Technological Background and Latest Market Requirements concerning "Static Viscosity" Measurement with a Tuning-fork Vibration Viscometer

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ABSTRACT

We introduce a new method viscometer "Sine Wave Vibro Viscometer" which principle is different from conventional viscometers, such as the capillary viscometers or the rotational one.

And also We propose a new viscosity unit "static viscosity[sv] $=$ viscosity[Pa·s] $\times$ density[kg/m^3]".

This sine wave vibro viscometer features a small amount of sample and wide range measurements without replacing the sensor.

The SV-1A requires only 2ml sample and has measuring range from 0.3mPa·s to 1000mPa·s.

The SV-10A requires only 10ml and has measuring range from 0.3m Pa·s to 10000m Pa·s.

Also describing the measuring method and features of this vibro viscometer. And explaining about JCSS and the measurement uncertainty evaluation for viscosity.

Finally showing the viscosity measurement result of various substances measured with this vibro viscometer.
(For example: the cloud point of a surface-active agent, the concentrations for ethanol solutions, the cure process of silicone adhesive and the coagulation process of egg white.)

1. INTRODUCTION

Various methods have been invented for measuring viscosity. Each of these methods is selected and used in the industry where it is most suitable. However, applications of viscosity measurements are recently expanding into new fields such as measurements of polymeric solutions, adhesive agents, coating materials, abrasives, engine oils, biodiesel fuels, and even soft drinks, cosmetics and human blood. Meanwhile, demands are rising for a measuring system that can minimize the energetic interference to a sample liquid such as rotative force and barycentric shift in order to measure the viscous property that is inherent to the liquid. Moreover, there are increasing requirements for measuring continuously a wide range of viscosities in order to observe a viscosity change caused by a temperature change, the curing of an adhesive agent, etc. The following will present an explanation of the tuning-fork vibration viscometer as a device that satisfies the above requirements, the technical background of its JCSS standardization and actual measurement examples. In addition, the physical quantity measured by the new viscometer, "static viscosity (sv)" [viscosity $\times$ density] will be discussed.

2. TUNING-FORK VIBRATION VISCOMETER

In the field of liquid viscosity measurements, the capillary viscometer and the rotational viscometer have a long history and are widely recognized. Meanwhile, although the principle for the vibration viscometer was proposed a long time ago, it was only about 20 years ago that the theory was put into actual practice due to various technological difficulties. The recently developed, tuning-fork vibration viscometer not only realized downsizing and price-reduction of the instrument but also made it possible to perform wide-range, continuous measurements from 0.3 mPa·s (equivalent of acetone) up to 10,000 mPa·s. More recently, measurements with as small as 2ml sample liquid have become possible, whose applications including the viscosity measurements of such fluids as resist inks for liquid crystals and human blood. The high-performance, tuning-fork vibration viscometer is rapidly expanding its scope of applications to where viscosity measurements used to be impossible. Meanwhile, due to quality control requirements in offshore manufacturing, the precision and the user-friendliness of the tuning-fork vibration viscometer have also been gaining attention at the production level (although delocalization has been decreasing lately).

2.1 MEASUREMENT PRINCIPLES OF THE VIBRATION VISCOMETERS

The damped vibration of a spring in a liquid is influenced by the restorative force of the spring and the viscous resistance of the liquid. Based on this idea, the characteristics of the damped vibration can be represented in a differential equation, which is then integrated to obtain a viscous resistance. This viscous resistance is then used to calculate the viscosity value. The formula that expresses this principle is a linear motion equation involving the inertial force due to the mass of the oscillator, the restorative force of the spring and the damping force due to the viscous resistance. Based on the solution of the equation, it could be deduced that the product of viscosity and density governs damping. When the oscillator is vibrated at the frequency f, the mechanical impedance R_z that the oscillator receives from the liquid will be:

