of approximately 3 min and the resulting mixture of brake fluid contained water was then used as a sample. The brake-fluid boiling points were measured by using special-

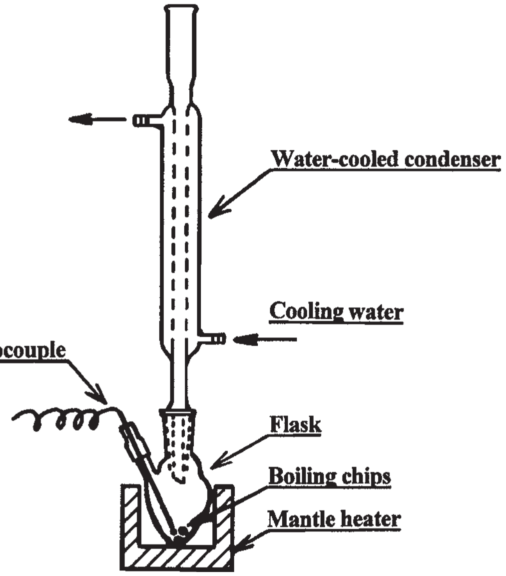

FIG. 1—*Schematic illustration of boiling point test equipment by thermocouple.*

made pear shape flask with two neck and capacities of 10 mL as container.

Testing of the Absorbed and Stirred Brake Fluid in Air

Brake fluids possess a water-absorbing property and become undesirable for practical use when their boiling points drop sharply after a large increase in the amount of water that has been absorbed. Brake fluid was stirred in air to force the absorption of moisture and then investigated the extent of the drop in the boiling point.

Measurements of the Boiling Point of Brake Fluid Taken from Automobiles

We extracted as samples approximately 50 mL of brake fluid from the reserve tanks and rear-wheel cylinders of automobiles that were operated during automobile inspections or while receiving maintenance in garages. Then, using this newly introduced method, measured the boiling points of approximately 30 mL of the brake fluid.

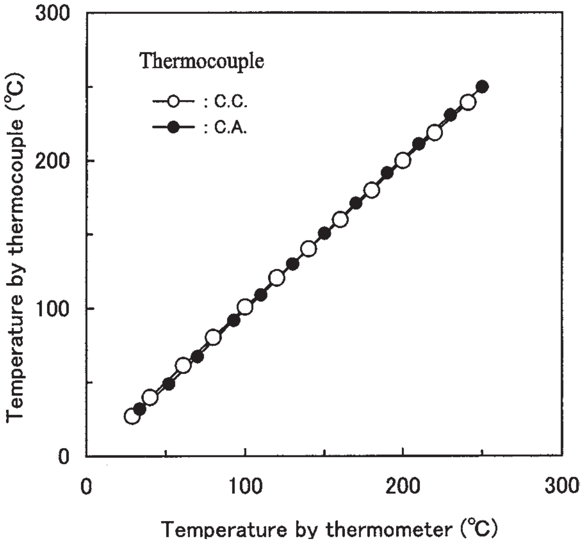

FIG. 2—*Relationships between temperature by thermocouple and by thermometer.*

Test Results and Considerations

Comparison Between Thermocouple and Thermometer

Figure 2 shows the thermocouple temperature-dependent characteristics. The horizontal axis shows the values obtained from the pre-calibrated thermometer readings and the vertical axis shows the temperatures as converted from the values of the thermo-electromotive force of the thermocouple. In Fig. 2, the symbol "○" represents the values from the copper-constantan thermocouple and the symbol "●" represents the values from the chromel-alumel thermocouple. The differences between the indicated temperature values between both thermocouples and the thermometer were within 1.5°C at maximum. Significantly, the difference was 0.0°C when the temperature of the brake fluid was approximately 250°C and the brake fluid was in a boiling state in which the generation of bubbles was continuous and convection conditions were severe.

It was thus confirmed that the temperature measurements by means of the thermocouples were accurate. And it was subsequently decided to use the chromel-alumel thermocouple for testing purposes.

