

TABLE III

The Variation of Relative Viscosity with Temperature of Nonaqueous Solutions of Magnesium Laurate

Solvent	Conc. g./100 g. of solvent	Relative viscosity $d/dt(\eta_s/\eta_0)$		
		50°C.	60°C.	70°C.
Toluene.....	2.259	1.127	1.126	1.121
<i>o</i> -Xylene.....	2.056	1.118	1.113	1.095
<i>p</i> -Xylene.....	1.553	1.119	1.115	1.104
<i>m</i> -Xylene.....	2.210	1.141	1.142	1.136
Butanol-1.....	2.106	1.073	1.066	1.050
3-Methyl butanol-1.....	1.486	1.090	1.070	1.050
Hexanol-1.....	2.046	1.070	1.065	1.058
Octanol-2.....	2.027	1.080	1.067	1.050

solutions of magnesium soaps, fluorescence was observed. This indicated the presence of micelles in the solutions. The formation of soap micelles is further supported by the fact that the solubility of water in these solvents is increased by magnesium soaps. Additional quantitative work is in progress in this laboratory. Pink and Martin (13) have determined by molecular weight measurements that each micelle contains 5 to 6 molecules of zinc soap and that the molecular weight of the micelle changes with the concentration of soap. Soyenkoff (15) has also detected particles of colloidal dimensions in solutions of iron and nickel soaps in benzene.

Viscosity Concentration Relationship

The equation of Schulze and Blaschke (6)

$$\eta_{sp}/c = (\eta_{sp}/c)_0 = 0 (1 + k \eta_{sp})$$

has been applied to these solutions by plotting c/η_{sp} against the concentration. The graphs are smooth curves and not straight lines as had been obtained in the case of aluminum soaps by Alexander and Grey (5). This difference probably results from the change in the size of the micelles of magnesium soaps with the concentration.

The change in the size of the soap micelles with concentration is further evidenced by the fact that the value of $\log(\eta_s/\eta_0)/c$ decreases with increasing concentration of the soaps, where η_s is the viscosity of the solution and η_0 is the viscosity of the solvent. Kemp and Peters (16) as well as Alexander and Grey (5) pointed out that, if the size of the particles does not change with the concentration, the value of

$\log(\eta_s/\eta_0)/c$ should approach a constant value. In the case of aluminum soaps the value obtained by Alexander and Grey was 2.6, but for the solutions studied in the present communication no constant value for $\log(\eta_s/\eta_0)/c$ was observed.

Summary

The viscosities of nonaqueous solutions of magnesium caprate and magnesium laurate have been determined at different concentrations and temperatures. Because Arrhenius' equation was found to be applicable to these solutions, it has been concluded that the size of the micelles does not change with the increase in temperature.

The variation of relative viscosity with temperature was also calculated. The fact that the value of $d/dt(\eta_s/\eta_0)$ does not change much with temperature further supports the conclusion that the molecular aggregation of the soap molecules in the solvent is not affected by the temperature.

The equation of Schulze and Blaschke is not applicable to these solutions within the concentration range studied in the present work, probably because the size of the micelles changes with the increasing concentration of the soaps.

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Melting and Crystallization of Vegetable Waxes

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PHENOMENA related to phase changes are most important in the analysis of waxes. Data are presented here which were obtained by a practical, rapid, and sufficiently accurate method (about 20 minutes for each sample). It is suggested that the following five tests be adopted as a routine procedure for waxes: a) odor, b) surface appearance, c) initial melting-point, d) melting point, e) crystallization point.

Method

From the wax submitted for analysis a small part is taken with the necessary care to make it truly representative. The quantity taken must be sufficient to form a big drop on a half microscope slide, over a hot plate at 100–110°C. If the sample is dirty, a

suitable method of purification, such as centrifugation of the melted wax, must be used (1). When the wax is being heated, its characteristic odor becomes stronger. The melted wax on the half-slide is well mixed with a glass rodlet (1 to 2 mm. in diameter), and a droplet is transferred to a circular cover slide (No. 1 thickness, 12-mm. in diameter). The droplet must be spread so as to form a thin layer.