$$R_z = A\sqrt{\pi f \eta \rho} \qquad (1)$$

In the above equation, f is vibration frequency (Hz), A is planar dimensions of the both sides of the oscillator in the liquid, η is the viscosity of the liquid, and ρ is the density of the liquid. Then if the force by which the electromagnetic driving unit gives the oscillator the constant vibration velocity $Ve^{i\omega t}$ is F, the following equation is valid:

$$R_z = \frac{F}{Ve^{iwt}} = A\sqrt{\pi f \eta \rho} \qquad (2)$$

Therefore, it is evident that the force generated in the electromagnetic driving unit to maintain the constant amplitude of the oscillator against the viscous resistance is proportional to the product of the viscosity η and the density ρ; that is, the "static viscosity."

2.2 STRUCTURE OF THE TUNING-FORK VIBRATION VISCOMETER

The tuning-fork vibration viscometer utilizes the same measurement principle as the vibration method, which was proposed a long time ago. However, the difference is that with the tuning-fork vibration viscometer, the vibromotive force generated due to the vibration—a problem inherent in the vibration method—has been eliminated by the adoption of a tuning-fork structure with two oscillator plates. The tuning fork and two oscillator plates function as a resonance system that is a highly sensitive viscosity sensor. Moreover, the viscous resistance of the liquid and the driving force generated in the electromagnetic unit are successfully balanced because the amplitude of the oscillators is always feedback-controlled to remain constant. By adopting the same measuring system as the electromagnetic weighing sensor of a balance (called the "null method"), it is now possible to perform a wide, dynamic range of highly sensitive viscosity measurements.
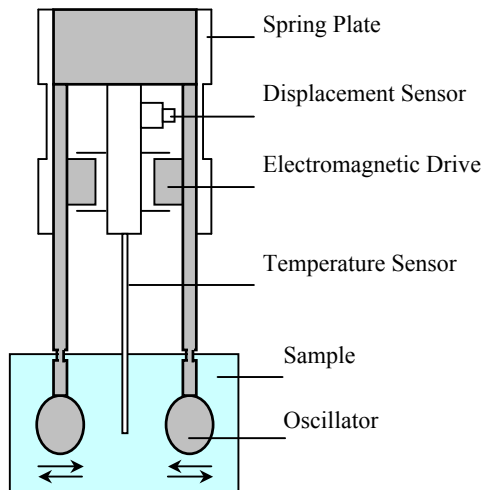

Figure 1: Structure of Viscosity Detection Unit

Figure 2: Tuning-fork Vibration Viscometer SV-A

(2ml sample measurement is possible)

Recently, viscosity measurements that require only 2ml sample liquid while measuring the temperature of the liquid have been realized, responding to the need for small sample measurements for expensive liquids. When the sample volume is 2ml, the size of a sample cup becomes very small. Therefore, in order to make the positioning of the sample cup easier, the precisive X-Y-Z stage is provided as standard. In addition, the oscillator and the temperature sensor are now made of titanium because there are growing demands for measuring the viscosities of strongly-acid or strongly-alkaline liquids along with the expansion of viscosity measurement applications.

3. "STATIC VISCOSITY" MEASURED BY THE TUNING-FORK VIBRATION VISCOMETER

As illustrated in the solution of the motion equation (1), the physical quantity measured by the vibration viscometer is viscous resistance, and this viscous resistance consists of "viscosity × density." If we define "viscosity × density" as "static viscosity," the relationships between each viscosity measuring method and physical quantity to be measured will be the "kinetic viscosity" (viscosity / density) for the capillary viscometer, the "viscosity" for the rotational viscometer, and the "static viscosity" (viscosity × density) for the vibration viscometer. The following is a brief summary of each viscometry device, its features and unit system:

- Kinetic viscosity: Determined by measuring the time taken by a liquid to go through a flow channel in accordance with gravity. This method is accompanied by a barycentric shift of the liquid, and the measured time is proportional to the viscosity, but inversely proportional to density.
- Viscosity: Determined directly from the difference in the rotational torque generated within a liquid in accordance with rotational movement. The liquid is always measured in a rotational state.
- Static viscosity: Determined based on the driving force torque loaded on the oscillator within a liquid. The driving force is proportional to the product of viscosity and density, and there is no barycentric shift of the liquid. The minute amplitude of the oscillators causes little change to the physical properties of the measured sample.

