Calorimetric Analysis of Commercial and Dental Waxes

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Calorimetric analysis was used to determine heats of transition and fusion of waxes between 0 and 100 C. In general, hydrocarbon waxes had higher total heats of transition than did ester waxes. Calorimetric measurements on binary mixtures showed that carnauba and beeswax interacted with paraffin, the former having the greater effect.

Dental waxes are often a blend of several waxes that are necessary to develop the most desirable qualities. In general, more information is available on physical properties and manipulation of dental waxes than on the composition or nature of the ingredients. Since heats of transition are fundamental in characterizing the chemical nature of matter, this information was obtained from waxes and blends and was correlated with other known properties to establish the behavior of the waxes and to eventually maximize the individual characteristics of each in blends.

Calorimetric analyses of paraffin waxes have been conducted by several authors.[1-4] These analyses characterized the heats of transition and the heats of fusion of commercial paraffin waxes and of comparable pure n-paraffins. A differential thermal analysis (DTA) study of waxes was done by the authors[5] of the present study.

The purpose of this study was to apply calorimetric analysis to the waxes used in dentistry. These waxes included binary mixtures of paraffin wax with carnauba and beeswax and several commercial dental waxes. Heats of transition were determined, and the interactions between waxes in the mixtures were evaluated as a function of composition and wax.

Materials and Methods

The waxes were used as purchased* and were blended as indicated for the mixtures. Calorimetric analysis† was carried out at 0 to 100 C in a nitrogen atmosphere with a Du Pont 950 Calorimeter Cell at a heating rate of 5 C/minute. The cell was calibrated using pure metals that have known heats of fusion over the temperature range of interest.

The areas above the calorimetric curves used in the calculation of the heats of transition and fusion were determined as shown in Figure 1. A planimeter‡ was used to measure the areas. ΔH_a, ΔH_b, and ΔH_{cd} represent the solid-solid transitions of paraffin, the melting transition of paraffin, and the melting transitions of carnauba wax, respectively. The total heat of transition, ΔH_t, represents the sum of the individual transitions over the entire temperature range studied. The determination of the areas for the individual components of binary mixtures of waxes was difficult because of incomplete resolution of the various peaks.
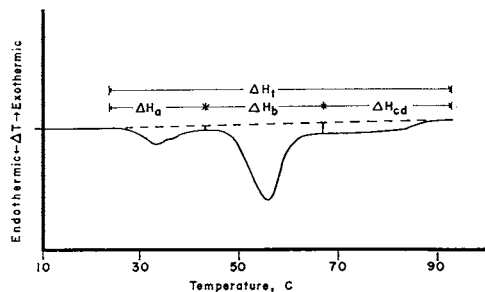
FIG 1.—Area determination of a calorimetric curve for a binary wax mixture.

This problem was resolved by choosing the closest return to the base line as the best estimate of the area, realizing that the melting peak of paraffin contributes to the area left and right of the vertical lines and that the solid-solid transitions of paraffin and the melting transitions of carnauba contribute an approximately equivalent amount to the area of the paraffin-melting transition.

In all instances, the values reported are means of five separate replications. Statistical inference of the data was accomplished by analysis of variance,[6] and where significant differences were observed, the means were ranked with Duncan's Multiple Range Test.[7] Regression and correlation analysis[8] were used to evaluate the interaction of the heats of transition on composition and waxes.

Results

The waxes generally used in compounding dental waxes are paraffin, carnauba, and beeswax; therefore, the variation in heats of transition of various batches of wax of the same grade was determined. Four batches each of paraffin, carnauba, and beeswax, which were selected at random by the manufacturer, showed variations of 5.1, 4.5, and 5.3 cal/gm, respectively, in the total heats of transition. The various batches tested were ranked as shown in Table 1.

The heats of transition for ester, plant, hydrocarbon, and commercial dental waxes are shown in Tables 2 and 3.

The ester-containing waxes (Table 2) were characterized by lower total heats of

TABLE 2
HEATS OF TRANSITION OF SEVERAL NATURAL, COMMERCIAL, AND DENTAL WAXES

Wax	Transition	ΔHi(cal/gm)
Montan	Total	38.4 (3.7) *
Candelilla †	Total	40.7 (3.4)
Ouricury	Total	43.6 (3.6)
Beeswax	Total	42.8 (2.1)
Carnauba	Premelting	3.8 (1.1)
	Melting	45.5 (1.3)
	Total	49.4 (2.0)
Kerr Blue Inlay Casting Wax-Hard	Total	45.9 (4.3)
Kerr Blue Inlay Casting Wax-Regular	Total	47.6 (4.6)
Dr. Peck's Inlay Wax-Purple Hard	Total	50.5 (1.6)

* ΔHi is the mean of five measurements. Standard deviation is given in parenthesis.
† Braces connect waxes for which the total heats of transition could not be distinguished at the 0.05 level.

transition (38.4 to 43.6 cal/gm). The small premelting transition of carnauba wax was not observed in the other ester-containing waxes. Beeswax was found to have a total heat of transition of 42.8 cal/gm. The total heats of transition for the commercial dental waxes were between 45.9 and 50.5 cal/gm.