Confirmation of the Boiling Points by Means of a Thermocouple

In order to study how to judge the boiling state by means of a thermocouple, a 60 mL-capacity round-bottom flask with two necks was used as the container. Figure 3 shows an example of the thermo-electromotive force of the thermocouple. A mantle heater performed heating and the temperature of the brake fluid was slowly raised. In regard to the state of the brake fluid during heating, small bubbles began to form at approximately 220°C and larger bubbles formed continuously from approximately 230°C. Dripping started from the bottom end of the water-cooled condenser at approximately 235°C and the continuous generation of

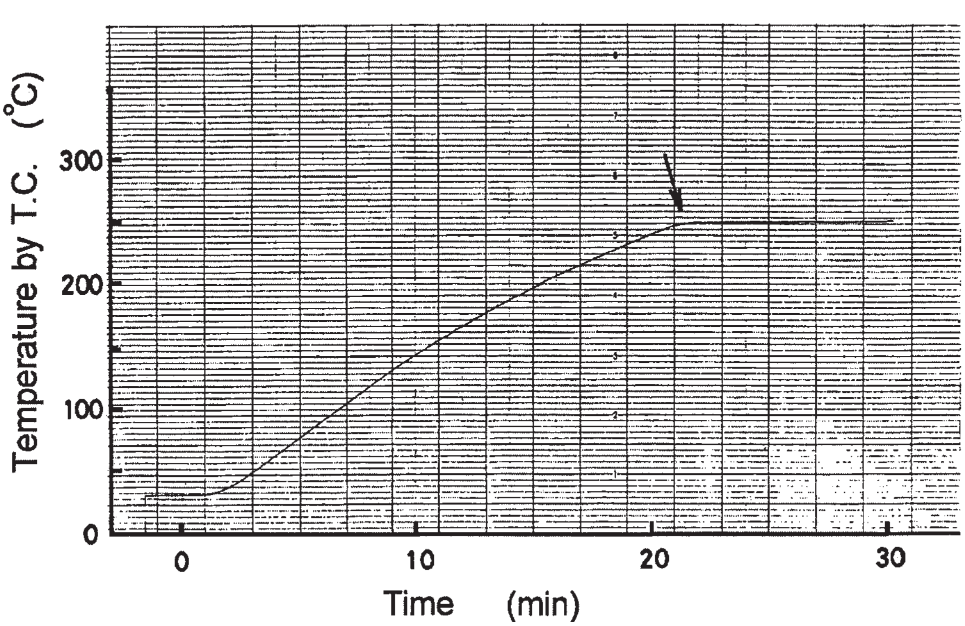

FIG. 3—*Temperature record conformed to JIS K 2233 standard. Arrow shows an inflection point.*

bubbles became pronounced at approximately 240°C. We were able to confirm that a boiling state had been established when the constant state was achieved at approximately 250°C. An inflection point, which is indicated by the arrow in Fig. 3, was abruptly displayed from approximately the level of 250.5°C, after which an almost constant temperature was maintained.

When the thermo-electromotive force had attained this constant state, we were able to conclude: (1) that the brake fluid was in its boiling state and, furthermore, (2) that the temperature value of 250.5°C, as indicated by the thermocouple, was the boiling point of the brake fluid in view of the fact that balanced reflux was established.

Reflux Speed

The relationship between the intervals of the drops (reflux speed) and the temperatures obtained from the thermometer and thermocouple is shown in Fig. 4. It can be assumed that the errors caused by the reflux speed on the brake-fluid boiling points were on the level of −0.5°C on the minus side and +1.0°C on the plus side. It was considered that the boiling points of brake fluids was measured within ±1°C accuracy even though the brake fluid was boiling state, and reflux speed will not affect intensely the boiling point of the brake fluid in this experiment.