Terms	Kinetic Viscosity	Viscosity	Static Viscosity
Definition	Viscosity / Density	Viscosity	Viscosity × Density
SI Unit	m^2/sec	$Pa \cdot s$	$Pa \cdot s \times kg/m^3$
Dimension	L^2/T	$ML^{-1}T^{-1}$	$M^2L^{-4}T^{-1}$
CGS Unit	St	cP	$cP \times g/cm^3 = sv$
Unit Conversion	$1\ m^2/sec = 10^6\ cSt$	$1\ Pa \cdot s = 10^3\ cP$	$1\ Pa \cdot s \times kg/m^3 = 1\ sv$
Measurement Method	Capillary method, etc.	Rotational method	Vibration method
Conversion to Viscosity	Density correction required	— —	Density correction required

Table1: Comparison between Kinetic Viscosity, Viscosity & Static Viscosity

4. JCSS STANDARDIZATION OF VISCOSITY

After modeling the above measurement principle and determining the uncertainties based on the measurement errors inherent in the product, the vibration viscometers were accredited as a Japan Calibration Service System (JCSS) standard device along with the standard liquids of viscosity, capillary viscometers and the rotational viscometers as of April 24, 2006, although at present the JCSS of viscosity is yet to be put into practice. The documents demonstrating the modeling and the uncertainties of the vibration viscometers have greatly contributed to the JCSS standardization of the other viscometry devices as well. Fore reference, the uncertainties estimated for the tuning-fork vibration viscometer SV-10 when calibrated using standard liquids for calibrating viscometers under a temperature of 20˚C are shown in Table 2.

Uncertainty Factor	Uncertainty Component	Distribution	Relative Contribution Of Uncertainty (%)	
			JS20	JS14000
Uncertainty based on Calibration Liquid	Calibration Liquid	Normal	0.062	0.111
Uncertainty based on Temperature Measurement	Accuracy	Rectangular	1.20	2.58
Uncertainty based on Calibration Procedure	Liquid Surface Adjustment	Rectangular	0.72	0.72
Uncertainty based on Other Factors	Repeatability Rounding Error	Normal Rectangular	1.00 0.21	1.00 0.04
Combined Standard Uncertainty Expanded Uncertainty (k = 2)			1.74 3.48	2.86 5.72

Table 2: Estimated Uncertainties of a Tuning-fork Vibration Viscometer
(2 Standard Liquids for Calibrating Viscometers, 20˙C)

What follows is an explanation of some distinctive uncertainty components of the tuning-fork vibration viscometer. From the certificate of properties for the standard liquids for calibrating viscometers based on JISZ8809, the uncertainty based on the calibration liquid u_s and the static viscosity S can be obtained as follows where η: Viscosity, v : Kinetic viscosity, ρ: Density

$$S = \eta \times \rho = v \times \rho^2 \qquad (3)$$

When the standard uncertainty of kinetic viscosity is u_v and that of density is u_ρ based on the certificate of properties, the below formula is valid:

$$u_s = \sqrt{\left(u_v \big/ v\right)^2 + \left(2 \times u_\rho \big/ \rho\right)^2} \qquad (4)$$