The hydrocarbon waxes were characterized by higher total heats of transition (50.7 to 55.6 cal/gm), with the exception of ceresin (45.6 cal/gm), as seen in Table 3. Several of the hydrocarbon waxes showed solid-solid premelting transitions. The two premelting transitions observed for both paraffin and ceresin were not sufficiently resolved in the calorimetric curves; thus the values of 11.4 and 6.6 cal/gm represent the sum of the solid-solid heats of transition. Polyethylene wax showed a solid-solid transition of 5.3 cal/gm. The solid-solid transi-

TABLE 1
TOTAL HEATS OF TRANSITION OF VARIOUS BATCHES OF WAXES

Wax	Batch No.	ΔHi(cal/gm)
Paraffin	193	50.6 (2.5) *
	303 †	54.3 (3.4)
	274	55.1 (1.5)
	319	55.7 (3.2)
Carnauba	B-1845s	47.0 (1.9)
	B-2318	47.8 (3.3)
	B-1845c	51.2 (5.6)
	B-1956	51.5 (1.7)
Beeswax	B-2183	40.3 (2.5)
	B-2170	41.9 (2.5)
	B-1788	43.7 (2.8)
	B-2247	45.3 (1.1)

* Numbers in parentheses are standard deviations determined from five individual determinations of ΔHi.
† Braces connect batches that could not be distinguished statistically at the 0.05 level of significance.

TABLE 3
HEATS OF TRANSITION OF SEVERAL HYDROCARBON WAXES

Wax	Transition	ΔHi(cal/gm)
Ceresin	Solid-Solid	6.6 (1.4) *
	Total	45.6 (5.0)
Polyethylene †	Solid-Solid	5.3 (0.7)
	Total	50.7 (4.6)
Barnsdahl	Total	53.1 (3.0)
Paraffin	Solid-Solid	11.4 (0.6)
	Melting	42.4 (1.9)
	Total	53.9 (2.5)
Litene	Total	55.6 (5.1)

* ΔHi is the mean of five measurements. Standard deviation is given in parenthesis.
† Braces connect waxes for which the total heats of transition could not be distinguished at the 0.05 level.

tions of paraffin, ceresin, and carnauba wax were 27, 17, and 8.3% of the melting transitions, respectively.

An analysis of variance for the total heat of transition associated with a given wax was determined for the natural, commercial, and dental waxes studied. $F_{18.76}$ of 14.20 compared with a critical value of 2.57 at the .001 level rejected the null hypothesis that all waxes were identical with respect to their total heat of transitions. Statistically, the calorimetric data showed that montan was different from ouricury, but candelilla could not be statistically distinguished from either. The commercial dental waxes* could not be statistically distinguished from each other on the basis of the total heat of transition. Of the hydrocarbon waxes, polyethylene, barnsdahl, and paraffin could not be statistically distinguished from each other on the basis of total heat of transition, nor could barnsdahl, paraffin, and litene. This ambiguity arises from rather high coefficients of variation, which are related to the standard deviations of 4 to 12%, with a mean coefficient of 8%. Tables 1, 2, and 3 summarize the results of ranking the data.

The solid-solid and melting heats of transition of paraffin and the total heats of transition were determined in binary mixtures of paraffin with carnauba and beeswax and analyzed as a function of composition (weight percentage) and wax to examine the question of whether true mixtures are formed in dental waxes derived from these components.

The solid-solid heats of transition of paraffin, ΔH_a, per gm of mixture were plotted as a function of composition of carnauba-paraffin mixtures as shown in Figure 2. The heat of transition vs composition relationship was statistically shown to be quadratic by regression analysis, as indicated by the equation below the graph. The curve showed regression with a high correlation coefficient, r, of -0.956; ie, as x increases, y decreases, where perfect correlation has r equal to ± 1.