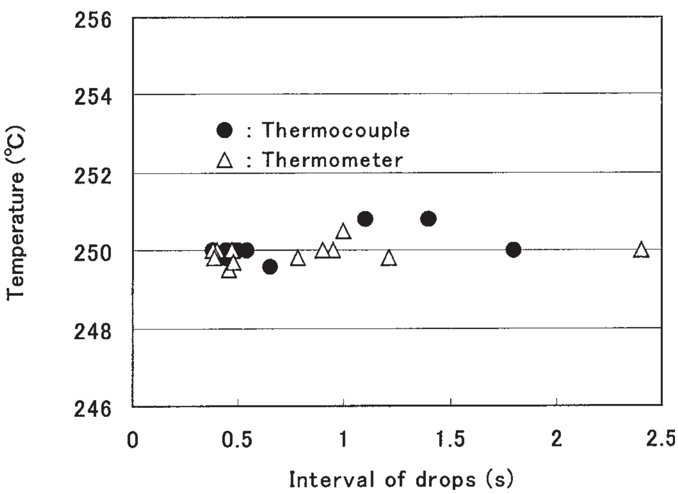

FIG. 4—*Relationships between temperature and interval of drops.*

Boiling Points of Small Volumes of Brake Fluids

The boiling points of small volumes of brake fluid were measured. In this test, 30 mL- and 50 mL-capacity pear shape flasks were used and the volumes of brake fluid samples were reduced in stages down to a minimum quantity of 2 mL. Figure 5 shows an example of the results when the 30 mL-capacity pear flask was used, the boiling point of a 2 mL sample was measured, and the thermo-electromotive force of the thermocouple was also recorded. The temperature of the brake fluid was gradually increased over time and achieved a constant temperature. The temperature of 253.3°C at this time was then considered to be the boiling point. It thus became evident that boiling points can be measured even when the volume of the sample of the brake fluid is as small as 2 mL. In addition, it was found that the intervals of the drops were not dependent on the capacity of the flask. The interval was from 3 to 100 s when the sample volume was more than 10 mL. Direct dripping from the bottom end of the water-cooled condenser could not be observed when the volume was less than 5 mL, however, since the brake fluid was carried to the inner wall of the flask when reflux occurred.

Figure 6 shows the influence of the sample volumes on the boiling points. The symbols "◆" represent the use of the 50 mL-capacity pear shape flask and it can be seen that the boiling points rise from the position at which the volume of the sample becomes less than 20 mL. A boiling point of 257.8°C was indicated when the volume of the sample was 2 mL. This is a value that is 7.8°C higher than the value of 250°C that is measured by the JIS measuring method. The "○" symbols, on the other hand, represent the use of the 30 mL-capacity flask. In this case, the boiling point was 253.3°C when the volume of the sample was 2 mL. As the volumes

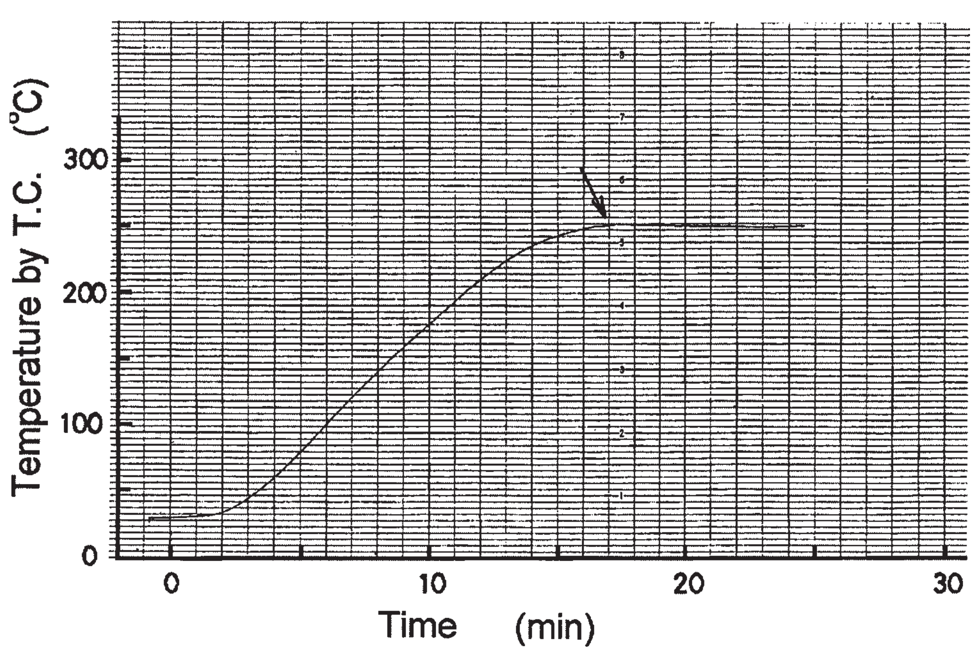

FIG. 5—*Temperature record obtained from 2 mL brake fluid using a 30 mL-capacity pear shape flask. Arrow shows a boiling point.*