As shown in Table 2, the uncertainty based on calibration procedure is largely influenced by the uncertainty based on temperature measurement. This is due to the fact that the temperature coefficient of the static viscosity is −4.1%/˚C for JS20 and −9.8%/˚C for JS14000. In order to minimize the uncertainty based on calibration procedure, it is necessary to lessen the temperature distribution inside the sample cup and the difference in temperature between the temperature sensor and the oscillators. The sample cup of the SV-10 is as small as 35ml (the optional cup of 10ml is also available), and it is possible to control the temperature of the sample liquid with a water jacket and a constant heat water tank. Therefore, the temperature distribution will be smaller than using a beaker, etc. However, it will be difficult to lessen the temperature distribution actively when the viscosity of a sample liquid exceeds 1000 mPa·s because the rotator of a stirrer for churning the liquid will not rotate. For example, when setting the liquid temperature of JS14000 at 40˚C under a room temperature of around 25˚C, a temperature difference by approx. 0.3˚C between the temperature sensor and the oscillators will be present, which will result in an error of approx. 3% in viscosity value. To combat this, the viscometer and the standard liquids for calibrating viscometers were placed in a temperature-controlled chamber so that the temperature difference could be reduced to within 0.02˚C, virtually eliminating any influence of temperature. Consequently, the uncertainty based on the temperature measurement was narrowed down to the uncertainty based on the temperature sensor, which was 2.6%. The uncertainty based on calibration procedure is attributable to the uncertainty caused by an operator being unable to position the oscillators always on the same level against the liquid surface. With viscometers other than the capillary type, the display value will be by principle influenced if the depth of the oscillator in the liquid varies. This problem was solved by making a narrow area in each oscillator as well as equipping the device with a liquid level adjustment plate, which reduced the uncertainty to 0.7%.

5. MEASUREMENT EXAMPLES OF THE TUNING-FORK VIBRATION VISCOMETER SV-10

Now, let us examine various examples of static viscosity measurements using the tuning-fork vibration viscometer SV-10. The physical quantity measured in these examples is the "static viscosity" (sv). However, to avoid confusion, the vertical axis of the graphs will indicate the "viscosity" with the unit being either Pa·s or mPa·s, assuming that the densities of the samples were all 1.0 g/cm³.

5.1 MEASURING THE CLOUD POINT OF A SURFACE ACTIVE AGENT (SEE FIGURE 3)

This is an example of a cloud-point measurement of a nonionic surface-active agent. The viscosity increased gradually as the liquid temperature was raised, but there was an abrupt fall in viscosity at 35.4°C. This point is the cloud point of this liquid, where the surface-active agent starts dissociating its hydrogen bond and becoming oil soluble and cloudy. Detecting the cloud point of a surface-active agent is the most important measurement in designing the basic performance and function of the surface-active agent. In the past, there existed cloud-point meters with which a cloud point was optically measured. On the other hand, being able to detect a cloud point by measuring changes in static viscosity, which is a physical property, is groundbreaking, and for this reason the tuning-fork vibration viscometer is highly evaluated.

Figure 3: Cloud-point Measurement of a Surface-active Agent

5.2 RELATIONSHIP BETWEEN THE CONCENTRATION AND THE VISCOSITY OF ETHANOL SOLUTION (SEE FIGURE 4)

Viscosity measurement examples of solutions of different alcohol/water ratios. The viscosity value increases as the alcohol concentration becomes higher until 40%. After 40%, the viscosity value decreases the higher the alcohol concentration. This phenomenon is consistent with past experiments, and the same viscosity change was observed with the tuning-fork vibration viscometer.
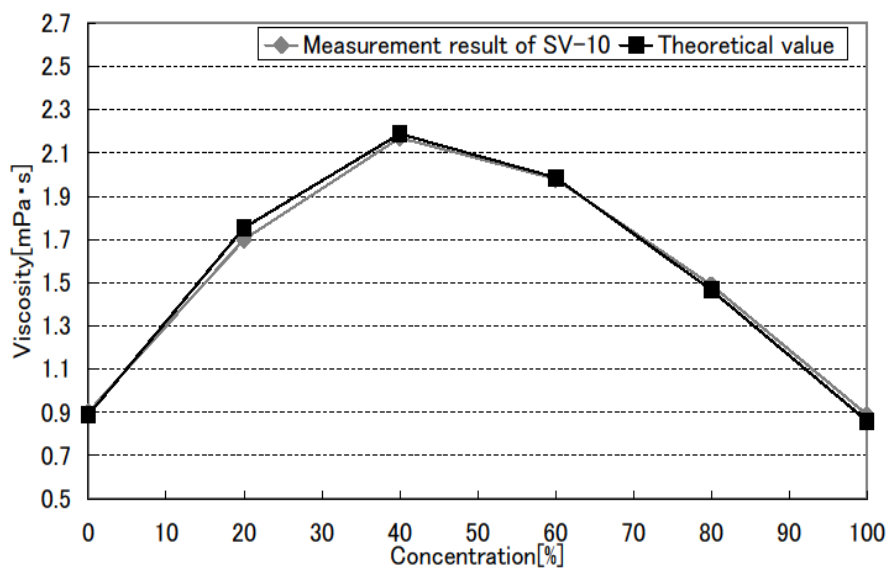
Figure 4: Concentration and Viscosity of Ethanol Solution

