A MELTING POINT METHOD FOR WAXES

R.A. Siddiqui, K.M. Bhatti and Nikhat Shaukat

Physical Research Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

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A new technique based on the variation of physical state under the influence of surface tension near the transition point has been evolved for the determination of melting point of waxes. An apparatus employed in this technique has been devised and successfully operated. Using this technique two methods have been developed, one of moderate accuracy of the order ± 1.5 C and the other of considerably improved accuracy. The latter method employs graphical extrapolation. Results of the melting point determination for three waxes are given and compared with those obtained by a conventional method.

Introduction

Waxes in general are complex mixtures of various compounds having melting points scattered over a wide range of temperature; consequently the "melting point of wax" does not carry the same connotation as accorded to that of a pure compound or to that of a relatively simple mixture of substances.

In the process of melting, in addition to the phenomenon of "premelting", waxes undergo a number of changes in the physical state, manifested by the phenomenon of softening. The process of softening of a wax begins with the melting of the lowest-melting point constituent followed by others in the order of ascending melting points. The relative abundance of the constituents of a given specimen of a wax determines its physical characteristics at any given temperature.

The methods for the determination of melting point of waxes in use are rather unsatisfactory because these methods do not provide any precise information about the transitional state of the wax under examination. At best they yield values corresponding to the arbitrary definitions of melting points which are invariably given with these methods.[2–6]

On close examination these definitions are found to have no theoretical support. For example, the definitions of melting point given with "ball and ring" method or Pohl's method are only a means of providing a convenient index for waxes.

On account of the complex nature of the wax composition, it is difficult to give a theoretical definition of melting point of waxes. However, some physical property should be used as a criterion for melting point of waxes to indicate the behaviour of the state of wax at the melting point. The melting point obtained would then provide a better index in comparison to those obtained by the conventional methods.

Methods developed on the basis of viscosity as the physical criterion have been tested by Marshall.[1] In the case of the crystalline paraffins and the plastic microcrystalline waxes there is no pronounced rise in viscosity as the soldification point of the wax is approached from either the rising temperature or the falling temperature side. In case of the hard microcrystalline waxes complications are introduced due to pronounced hysteresis in viscosity on the rising temperature curve. The viscosities immediately above the melting point are very high in comparison to the "falling temperature" values of the viscosity in this temperature range.

On account of these drawbacks in the viscometric method of melting point it is necessary to explore the use of other physical properties for a dependable criterion for melting point of waxes. The present work describes a method based on the effect of surface tension. The actual measurement of the surface tension is not, however, required to arrive at the melting point. It is the difference of behaviour of physical states of the wax under the influence of surface tension that is used to determine the melting point.

Liquids show a characteristic tendency to acquire a minimum surface area under their own surface tension almost instantaneously, whereas in solids the effect of this tendency is delayed or offset due to the forces responsible for their rigid form. In waxes an intermediate effect is observed over a considerable range of temperature.

In the viscometeric method, the viscosity of wax is determined at different temperatures in its softening range and a plot of viscosity against temperature is obtained. The melting point of the wax is indicated by a pronounced change in the slope of the curve. However, in the present method the time τ required for retraction of a thread of the wax drawn at different temperatures is determined and a plot of the time against temperature is obtained. The melting point

is indicated by the lowest temperature at which the time of retraction reaches a minimum value. The melting point thus obtained signifies that the state of the wax is sufficiently fluid to behave like a liquid and therefore acquires the shape with minimum surface area almost instantaneously. The time of retraction of the thread of differenet waxes at the melting points is in general different but always within a few seconds. This may enable the observer to arrive at the melting point of the wax by direct observation without any actual measurement of time. The results obtained by the "τ method" and the "direct observation method" are discussd below along with comparative study of the melting points of the waxes obtained by a standard conventional method, namely, Pohl's method.

Experimental

An apparatus was designed and constructed to work on the principle of the present method developed on the basis of the effect of surface tension on the state of wax at different temperatures.

The apparatus consists of a metallic box D ($6'' \times 6'' \times 12''$) shown in Fig. 1. It is made of a 1/8″ thick brass sheet covered on all sides with a 1/8″ thick asbestos sheet and is placed on an electrical hot-plate E. Two glass windows (not shown) are provided, one on each of the two facing walls. One is used to allow the illumination of the interior of the box and the other is used for the observation of the state of wax. Through the right hand side of the box an adjustable brass probe carrier B is fixed. The probe is made of a glass rod having a thin platinum wire at one of its ends to draw fine threads of wax. Two thermometer holders are provided on the top of the box to allow the thermometers to be placed inside the box. One of the thermometers, A, is for carrying and registering the temperature of the test wax attached to its bulb. The other thermometer C is placed in the holder with its bulb slightly above the heating surface, that is, the bottom of the box, for controlling the rate of heating.