The cover slide is rapidly transferred from the hot plate to a metal cooling block at room temperature to solidify the wax quickly. The surface of the droplet is then examined. This corresponds to the "spot melting test" (2). The surface may be dull (carnauba wax) or light-reflecting, varnish-like (licuri wax). The cover-slide with the droplet is then adapted to a

hot stage on a microscope. The hot-stage used for this work was designed by the author and made under his supervision at the Instituto de Óleos (see figures). It is simple but accurate and has been carefully checked. Sample temperature and thermometer reading agree very well. The thermometer is divided in $\frac{1}{2}^{\circ}\text{C}$., but interpolation is easily done; and 1-2 tenths of a degree centigrade can be evaluated and are fully significant. The microscope can be of the common type, with simple polarizer and analyzer, and optics for observation 100 times. The usual 10-fold objectives can be employed with this hot-stage.

Heating is controlled by a rheostat. The specimen is first observed without the analyzer. Readings are taken under temperature variations of 1°C . in 1.5 to 2 minutes. Vegetable waxes are complex and melt slowly. Under the microscope the liquid phase can be detected in most cases more than 10°C . below the melting point.

In the present method initial melting point is the temperature at which minute drops are first seen. In most cases they are very clearly perceptible, especially if the microscope tube is moved up and down, slightly above and below focus, when the droplets appear, respectively, brighter and darker than the surrounding medium. Heating is continued, and the specimen is now observed between crossed polarizers. Up to the present time all the vegetable waxes that have been examined by the author have a crystalline structure and are birefringent when solid. As melting proceeds, the birefringence gradually weakens and finally disappears. At this moment the melting point is recorded.

Cooling is now started. Melted waves are homogeneous and optically isotropic. The microscope field is uniform and dark. As cooling proceeds, a moment comes when crystallization begins, and the solid phase is strikingly visible, owing to its birefringence. The corresponding temperature is the crystallization point.

Discussion

The difference between melting and crystallization points is of great significance for vegetable waxes. For instance, it provides an easy distinction between carnauba and licuri (ouricuri) waxes, even for low grades or waxes recovered from residues. The initial melting point must be related to the liquefying point (3), but observation under the microscope is much more accurate and really seems to show the first steps in the separation of liquid. This value proved to be very significant in the detection of some adulterations of carnauba wax. Some samples however fail to show clearly the beginning of melting, and consequently their initial melting point was not recorded.

The determination of the melting point is usually made by a capillary. Well-known difficulties (4) have directed research into two different channels. Francis and Piper (7) abandoned the capillary tube and adopted a wider, thin-walled tube 3 to 4 mm. in diameter. With the aid of a telescope a minute particle of the material to be examined, fused on the side of the tube, is watched. Melting and resolidification points are thus recorded. The latter is the temperature at which the partly molten specimen commences to solidify, on slow cooling. On the other hand, Marsel *et al.* (6) chose a method based on a fact related to the melting process but easier to ascertain, such as the flowing of the wax in the capillary tube, forced

by the buoyancy of the air in the lower part of the tube.

The melting point determined under the microscope should turn out to be very close to that obtained by Francis and Piper's method. The similarity between the distribution of Marsel's melting points (Figures 3 and 8) and those determined by the author (Figures 2 and 6) is striking. Nevertheless there are some differences in individual samples. Melting points under the microscope are frequently higher, as might be expected. There may be two causes for differences between capillary (6) and microscope melting-points: a) heat transfer to the sample is readier in the microscope method; all other factors being equivalent, this would lead to higher results with the capillary tube method; b) methods based on wax flow are likely to give lower results because the wax may be liquid enough to flow and yet include minute crystals. In Table I are listed values for comparison of the two methods.

TABLE I

Sample number	Melting point $^{\circ}\text{C}$.		Sample number	Melting point $^{\circ}\text{C}$.	
	Microscopic	Capillary tube		Microscopic	Capillary tube
2	84.0	83.6	14	84.7	83.9
3	84.5	84.4	16	84.5	84.2
4	84.0	84.0	17	83.8	83.9
7	85.0	83.4	18	84.0	83.6
8	83.8	83.9	21	85.0	83.8
11	84.0	82.9	32	84.5	85.6
12	83.3	82.8			
13	84.0	84.4	Average	84.2	83.9

NOTE: Capillary-tube method as described by Marsel *et al.* (6). This method does not work well with licuri wax (No. 32) on account of its high viscosity (1).