5.3 INFLUENCE OF AMBIENT TEMPERATURE ON THE CURE PROCESS OF MORTAR(SEE FIGURE 5)

The viscometer and a commercially-available mortar material were placed inside a temperature-controlled room, where water and the mortar were mixed under different temperatures in order to measure the influence of differences in ambient temperature on curing. It is possible with the SV-10 to measure the cure process while checking directly the temperature of the sample since the temperature sensor is placed between the two oscillators of the device. Consistent with what is already known from experience, a relationship was found to exist between the temperature and the cure process by means of the static viscosity measurement. When the cure process was under a temperature of 40°C, there existed an unstable viscosity variation around 8000 mPa·s. This is supposedly due to slipping between the sample and the oscillators, which means that a state change of the sample around the oscillator surfaces was measured as a variation in viscosity value.
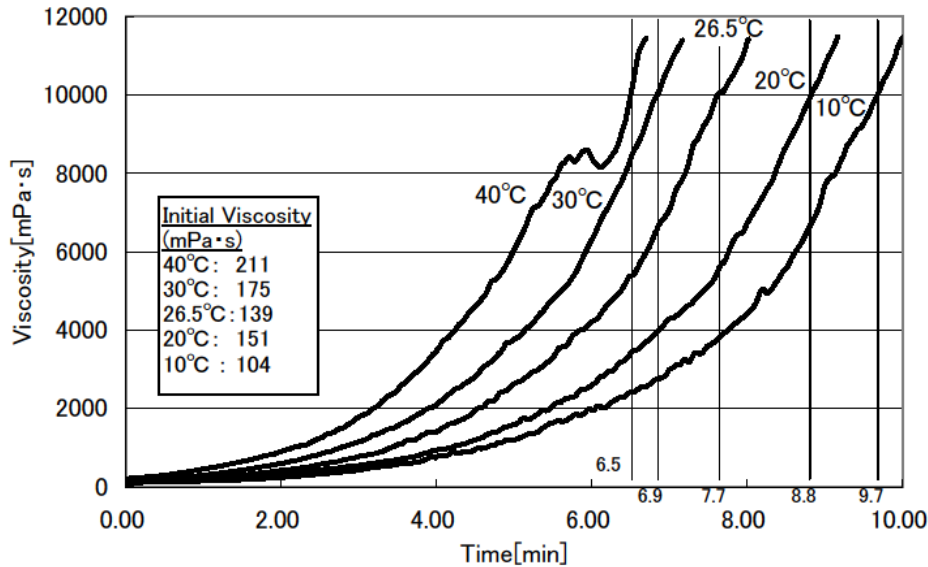
Figure 5: Cure Processes of Mortars under Different Ambient Temperatures