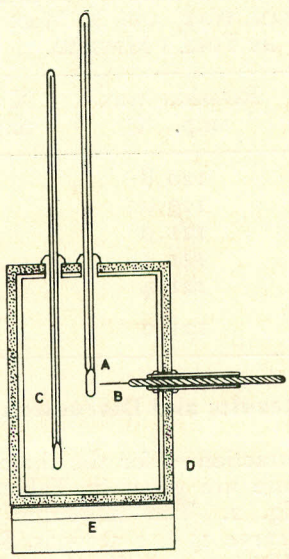

Fig. 1.—Schematic arrangement of the melting point apparatus (A, Melting point thermometer; B, Adjustable brass probe; C; Control thermometer; D, Metallic box; E, Hot plate).

Method

The two methods namely "τ method" and the "direct observation method" differ only in some experimental details, otherwise their procedures are the same. Therefore only the "τ method" is given in detail below and the direct observation method is dealt with briefly.

"τ *method*".—The melting point apparatus is set for observation by heating the box D to attain some steady temperature in the softening range of the test wax. The heavy thermal insulation of the box D and the controlled rate of heating ensures the temperature stability of the apparatus to a fluctuation of about $\pm 0.5°$C. A small piece of the wax sample is placed on the bulb of the thermometer A by gently pressing it against the bulb. Sufficient time is allowed for the attainment of temperature equilibrium. The probe is adjusted in level with the wax sample and a thread of the wax is drawn to a convenient but constant size. As soon as the thread breaks from the probe the stop-watch is started. The thread slowly retracts back to the bulb under the surface tension of the wax. The stop-watch is stopped when the thread merges back completely into the bulk. The temperature of the box is raised gradually in steps of small interval to new equilibrium values. Threads are made repeatedly and their time of retraction recorded for each equilibrium temperature. The thread at temperatures well below the melting point normally takes a few minutes for the retraction time but at higher temperatures "τ" decreases until it acquires a constant minimum value. Further rise in temperature has no significant effect on the time of retraction. The set of observations is repeated with a fresh sample. The τ values are plotted against the temperature and the lowest temperature against the minimum time of retraction τ is recorded as the melting point of the wax.

Direct Observation Method.—All the steps of the procedure given in the "τ method" from the

beginning to the formation of the wax thread are the same for the direct observation method. It is the recording of the time of retraction that is replaced by the visual estimation of the minimum time of retraction. An observer may acquire sufficient skill to note the minimum time without any use of stop-watch. The threads at increasingly higher temperature are formed, as before until the time of retraction has reached its lowest value. The temperature recorded is the melting point of the wax. The set of observations is repeated with fresh samples of the wax and an average value of the readings is given as the melting point of the wax.

Pohl's Method.—In order to compare the performance of the above two methods with some standard conventional method observations on the same waxes were obtained with Pohl's method.

The results obtained with the three methods are compared in Tables 1, 2 and 3.

TABLE 1.—THE VALUES OF TIME OF RETRACTION τ AND TEMPERATURE t°C FOR APIEZON W, ROWSHAN WAX AND THE UNKNOWN X OBTAINED BY "τ" METHOD.

Apiezon W		Rowshan wax		Unknown X wax	
Temp t°C	Time τ sec.	Temp t°C	Time τ sec.	Temp t°C	Time τ sec.
92	105	91	125	90	120
107	94	93	87.5	92	62
112	90	94	76.0	100	20.5
115	72	98	38.0	103	13.0
119	57	100	28.0	105	7.0
122	25	102	16.0	107	3.0
128	21	103	15.0	108	1.5
130	9.0	105	13.0	109	1.5
132	9.0	107	13.0	110	2.0
134	9.0	108	11.5	111	1.5
136	6.0	109	6.0	112	2.0
138	6.0	111	6.0	113	1.5
140	2.0	112	6.0	115	1.5
141	2.0	113	6.0	116	—
143	2.0	115	5.0	117	1.5
144	2.0	116	3.0	118	1.5
145	2.0	117	2.0	119	1.8
146	2.0	119	2.0	120	1.5
149	2.5	121	0.5	122	—
150	2.0	122	0.75	124	1.5
151	2.0	123	0.5		
152	2.75	125	0.75		
152	2.0	127	0.5		
156	2.0	128	0.5		
157	2.0	130	0.5		
158	2.0	133	0.5		
		135	0.5		
		138	0.5		
		140	0.5		

TABLE 2.—THE VALUES OF MELTING POINTS FOR APIEZON W, ROWSHAN WAX AND THE UNKNOWN X WAX OBTAINED BY DIRECT OBSERVATION METHOD.