The solid-solid heats of transition, ΔH_a, for mixtures of paraffin with beeswax are plotted in Figure 3. Again the heat of transi-
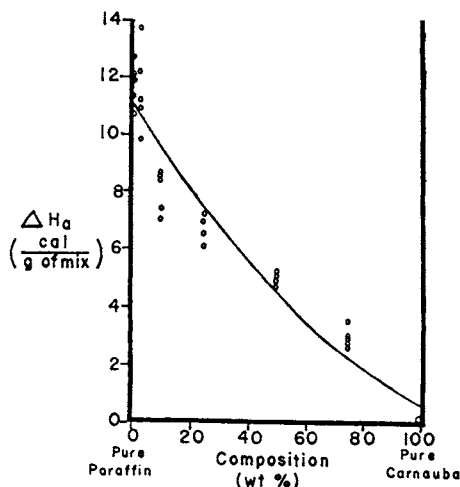
$$y = 11.0 - 0.157\,x + 0.0005\,x^2 \quad ; \quad r = 0.956$$

FIG 2.—ΔH of the paraffin solid-solid transition in carnauba-paraffin mixtures as a function of composition.
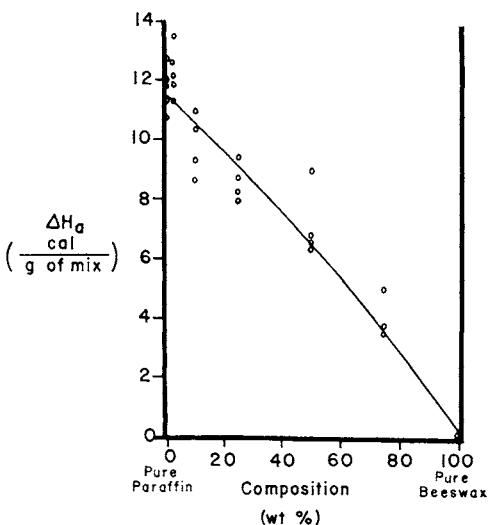
$$y = 11.6 - 0.0931\,x - 0.0002\,x^2 \quad ; \quad r = 0.976$$

FIG 3.—ΔH of the paraffin solid-solid transition in beeswax-paraffin mixtures as a function of composition.

tion vs composition relationship was statistically found to be quadratic, with a correlation coefficient of r equal to -0.976. This curve was concave down rather than concave up (convex) with respect to the composition axis as observed for the carnauba-paraffin ΔH_a relationship.

The heats of fusion for carnauba-paraffin mixtures and the total heats of transition for mixtures of paraffin with carnauba and beeswax were also plotted as a function of composition. These relationships, which were statistically shown to be quadratic, are summarized in Table 4.

Statistical analysis of the data for the binary mixtures was performed with a computer program that provided the following output: a least-squares regression line, a least-squares exponential equation, a least-squares quadratic equation, prediction errors resulting from the above output, and a linear correlation coefficient. Selection of the equation best fitting the data was made on the basis of least error between observed and predicted values of ΔH_i.

Discussion

The values for the heats of transition for different batches of paraffin, carnauba, and beeswax indicate the variation in composition of waxes of the same grade. In general, the hydrocarbon waxes had higher total heats of transition (premelting and melting) than the ester-containing waxes; ceresin and carnauba wax were exceptions. Beeswax was found to have a heat of transition that suggested its partial ester nature. The premelting combined with the unusually high melting transition of carnauba wax indicates its microcrystalline nature. The total heats of transition for the commercial dental waxes indicate their complex nature.

The premelting values reported for the paraffin waxes* are lower than those reported by Kawasaki, Komizu, and Uchida[1] and by Barnby, Bostwick, and Huston.[2] Kawasaki, Komizu, and Uchida[1] reported heats of premelting of 14 to 22 cal/gm and heats of fusion of 36 to 44 cal/gm for the commercial paraffin waxes. Barmby, Bost-

* Ross Fully Refined Paraffin Wax, Ross Company, Jersey City, N.J.

wick, and Huston[2] reported a heat of transition for a C_{23}-C_{24}-n-paraffin as 17.4 cal/gm. Mazee[3] reported heats of transition for $C_{23}H_{48}$ and $C_{24}H_{50}$ waxes as 16.6 and 21.0 cal/gm, respectively. These values suggest that the commercial paraffin waxes studied by the above mentioned authors were narrower fractions. Broadhurst[4] has collected, summarized, and interpreted information published on the solid phase behavior of n-paraffins. Those from C_{22} to C_{30} had heats of transition that were 50% or more times the heats of fusion, compared with 27% found in this study for commercial paraffin waxes. The premelting heats of transition of ceresin and paraffin of 6.6 and 11.4 cal/gm may be the result of the paraffin being a narrower fraction and of the influence of the impurity in ceresin as suggested by the authors' previous DTA work.[5] The comparison of the solid-solid transitions percentage of the melting transition for paraffin, ceresin, and carnauba wax suggests that paraffin is the most and carnauba the least pure of the three waxes.