5.4 CURE PROCESS OF PLASTER (SEE FIGURE 6)

The cure processes when the water-plaster ratio was 67, 60 and 50% are shown. Here, it is easy to understand how plaster hardens rapidly in a few minutes and that curing speed varies greatly depending on the mixing ratio.
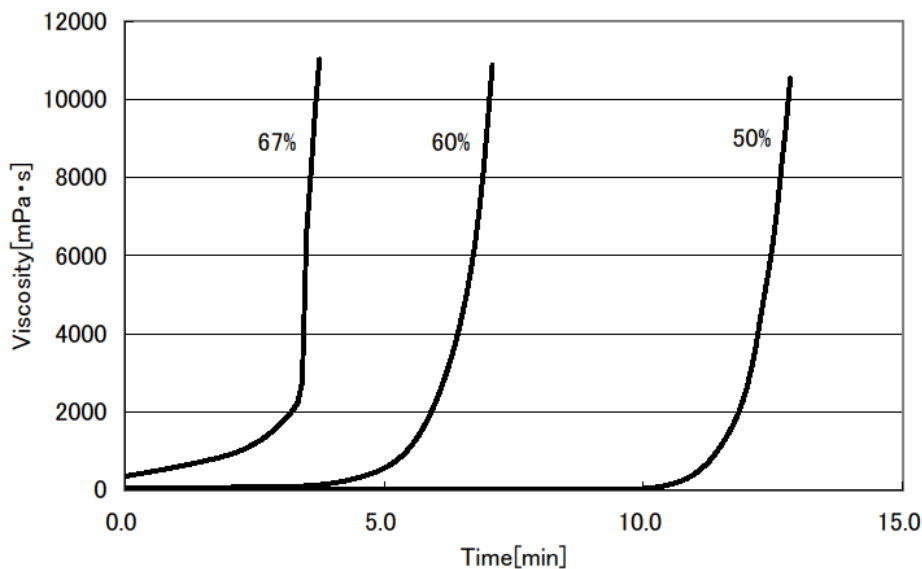
Figure 6: Cure Process of Plaster at Different Temperatures

5.5 CURE PROCESS OF A SILICON ADHESIVE AGENT (SEE FIGURE 7)

In general, silicon adhesive agents require a long time for curing. As shown in the example in Figure 7, the measured sample took 22 hours for its slow curing. This and other measurement examples of a long curing process are very rare, but these kinds of measurements are important for examining the physical properties of an adhesive agent during its cure process and for designing its adhesion characteristics.
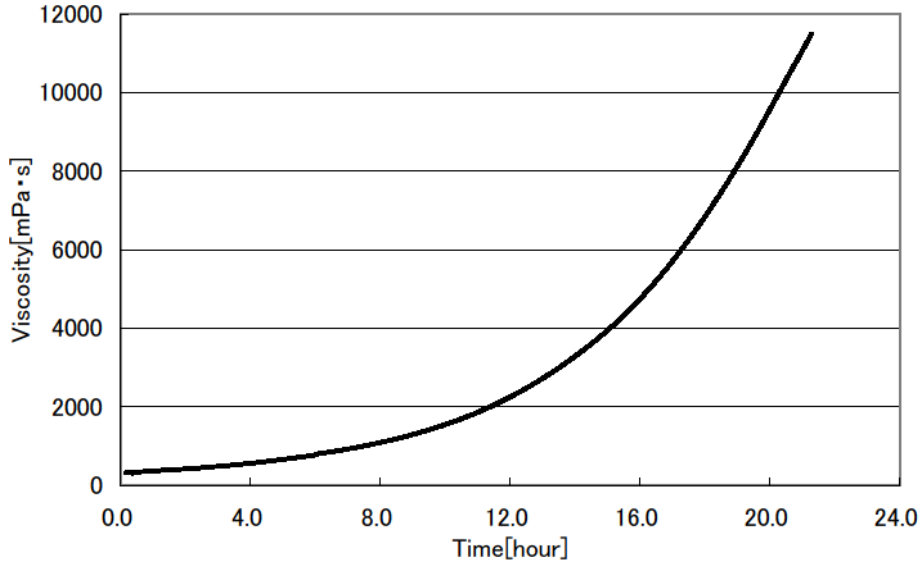