The crystallization point will probably have about the same value as the resolidification point. As Warth emphasizes, the clouding, solidification, and resolidification points are very close to each other. The clouding and solidification points of waxes do not vary more than 0.5°F .; the latter is normally higher than the former. A table from Francis and Piper (3) shows solidification, resolidification, and melting points for n-aliphatic acids from C_{14} to C_{34} . For this kind of substance the difference between solidification and resolidification points is very low. The solidification point is a little higher except for C_{14} acid.

The solidification point is the temperature which remains constant for a certain period when the wax is cooled under specified conditions. This is apparent in the cooling curve of vegetable waxes. Figure 16-A is a curve of carnauba wax. The sample filled two-thirds of a common titer test tube. After the wax completely melted, the tube was immersed in a constant temperature water bath at 70°C ., a stop-watch was started and the temperature was recorded at intervals. The sample was continuously agitated by moving a glass ring fixed at right angles to the end of a glass rod, up and down. With the hot stage the crystallization point of the same sample was found to be 79.5°C ., and the melting point 84.0°C .

Figure 16-B is the curve of a sample of licuri (ouricuri) wax. It was determined the same way as above, but the bath was set at 60°C . The arrow shows the moment when agitation was no longer possible. If agitation is interrupted before the temperature begins to rise, the solidification point will be less well-defined and considerably lower. It should be pointed out that although crystallization and resolidification

points of licuri waxes must be close to each other, this curve suggests that both will be lower than the solidification point by, perhaps, several degrees.

Graphs are included that show the data for the two commercially important Brazilian vegetable waxes (carnauba and licuri) and a few others. From the samples belonging to the Instituto de Óleos the author selected those supposed to be true adulteration-free natural waxes. The five official types of carnauba wax were grouped according to their natural origin: olho—wax from the still closed leaves, yellow or yellowish, Types 1 and 2; and palha—wax from the open leaves, brownish (fatty), Types 3 and 4, and chalky, Type 5.

Olho carnauba waxes show very uniform behavior. The beginning of melting is very clearly seen and normally occurs at 73°C. The differences between melting and crystallization points is narrow, from 2 to 3°C., for all samples examined (Figures 1 to 5).

Palha carnauba waxes seem to present two different tendencies. Some samples follow closely to behavior of olho wax (*e.g.*, Nos. 17, 18, and 19). There are

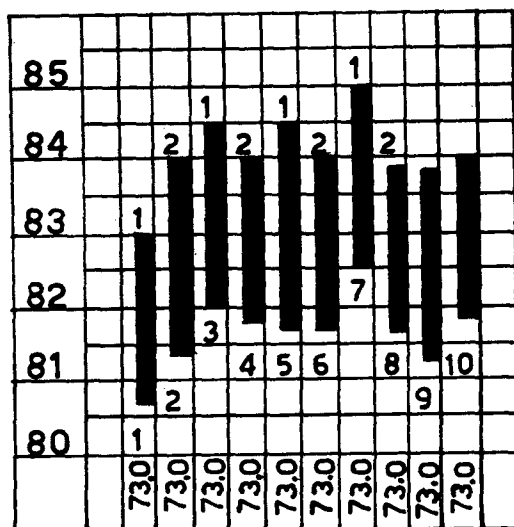


FIG. 1. Olho carnauba wax. Intervals between melting and crystallization points. Upper numbers indicate types. Lower numbers indicate samples (1 to 10). Vertical scale (left) shows centigrade temperatures. Bottom numbers are initial melting points.

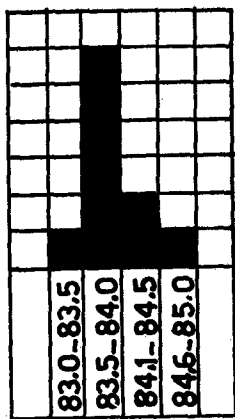


FIG. 2.