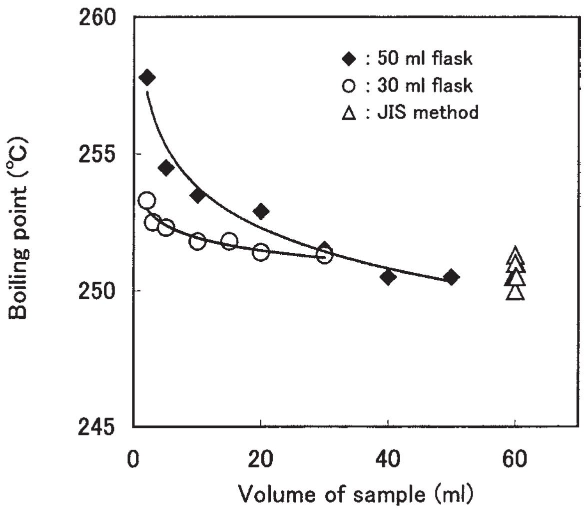

FIG. 6—*Boiling point dependence of volume of sample.*

of the samples were reduced in this way, higher measurements than those conforming to the JIS method were obtained. For the small volume samples (less than 20 mL), the boiling point was higher than the value of 250 to 251.5°C that is measured by the JIS method. The reason for this is thought to be that the mantle heater may be heating the thermocouple even though the thermocouple is immersed in the brake fluid. It is also thought that the smaller the container is when measuring the boiling points of minute volumes of brake fluids, the closer will be the measured temperatures to those that can be obtained by the JIS method.

In an actual automobile accident that is caused by trouble in a hydraulic braking system, the volume of brake fluid that can be collected for analyses is limited. For this reason, this method is worthwhile and has a high practical value since it sheds light on the vapor lock phenomenon by making possible the measurements of the boiling points of minute volumes of brake fluids in quantities as low as 2 mL at 3°C higher than those that can be obtained from the boiling points that conform to the JIS method.

Compensating of Boiling Points for Atmospheric Pressure

Since boiling points change depending on the atmospheric pressure, JIS K 2254 (5) prescribes a method for compensating for this phenomenon. In this method, the measured temperature is compensated by the compensation Eq (1) given below to the value for the standard atmospheric pressure (101.325 kPa), and this compensated value is then considered to be the measured result:

$$C = 0.0009 \{(101.3 - P)(273 + t)\} \quad (1)$$

Where,

C: Compensation value (°C) added to measured temperature
P: Atmospheric pressure (kPa) at time of measuring
t: Measured temperature (°C)

During the period of these tests, the atmospheric pressure was almost constant at 101.5 to 101.7 kPa. Assuming the measured temperature, i.e., the boiling point, to be 250°C, the compensation value from Eq (1) is 0.19°C at its maximum. Since this value is fairly small, no special efforts to compensate for the atmospheric pressure were made during these tests.

Percentages of Water Content and Boiling Points

Studies were conducted to determine whether or not this method could be used to obtain the boiling points of brake fluids that contain water. In these tests, a 10 mL-capacity pear shape flask was used. The volumes of the samples were 5 mL and 10 mL, and the percentage of water content in the brake fluid ranged between 0 and 10%. Additionally, boiling-point measurements were performed with a 60 mL volume of sample with a round-bottom flask and the measured values from these tests were considered to be the boiling point for standards.

Figure 7 shows the boiling points of brake fluids that contain various percentages of water. In the method prescribed by JIS (symbolized by "●"), the boiling point of pure brake fluid was approximately 250°C, but this dropped sharply to about 150°C when the percentage of water content in the brake fluid was made to be 2 to 3%. It dropped further to approximately 120°C when the percentage of the water content was increased to 10%. In addition, although the boiling points of small volumes of brake fluids containing water (as indicated by the symbols "○" and "△") were somewhat higher than in the method prescribed by JIS, these also dropped in a similar way. The value indicated for the boiling points of small volumes of brake fluids with percentages of water content of 3% was approximately 12°C higher than that obtained by the JIS method. In other words, it will be said that these values of the boiling points of small volumes of brake fluids with percentages of same water content were almost same in this experiment.