Figure 7: Cure Process of a Silicon Adhesive Agent

5.6 CONCENTRATIONS AND COAGULATION TEMPERATURES OF GELATIN (SEE FIGURE 8)

The graph shows an example of viscosity measurement of 2.5% and 5% gelatin solutions while varying the temperatures. It can be observed that the coagulation point depends on the concentration of the solution.
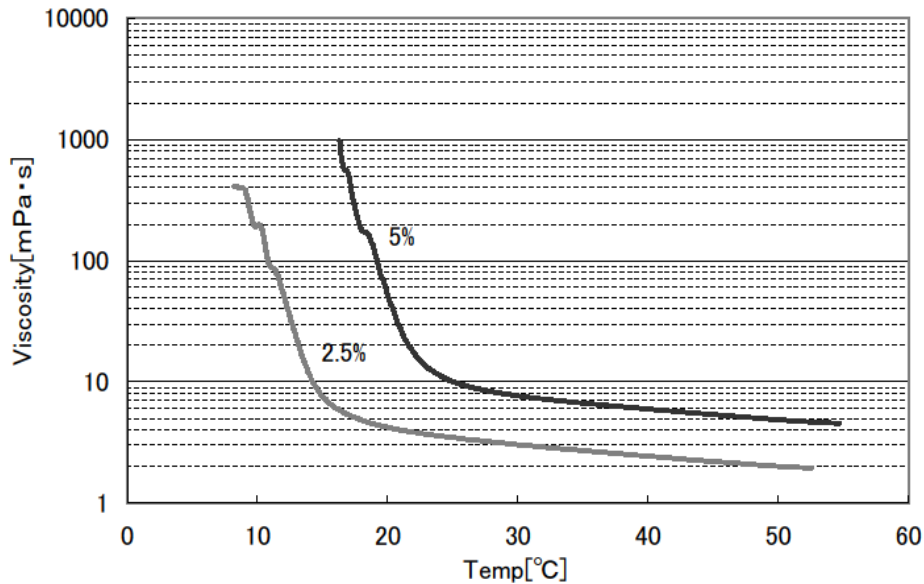

Figure 8: Concentrations and Coagulation Temperatures of Gelatin

5.7 CURING OF EGG WHITES DUE TO TEMPERATURE (SEE FIGURE 9)

The process in which protein becomes irreversibly hardened was measured by heating egg whites. Based on the thermal history of the graph (the horizontal axis indicates temperature and the vertical axis viscosity), the process can be described as (1) softening due to heat until 60°C, (2) starting to harden suddenly from 60°C, (3) passing a small peak around 68°C, and then (4) fully hardening. The peak around 68°C indicates that the egg white contains several kinds of proteins with different curing characteristics.
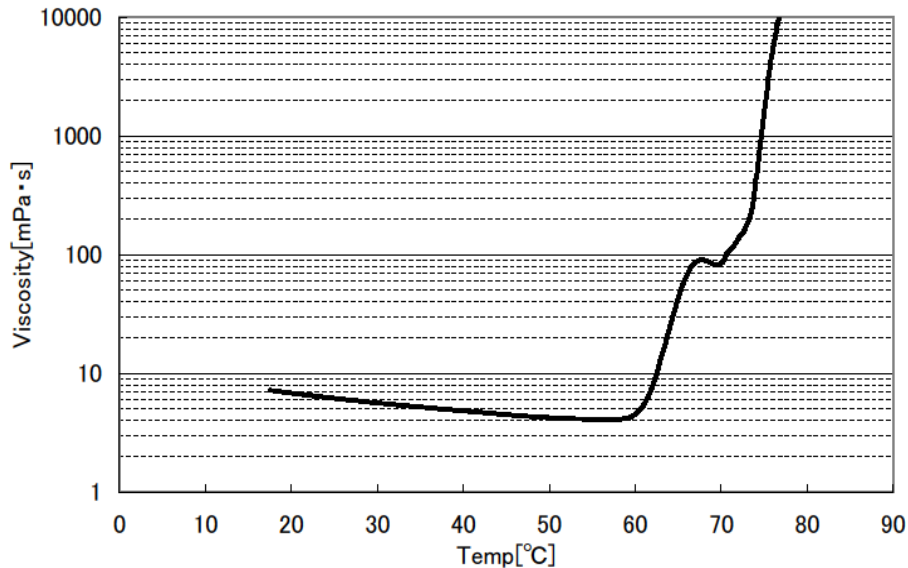