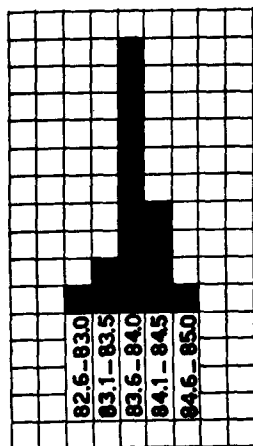


FIG. 3.

FIG. 2. Olho carnauba wax. Distribution of melting points.
FIG. 3. Distribution of melting points from Marsel *et al.* (6), only Types 1 and 2 (olho carnauba wax).

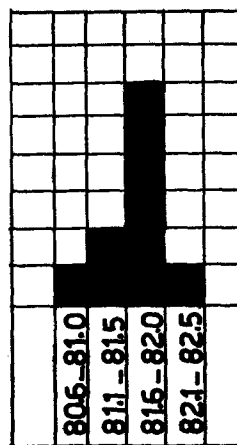


FIG. 4.

FIG. 4. Olho carnauba wax. Distribution of crystallization points.

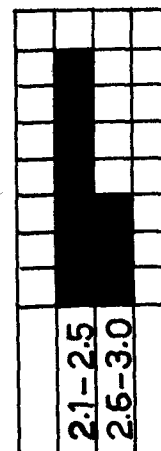


FIG. 5

FIG. 5. Olho carnauba wax. Distribution of differences between melting and crystallization points.

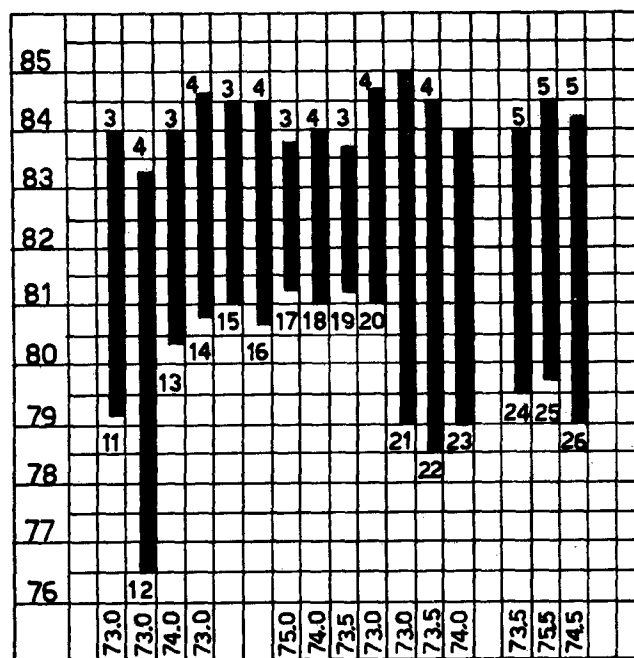


FIG. 6. Palha carnauba wax. Intervals between melting and crystallization points. Upper numbers indicate Types (3, 4, and 5). Lower numbers indicate samples (Nos. 11 to 26). Vertical scale (left) shows centigrade temperatures. Bottom numbers are initial melting points.

other samples however that show lower crystallization points, sometimes exceptionally low (sample No. 12) (Figures 6 to 10).

Lüdecke and Diena (5) point out that the so-called resinous matter can be responsible for the wide difference between melting and solidification points of licuri wax, also that this "resinous matter" presents different aspects and properties if the wax has been gathered a short or a long time previously. Perhaps this possible inhibiting effect of the "resinous matter" on the solidification (and, of course, on the crystallization) of waxes, has something to do with the varying behavior of palha carnauba waxes. This question, including the influence of wax age on the crystallization point, should be further investigated.

