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Softening Point Experiments Compare Methods' Ease, Accuracy

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A petrochemical product's softening point impacts performance; however, complex test sample preparation and varying heating requirements can present repeatability challenges that affect quality. Comparative softening point studies on bitumen samples using ASTM D 3461 (Mettler cup-and-ball) and ASTM D 36 (ring-and-ball) explored the accuracy and repeatability of each.

Softening and dropping point determination are established analytical tests that provide quality control for petrochemical products such as bitumen (asphalt). However, to be accurate, manual/semi-automated quality tests prescribed in ASTM standards must be performed in a standardized fashion. Unfortunately, manual processing bears inherent process risks that affect repeatability, which in turn can negatively affect end-product performance. Additionally, today's most prevalent softening point determination methods differ in terms of hardware. Do the methods provide similar results?

To answer this question and explore repeatability, this paper reviewed two softening point determination methods currently considered acceptable for quality control, ASTM D 3461 (Mettler cup-and-ball) and ASTM D 36 (ring-and-ball). The resulting study, Characterization of Bitumen (Asphalt) by Softening Point Determination, mounted independent experiments at different test locations using both pure bitumen and wax- or polymer-modified bitumen samples.

Softening point tests showed that while pure bitumen results were comparable between methods, modified samples produced greater deviation between Mettler cup-and-ball and ring-and-ball methods. Mettler cup-and-ball offered better repeatability overall, presumably due to its precise oven-controlled heat and lower heating rate of 2°C per minute (compared to the rate of 5°C per minute used in the ring-and-ball method).

Characterization of Bitumen (Asphalt) by Softening Point Determination

Bitumen physical properties are varied with heat and binder materials such as polymers and hard waxes to establish optimum softening point for particular applications such as road coverings and roof felt. Product quality can be controlled through precise softening point measurement. Two methods are widely accepted to determine softening point: the Mettler cup-and-ball (ASTM D 3461) and the ring-and-ball method (ASTM D 36). The following uses commercially-available bitumen samples to assess the workflow efficiency and repeatability of each method.

1. Principles of ASTM D 3461 (cup-and-ball) determination

According to ASTM D 3461, the softening point is the point at which a test substance escapes from a standardized cup in defined conditions – in this case, a heating oven at elevated temperatures – enforced by the weight of a standardized ball. A softened sample flows freely once it has escaped the cup to 19 mm (Figure 1). Using the METTLER TOLEDO DP70 Dropping Point System, video image analysis is performed concurrent to oven-temperature recording to determine softening point (Figure 2).

2. Principles of ASTM D 36 (ring-and-ball) determination

Using ring-and-ball, samples are confined in small brass rings loaded with a steel ball. After preparation, samples are suspended in a beaker of water, glycerin or ethylene glycol 25 mm above a metal plate. The liquid is heated, and the ball sinks through the brass ring. An automatic ring-and-ball dropping point instrument was used for the purposes of this experiment, which automatically detects progress using a laser beam light barrier. Bath temperature is also recorded (Figure 3).

3. Experiment methodology

Pure bitumen, wax-modified bitumen (2-4%) and polymer-modified bitumen (2-4%) were tested in two different labs/locations. Ring-and-ball tests using the automatic ring and ball instrument were performed by two different operators in one lab; cup-and-ball tests using the METTLER TOLEDO DP70 were performed by one operator in both labs.

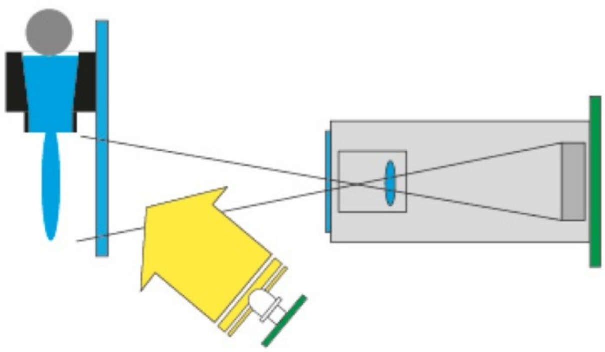

Fig. 1: Schematic of cup-and-ball detection principle

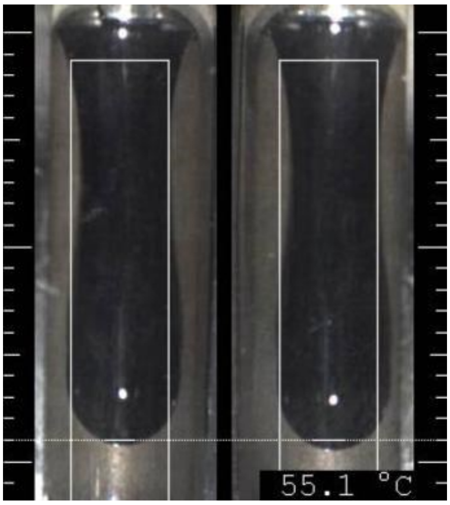

Fig. 2: Softening point of two pure bitumen samples with white dotted line indicating 19 mm distance from cup orifice

Samples were melted to 180°C on a hot plate and homogenized using a glass rod, then poured either directly into the DP70 sample preparation tool that enables four samples to be prepared in ASTM D 3461 cups simultaneously (Figure 4), or into ASTM D 36 brass rings placed on baking paper to facilitate sample release after cooling. The DP70 sample preparation tool facilitates the sample preparation significantly whereas repeatable ASTM D 36 sample preparation requires experienced operators. In both cases excess sample was removed with a hot knife and tests were performed within 2 hours. Repeat testing using the same sample was not permitted.