Apiezon W m.p.,°C	Rowshan wax, m.p.,°C	Unknow X wax m.p.,°C
139	120	107
139	121	108
142	122	106
140	120	108
140	123	107
141	120	106
139	119	108
141	120	106
140	121	108
140	118	108
140	120	107
142	120	108
140	121	109
139	125	108
140	123	106
140	120	107
141	121	108
140	122	107
139	121	108.6
141	120	109
139	120	107
140	119	106
Mean 140.09	120.73	107.39

TABLE 3.—VALUES OF MELTING POINTS OF APIEZON W, ROWSHAN WAX AND X WAX OBTAINED BY POHL'S METHOD.

Apiezon W m.p., °C	Rowshan wax m.p., °C	X wax m.p., °C
135.0	120.8	105.0
139.0	119.0	106.0
138.8	121.0	107.5
139.0	121.4	107.5
140.2	121.4	108.0
Mean 138.4	121.0	106.8

Results and Discussion

Time of retraction τ for the three waxes and the temperature are given in Table 1 and are plotted in Fig. 2. The minimum time τ for Apiezon W (curve 1) is 2 seconds, for Rowshan wax (curve II) 0.5 and for the unknown wax referred to as X wax it is 1.5 seconds. Temperatures read directly against these τ values from their respective curves in Fig. 2 give the

melting points of Apiezon W, Rowshan wax and X wax as 140°C 120°C and 108°C. Although "τ" is different for different waxes but for any given wax it is significantly constant over a considerable temperature, see curves I-III in Fig. 2. This is particularly advantageous for the determination of the melting points.

The results of the direct observation method are given in Table 2. It will be noted that the individual values for any wax are generally reproducible within a narrow limit of variation i.e. about ± 1.5°C. In the case of Rowshan wax, however, the variation is slightly larger because of one exceptionally high value of 125°C otherwise the reproducibility is of the same order as for other waxes. The melting point values for Apiezon W, Rowshan wax, and X wax are 140.09°C, 120.73°C and 107.39°C respectively. These values are in close agreement with the values obtained by "τ method".

Melting points of Apiezon W, Rowshan wax and X wax obtained by Pohl's method are given in Table 3, and the results of the three methods in Table 4. The mean melting point values are not very much different from those obtained by the "τ method" or direct observation method. But the values of Pohl's method do not give any indication about the physical state of the waxes, whereas the values of τ method or direct observation method have well-defined physical meaning.

Even at the present stage of the development of the τ method and the direct observation method the accuracy and reproducibility of the results are as good as or better than those obtained by conventional methods of determination of melting point of waxes (Table 4).

Marshall [1] in a comparative evaluation of the most general melting point methods for waxes, obtained melting points ranging from 54.5 to 59.0°C for 128 AMP paraffin wax, from 57.7 to 78.2°C for microcrystalline waxes, from 65 to 87.6°C for oxidized petroleum waxes and from 77 to 97°C for hard high melting microcrystalline waxes. The melting points of a particular wax sample obtained with one and the same method vary in the range of about 14°C for plastic microcrystalline waxes, of about 4°C for oxidised petroleum waxes and of about 5°C for hard high melting microcrystalline waxes.

Since these methods do not involve a common definition of melting point of wax, rather large variation in the melting points obtained with different methods are not surprising. The lack of reproducibility is probably due to the fact that the criteria of melting as defined by these methods involve a number of factors that may vary independently.

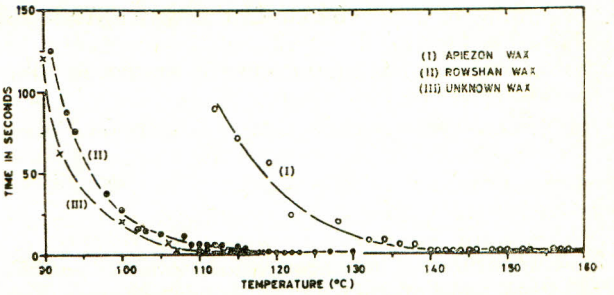

Fig. 2.—Dependence of time of retraction for waxes on temperature. (Curve I, Apeiezon wax; Curve II, Rowshan wax; Curve III. unknown wax).

TABLE 4.—MELTING POINT VALUES OF APIEZON W, ROWSHAN WAX AND X WAX OBTAINED BY "τ METHOD", "DIRECT OBSERVATION METHOD" AND POHL'S METHOD.

Samples	τ method m.p.°C	Direct observation method m.p.°C	Pohl's method m.p.°C
Apiezon W	140	140.09	138.4
Rowshan wax	120	120.73	121.0
X wax	108	107.39	106.8

In the present methods of determination of melting point of waxes only a few factors are involved, and therefore good reproducibility is achieved. The results obtained are within a narrow range of two or three degrees for all the three samples investigated. Moreover, the definition of melting point of waxes has been given a new form.

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