In order to investigate the effects of the volume of the sample on the boiling point, we conducted tests with the percentage of water content at 5% and used 10 mL- and 30 mL-capacity pear shape flasks. As shown in Fig. 8, the boiling points rose as the volumes of the samples decreased and the maximum difference was in the range of approximately 20°C. Consequently, even when the rise in temperature was in this range, it could nevertheless be concluded from the fact that the boiling points of small amounts of brake fluids could be measured that this method poses no special forensic problems from the standpoint of workability.

Testing of Absorbed Moisture

The test of absorbed moisture by stirred brake fluid was conducted in an environment in which the humidity was set at 74 to

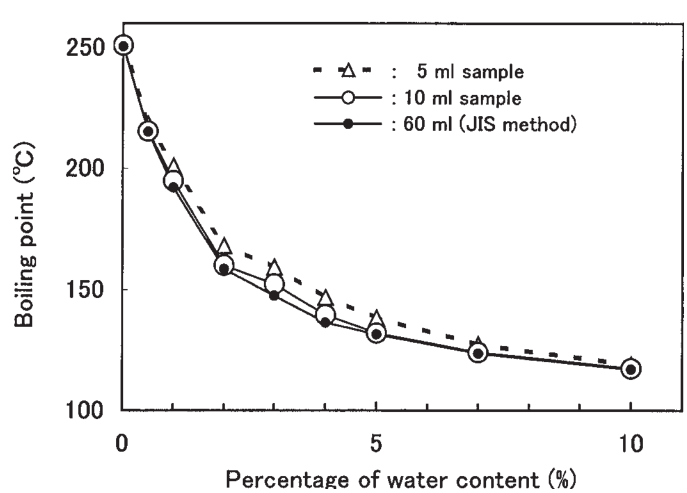

FIG. 7—*Boiling point dependence of percentage of water content by using 10 mL capacity pear shape flask for 5 mL and 10 mL samples.*

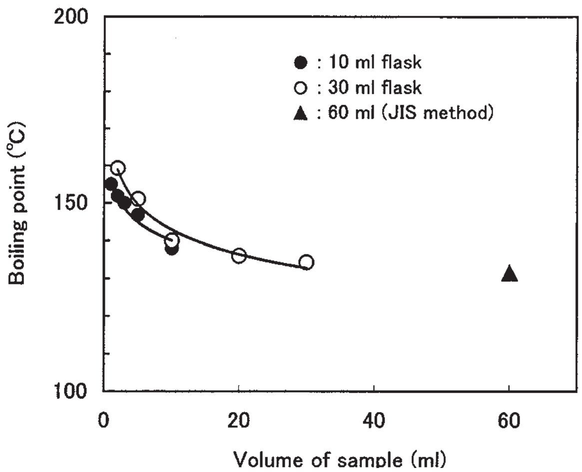

FIG. 8—*Boiling point dependence of volume of samples with the percentage of water content at 5%.*

82%, which is normal during the rainy season in Japan, and in which the temperature was set at 27 to 29°C. As shown in Fig. 9, the results made clear the fact that the boiling points for both BF-3 and BF-4 brake fluid dropped sharply to approximately 150°C within less 10 h than of stirring time and to approximately 120 to 130°C after about 30 h of stirring time had elapsed.

Whereas a tendency for the boiling points to drop was indicated as time elapsed, there were partial indications of somewhat high measured values, but these were thought to be due to the influences of the humidity and the stirring conditions at the time of the test. From the fact that the brake fluid was made to exhibit such a high degree of hygroscopicity in this way, the necessity of designing, properly maintaining and inspecting reserve tanks, etc., to assure perfect seal ability became readily apparent.

Boiling Points of Brake Fluids Taken from Automobiles

Samples of brake fluids were taken from the reserve tanks and rear-wheel cylinders of six automobiles. Since new brake fluid was replaced for old during automobile inspection for automobiles No. 1 and 2, it was learned from the records at that time that BF-4 brake fluid was used for automobile No. 1 and that BF-3 brake fluid was used for automobile No. 2. However, the types of brake fluid used in the other automobiles are not known.

The results of the measured boiling points are shown in Fig. 10. Although the boiling points of new brake fluids are assumed to be at least 200°C, the boiling points of the brake fluids sampled from the automobiles were found to have dropped to approximately 140°C.