Zocher (8) thinks it is more probable that this in-

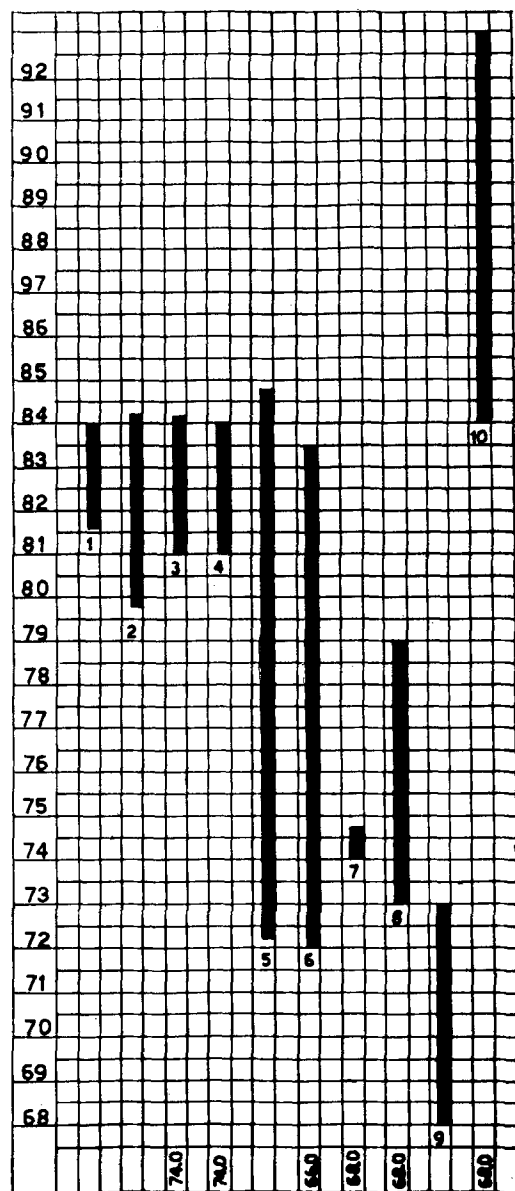


Fig. 15. Intervals between melting and crystallization points: 1. Olho carnauba wax, average of samples 1 to 10. 2. Palha carnauba wax, average of samples 11 to 26. 3. Carandá wax. 4. Cuban carnauba wax, sample received from Humberto Rodrigues de Andrade. 5. Licuri (ouricuri) wax, average of samples 27 to 39. 6. Sugar cane wax, Warwick Wax Company Inc. No. 500. 7. Heliconia farinosa wax, collected by the author from leaves of this *Musacea*, at the Jardim Botânico do Rio de Janeiro. 8. Heliconia pendula wax, same origin as 7. 9. Candelilla wax. 10. Caá-uassú wax, received from Belem (State of Pará), benzol-extracted.

vegetable waxes. The wax from the leaves of *Heliconia farinosa*, Raddi., surprisingly simulates the behavior of an almost pure substance. The difference between melting and crystallization is as low as 0.7° C., and the crystals are exceptionally well developed for a wax. Table II lists, for comparison, some values given by Warth. Relative to stearic acid it should be pointed out that, with the hot stage, it is possible to determine the temperature at which a small crystal can be maintained in equilibrium with the liquid phase. For Merck No. 674 stearic acid, 68°C. was found to be the equilibrium point.

The crystal habits of waxes may provide useful information. No reference is made to this subject here because it was thought better in due course to

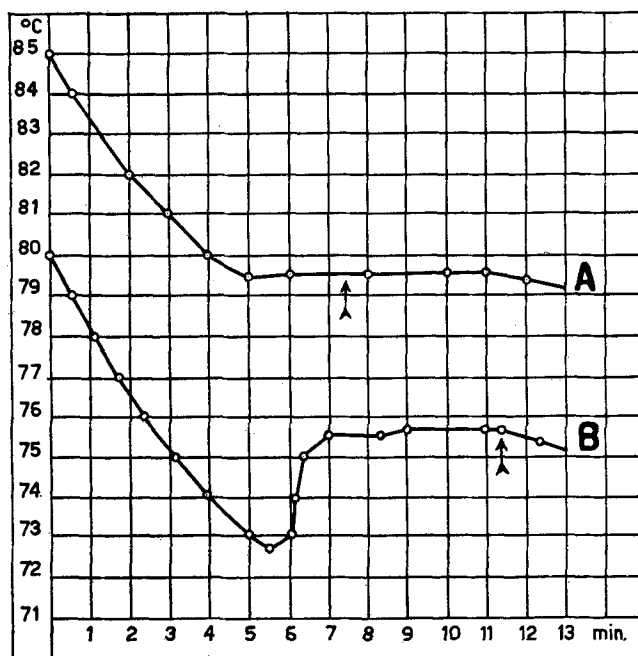


Fig. 16. Cooling curves of carnauba (A) and licuri (B) waxes. The arrow indicates the moment when agitation was no longer possible.