Figure 9: Increase in Viscosity of Egg White along with Rise in Temperature

5.8 MEASUREMENT OF THE GELATION POINT OF A SOLDERING FLUX DUE TO HEAT (SEE FIGURE 10)

In the graph, the horizontal and vertical axes indicate temperature and viscosity respectively. At around 70°C there is an inflection point where viscosity changes drastically. It can be inferred that a soldering flux is also designed to have a phase transition point at a certain temperature.
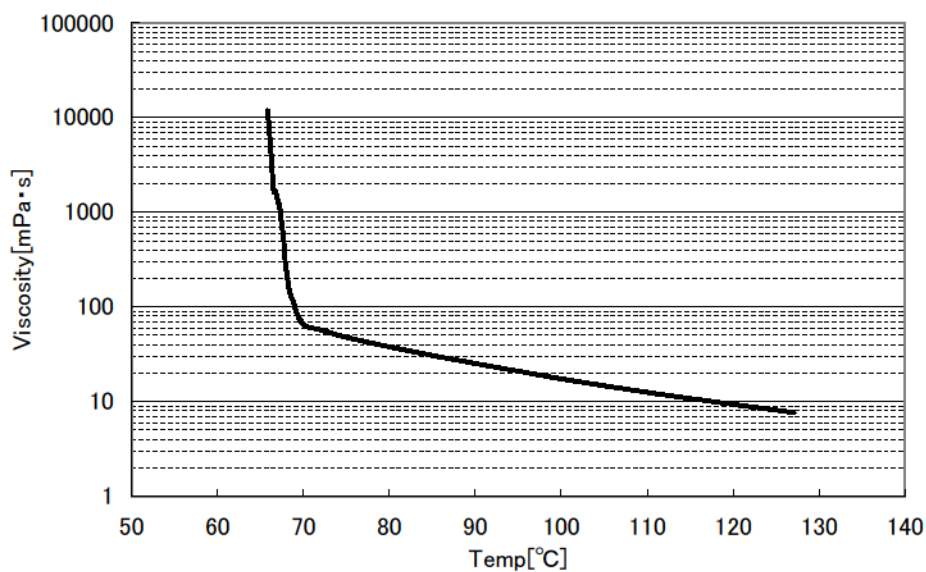

Figure 10: Measurement of the gelation point of a soldering flux due to heat

6. SUMMARY

For a long time, viscometers were limited to the capillary type, rotational type and the cup type, etc. It is true that these devices were forming a staple market. At the same time, advancing technological levels including the upgrading of R&D frameworks and enhancing sensitivities of measuring instruments has been increasingly an important issue in the industrial arena. In addition, standards and regulations concerning production lines are becoming more and more strict worldwide. For example, it is now essential to enhance qualities all the way from basic research to production lines, which involves evaluating and understanding the physical characteristics and properties of materials such as liquids. Consequently, there are emerging demands for measuring viscosities more accurately and efficiently as basic data that show the characteristics of the liquids. The tuning-fork vibration viscometer has the capabilities to satisfy such needs, and it should be possible to cultivate new technological fields through "static viscosity" measurements using this viscometer. For example, the tuning-fork vibration viscometer is already adopted and recommended by a leading engine oil manufacturer as a device for measuring viscosities of engine oils. It is also beginning to be used for blood viscosity measurements. As these examples indicate, it is expected that static viscosity measurements will be utilized in wider-ranging industrial fields including the medical industry in the near future.

7. REFERENCES

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