Moreover, in regard to the sampling location, the brake fluids from the wheel cylinders of some automobiles had boiling points that were approximately 40°C lower than those of the brake fluid taken from the reserve tanks. One of the causes of this is thought to be the presence of dirt in the brake fluid. In addition, the difference in the percentage of the water content between brake fluid taken from the wheel cylinders and brake fluid taken from the reserve tank will reduce the boiling point.

Consequently, while it is necessary to measure the boiling points of brake fluid in order to prevent accidents, such measurements must not be limited to brake fluids only from the reserve tank. It is also essential to take samples from the wheel cylinder since the cylinder is most easily subjected to heating and boiling point of brake fluid in wheel cylinder can differ from brake fluid in the reserve tank.

Conclusions

Measurements of boiling points of small volumes of brake fluids were performed using pear shape flasks as containers and thermocouples to measure temperatures. This new method was applied to measure the boiling points of brake fluid taken from automobiles.

It was demonstrated that there was a 1:1 correspondence between JIS-prescribed thermometers and the thermocouples when the brake fluid was in a boiling state. These tests measured the boiling points of small volumes of brake fluid, down to 2 mL, with an accuracy of approximately 3°C of the boiling points as determined by the JIS method. Even when the brake fluids contained water, it was possible to perform boiling point measurements of small volumes of brake fluid. Consequently, this method can serve as one means that can be used to analyze the forensic causes of automobile accidents.

When tests were conducted in which the brake fluid was stirred to cause it to absorb moisture, it became evident that the boiling

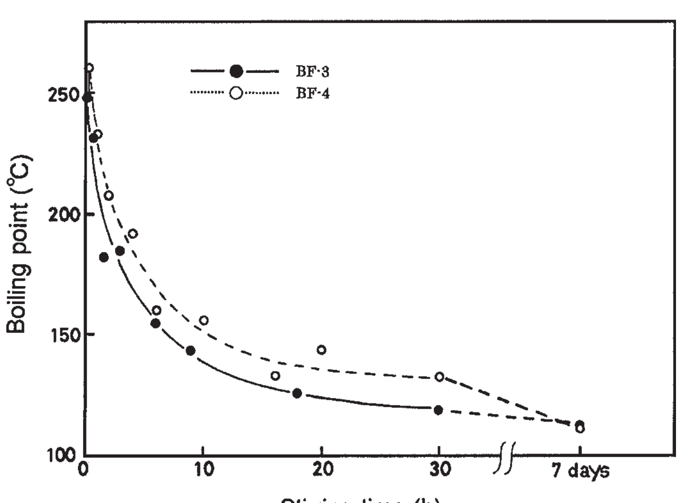

FIG. 9—*Boiling point dependence of stirring time in the air.*

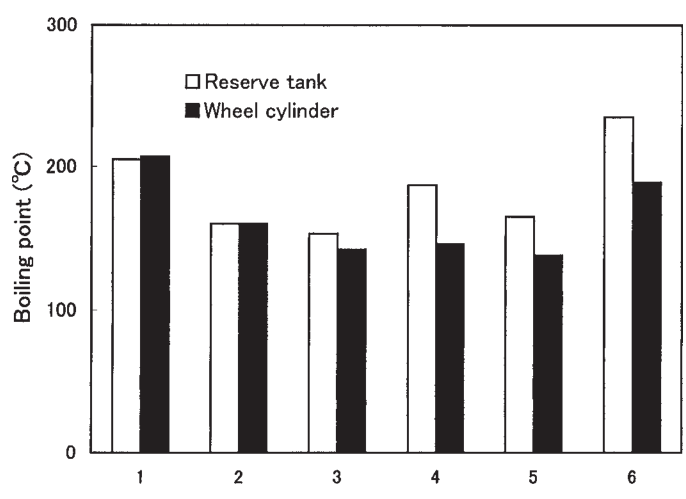

FIG. 10—*Boiling point of brake fluid taken from automobiles.*

point dropped to approximately 130°C after approximately 30 h of stirring. It was also confirmed that brake fluids possess a pronounced degree of hygroscopicity.

The boiling points of brake fluids that were taken from some automobiles dropped to approximately 140°C. In addition, the boiling points of brake fluids in the wheel cylinder of some automobiles were approximately 40°C lower than that taken from the reserve tanks.

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