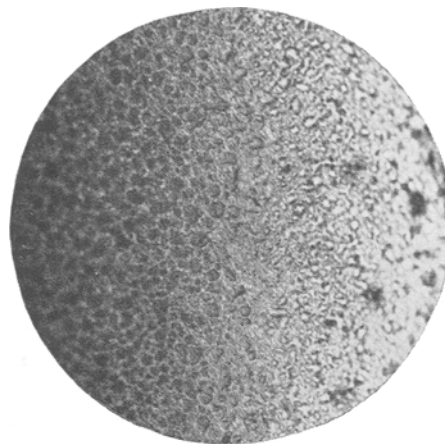


Fig. 17.

Fig. 17. Photomicrograph showing the aspect of the sample a little after the initial melting point. A markedly rounded drop was chosen in order to exhibit the just formed liquid droplets, which appear dark above focus (left) and bright below focus (right). Polarizers in parallel position. Magnification 100 times.

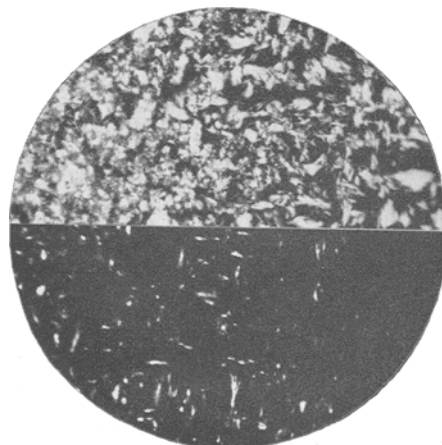


Fig. 18.

Fig. 18. Same field as in Fig. 17. Upper half, photomicrograph taken at 80.5°C. Lower half taken at 84°C, one degree below melting point. Crossed polarizers. Magnification 100 times.

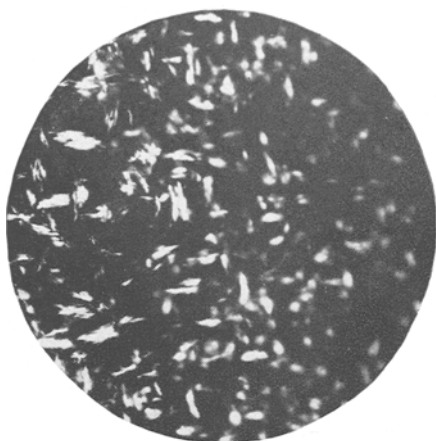


FIG. 19.

FIG. 19. Same field as in Fig. 17. Crystallization sets in. Photomicrograph taken at 81°C. Crossed polarizers. Magnification 100 times.

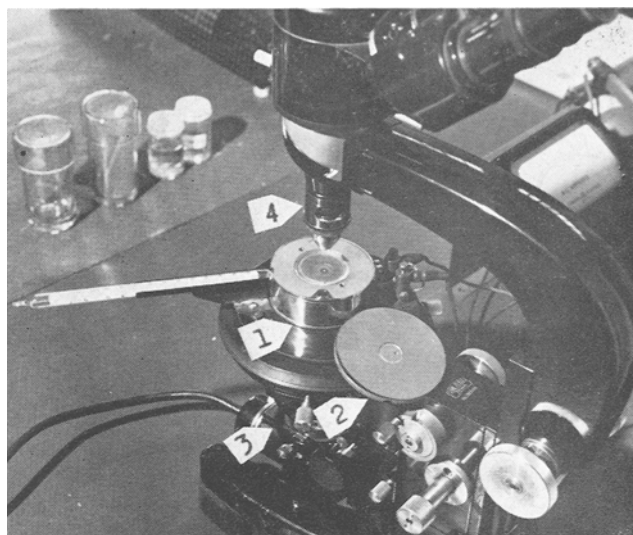


FIG. 21. Latest hot stage assembly in which the angle of the illuminating cone (I, Figure 20-A) has been widened in order to allow a larger aperture of illumination and even-phase contrast. For phase contrast it is necessary to remove the upper lens of the condenser and to use the 10-time magnification with the condenser ring for the oil-immersion objective. The chamber for the sample is wider and shallower. The size of the illuminating hole (H, Figure 20-B) has been maintained. This model was built in 1954. 1. Hot stage; 2. cover; 3. heat-absorbing glasses; 4. analyzer.