According to ASTM D 3641, starting temperature shall be 20°C below expected softening point with a heating ramp of 2°C until softening point is detected. For ASTM D 36, the estimated softening point of an individual sample determines both the heating temperature and bath medium with a final heating ramp of 5°C per minute until the actual softening point of the sample is automatically detected.

Each test was repeated two times to receive four softening points that were then averaged. Standard deviation was also calculated (Table 1).

4. Results and discussion

ASTM D 3461 Mettler cup-and-ball proved to be an easier to process to manage. Cups were easier to fill. Plus, the DP70 did not require cleaning between experiments due to the ability to fit it with new collector glasses. Finally, the oven offered faster, more controlled ballistic heating. No time preparing additional baths after determining softening point was required, as was required for multiple ring-and-ball tests according to ASTM D 36.

As far as results themselves, average softening point difference between test methods for pure bitumen was between 0.5 – 1.1°C, within ASTM D 36 repeatability of 1.2°C. Based on this, the methods can be considered equal for pure bitumen softening-point testing. Both tests also achieved repeatability as required by their individual standards; however, Mettler cup-and-ball achieved better repeatability 60% of the time, which is a statistically significant improvement.

Standard deviation in 85% of the Mettler cup-and-ball results sets were <0.5°C as required by standard. However, much higher differences between modified bitumen samples in each test method were recorded. Observed deviations seemed to be due to the visco-elastic properties of materials reacting to the different mechanical stresses imposed by each method at high temperatures.

Ring-and-ball seemed to enforce the softening point event by passing the material together with the ball through the ring, whereas the cup-and-ball only enforced sample outflow. Because of the latter, results of Mettler cup-and-ball methods are presumed to better reflect the unaltered, rheological characteristics of all bitumen samples.

5. Conclusions

When reviewing results, it is clear that test principles have an influence on rheology and therefore the softening point determination of respective bitumen samples. The difference is not significant for pure bitumen; however, it is pronounced in an unsystematic way for modified samples.

Based on the individual repeatability achieved, however, test results allow for intra-comparative studies of each method. Better repeatability with the Mettler cup-and-ball method is attributed to its precise, accurate oven-controlled heat, as well as its lower heating rate of 2°C per minute compared to 5°C per minute used in the ring-and-ball method.

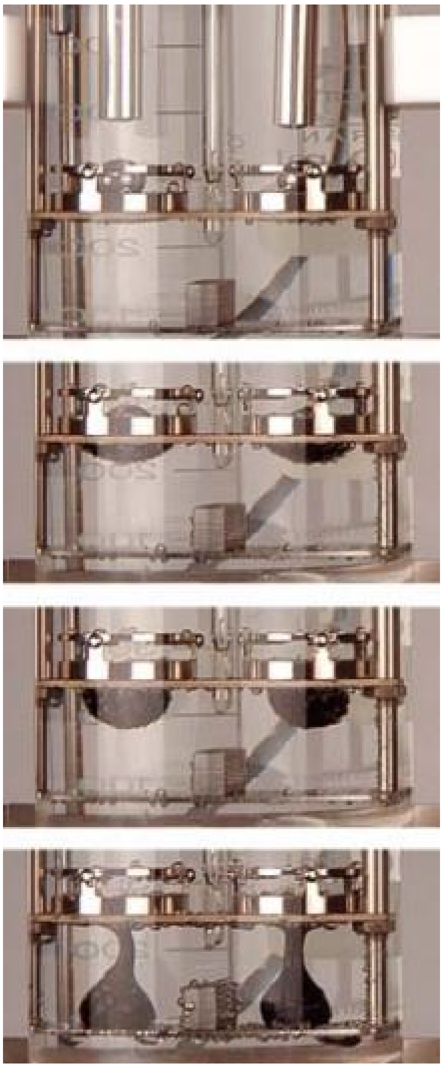

Fig.3: Ring-and-ball detection sequence with temperature increase sequenced from top to bottom

Fig. 4: The DP70 sample preparation tool

Tab. 1: Test results of ASTM D 3461 (Mettler cup-and-ball) and ASTM D 36 (ring-and-ball)

Bitumen type	Softening point ASTM D 3461 [°C]	Standard deviation [°C] (permitted: 0.5 °C)	Softening point ASTM D 36 [°C]	Standard deviation [°C] (permitted: 1.2 °C)	Difference SP (cup-and-ball – ring-and-ball) [°C]
Pure	51.0	0.08	50.3	0.24	0.7
	51.8	0.1	50.8	0.62	1.0
	55.0	0.14	54.0	0.10	1.0
	61.3	0.05	60.2	0.24	1.1
	85.1	0.56	84.6	0.42	0.5
Wax modified	85.0	0.24	83.4	0.17	1.7
	100.4	0.10	89.1	0.85	11.3
	91.7	0.17	90.0	0.42	1.7
	103.8	0.29	106.3	0.73	-2.5
Polymer modified	61.7	0.56	58.8	0.39	2.9
	65.3	0.25	61.6	0.57	3.7
	93.7	0.12	88.6	0.42	5.1
	92.5	0.24	91.1	0.21	1.4