The heat of transition vs composition relationships for the binary mixtures were all found to be quadratic in a manner that suggests a dependency of ΔH_i not only on composition but also on the waxes. Since in an ideal mixture the heat of transition vs composition would be a linear relationship, the observed quadratic behavior suggests that interaction is occurring. A qualitative representation of this nonideality was determined as shown in Figure 4. The deviation from ideality of a binary mixture is represented by the shaded area between the ideal and nonideal ΔH_i vs composition relationships and can be computed by the formula as indicated. The percentage deviation for each transition studied is given in Table 4.

As can be seen from Table 4, the solid-solid transitions of paraffin are the most

TABLE 4
ΔH vs Composition Relationship Summary

Wax	Transition	Correlation Coefficient (r)	Concavity	Deviation from Ideality (%)
Carnauba-Paraffin	ΔH_a	−0.956	up	−16.48
	ΔH_b	−0.968	down	+9.83
	ΔH_t	−0.096	up	−0.33
Beeswax-Paraffin	ΔH_a	−0.976	down	+5.57
	ΔH_t	−0.711	up	−1.40

Deviation of a Binary Mixture from Ideality

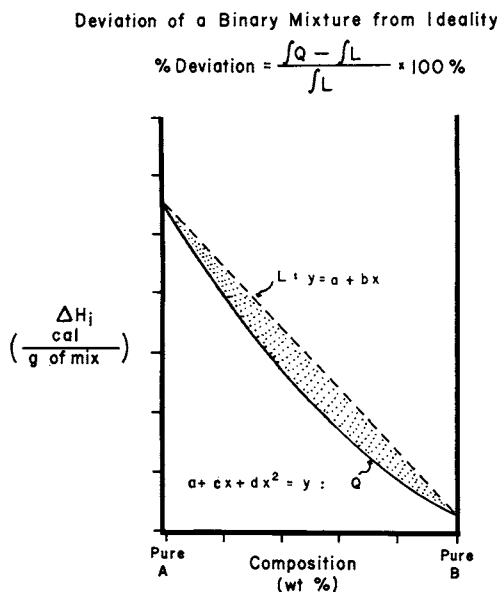$$\% \text{ Deviation} = \frac{\int Q - \int L}{\int L} \times 100\,\%$$

FIG 4.—Deviation of a binary mixture from ideality.

affected by variations in composition and wax. Furthermore, carnauba wax has a greater influence on the solid-solid transitions of paraffin than does beeswax. It is interesting to note that these observations are paralleled by flow measurements in the temperature region of the paraffin solid-solid transitions. Craig, Eick, and Peyton[9] found that additions of carnauba to paraffin wax resulted in a reduction of flow, whereas beeswax had comparatively little effect. The high resistance to flow was attributed to the presence of polar ester groups and the resulting intermolecular attraction. It therefore is not surprising that the heat of fusion of paraffin is less affected by composition variation than the solid-solid heats of transition, since at higher temperatures, intermolecular attraction would decrease. The relatively low percentage deviation of the total heats of transition can be explained by the close proximity of the total heats of the pure waxes.

Conclusions

Calorimetric analysis has been determined over a temperature range of 0 to 100 C for a number of natural, commercial, and dental waxes, including binary mixtures of paraffin with carnauba and beeswax. The interaction between waxes in these binary

mixtures was evaluated as a function of composition (weight percentage) and wax.

The values for the heats of transition for different batches of waxes of the same grade indicated a significant variation in composition. In general, hydrocarbon waxes had higher total heats of transition, followed by commercial dental waxes, and then by ester-containing waxes. Ceresin and carnauba wax were exceptions to this order, with carnauba wax having a premelting and an unusually high melting transition that indicated its microcrystalline nature.

Comparison of values obtained for commercial paraffin waxes with those reported in literature suggested broader fractions, ie, wider molecular weight ranges, in the former. Comparison of the solid-solid transitions percentage of the melting transition for paraffin, ceresin, and carnauba wax suggested that paraffin was the most and carnauba the least pure of the three waxes.

The heat of transition vs composition relationships for the binary mixtures studied were all found to be quadratic in a manner that suggested a dependency of ΔH_i not only on composition but also on the waxes. Since in an ideal mixture the expected relationship would be linear, the observed quadratic behavior suggested that interaction was occurring. The solid-solid transitions of paraffin were found to be the most affected by variations in composition and wax. Carnauba wax had a greater influence on the solid-solid transitions of paraffin than did beeswax. These observations were paralleled by flow measurements in previous work.

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