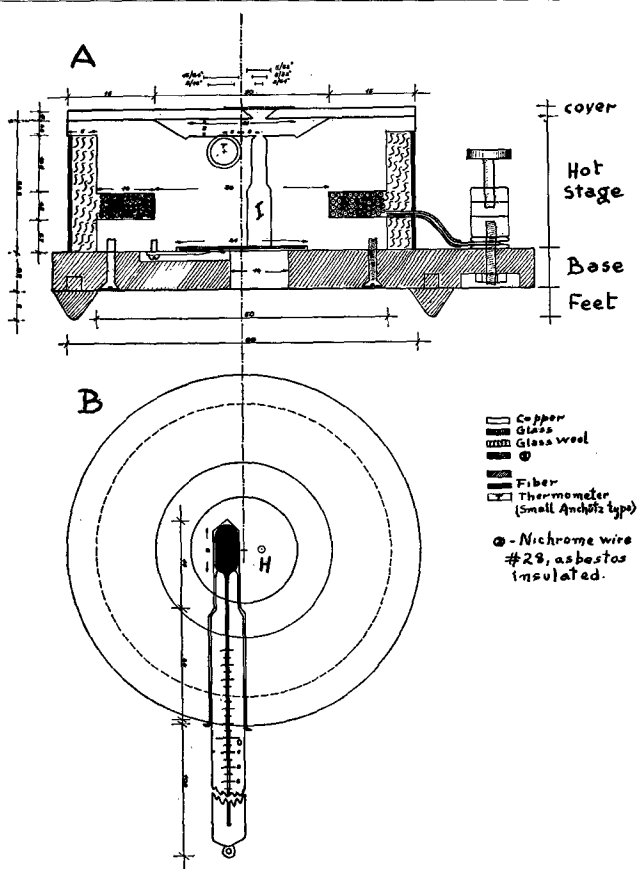


FIG. 20. Diagram of the hot stage designed by the author and used for the determinations described in this paper.

present more fully the results of an investigation still being carried out by Hans Zocher and the author.

Summary

A rapid but sufficiently accurate method is applied to the observation of phase changes in vegetable waxes and is suggested for adoption as a routine procedure. Five indications are obtained in about 20 minutes for each sample: odor, surface appearance, initial melting, melting and crystallization points. A hot stage is used, designed by the author, and made under his supervision at the Instituto de Óleos.

Data are discussed concerning carnauba (*Copernicia cerifera*, Mart.) and licuri or ouricuri (*Syagrus*

TABLE II^a

Wax	Melting point °C.	Solidifying point °C.	Dif.
Candelilla.....	70.6	66.7	3.9
Candelilla.....	75.8-77.4	63.8-67.7
Carnaúba No. 1.....	83.0	82.0	1.0
Carnaúba.....	83-86	80-84
Ouricuri, crude.....	84.3	72.2	12.1
Ouricuri, refined.....	83.3	72.9	10.4
Ouricuri double refined.....	79.0	68.0	11.0
Ouricuri, crude.....	83.87	72-76
Sugar cane, crude.....	55.0	51.0	4.0
Sugar cane, refined.....	77.8	70.9	6.9
Sugar cane, East Indian.....	60-62
Stearic acid, USP.....	56.1	54.2	1.9
Stearic acid.....	57.2	56.6	0.6
Stearic acid ^b	69.6	69.2 ^c	0.4

^a From Warth (3).
^b From Francis and Piper (7).
^c Resolidification point.

NOTE: It is supposed that the melting points have been determined by one of the capillary tube methods.

coronata, Mart., Becc.) waxes. Some results related to carandá (*Copernicia australis*, Becc.), cuban carnauba, sugar cane, *Heliconia farinosa*, Raddi., *Heliconia pendula*, Wawra., candelilla, and caá-uassú (*Calathea lutea*, Mey.) waxes are also included.

Acknowledgment

The author is indebted to his colleague, Carlos Gitahy de Alencastro, for the capillary tube determinations.

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