Thermogravimetric Analysis of Waxes

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Thermogravimetric analyses of various waxes were made. This manner of assessment was evaluated critically.

Differential thermal analysis and calorimetric analysis of commercial and dental waxes have been reported in the dental literature.[1,2] Thermogravimetric analysis is described in most textbooks on thermal analysis[3–5] and is essentially a method of measuring the weight of a sample as a function of temperature or as a function of time at a fixed temperature.

The purpose of this study was to examine the possibility of the thermogravimetric method in the quantitative analysis of some experimental and dental waxes.

Materials and Methods

The waxes investigated were the same as those described in a previous paper.[2] The thermogravimetric analyzer* consisted of a semi-micro balance of the null type. The cool portion of the balance is contained in a glass housing and the heated portion is contained in a quartz housing that allows the analysis to be conducted in a controlled gas atmosphere. The samples were heated at a linear rate of 15 C/minute from 25 to 500 C in a nitrogen atmosphere. A few isothermal runs were made at 50 C below the temperature where weight loss was observed for the same samples run at the rate of 15 C/minute. Some isothermal runs were made in air and others in oxygen.

The percentages of the various component waxes were determined by extrapolating the slopes of the thermogravimetric curves above and below an inflection temperature. The intersection of these slopes allowed the determination of the weight loss and thus the percentage of the components.

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* DuPont 950 Thermogravimetric Analyzer, E.I. du Pont de Nemours, Instrument Products Division, Wilmington, Del.

Results

The thermogravimetric curves for pure paraffin and carnauba wax plus mixtures of these two waxes are shown in Figure 1. The abscissa of the weight vs temperature plots (Figs 1-3) represent temperatures the values of which have not been corrected for nonlinearity of the chromel-alumel thermocouples. Temperatures reported in the text, however, have been corrected. The weight of paraffin decreased at 157 C and continued decreasing until most of the material had vaporized at 300 C. The paraffin appeared to contain a small amount of a higher boiling point component since 343 C was reached before a zero weight was observed. As expected, a higher temperature of 246 C was required before loss in weight of carnauba wax was observed and temperatures of 485 C were necessary before no residue remained. The mixtures of paraffin and carnauba wax had curves reflecting the percentage of these two components. When the weight at the break in the curve was used to calculate the percentage carnauba wax, the values in Table 1 were found.

Thermogravimetric curves for binary mixtures of beeswax and paraffin were more nearly alike because the melting and vaporization points of these components were closer than those of carnauba and paraffin wax. The percentage of beeswax in the standard mixtures and the percentage calculated from the thermogravimetric curves are listed in Table 1. The calculated values for mixtures containing 50 and 75% beeswax were low, although reasonable agreement was obtained at lower percentages of beeswax.

The thermogravimetric curves for three dental inlay waxes are presented in Figure 2.

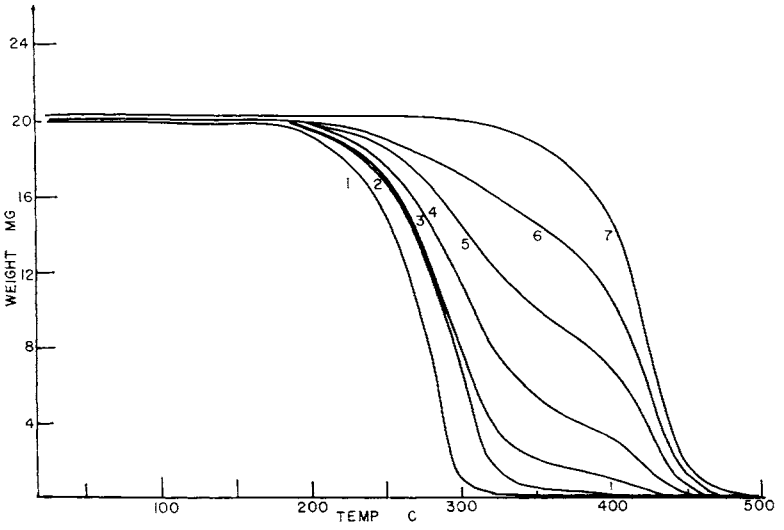

FIG 1.—Thermogravimetric curves for paraffin = carnauba binary mixtures. 1, 100% paraffin (P); 2, 2.5% carnauba (C) + 97.5% P; 3, 10% C + 90% P; 4, 25% C + 75% P; 5, 50% C + 50% P; 6, 75% C + 25% P; 7, 100% C.

TABLE 1
PERCENTAGE OF CARNAUBA OR BEESWAX IN BINARY MIXTURES WITH PARAFFIN

Sample	Carnauba (%)	Beeswax (%)
2.5% C*-97.5% P*	2.9, 2.8 > 2.9	...
10% C-90% P	11.1, 10.9 > 11.0	...
25% C-75% P	25.9, 27.0 > 26.5	...
50% C-50% P	51.5, 52.5 > 52.0	...
75% C-25% P	76.7, 72.5 > 74.6	...
2.5% B*-97.5% P	...	2.2, 2.4 > 2.3
10% B-90% P	...	8.9, 9.5 > 9.3
25% B-75% P	...	22.8, 23.5 > 23.2
50% B-50% P	...	44, 46 > 45
75% B-25% P	...	67, 65 > 66

* C, P, and B represent carnauba, paraffin and beeswax, respectively.

The higher melting component was assumed to be carnauba-based on previous differential thermal analysis.[1] The percentage of this component wax is given in Table 2. Kerr regular and Peck's Purple hard had the highest values of 24.9 and 24.3%, respectively, and Kerr hard had the lowest value of 17.4%.

The thermogravimetric curves for a variety of hydrocarbon waxes are shown in

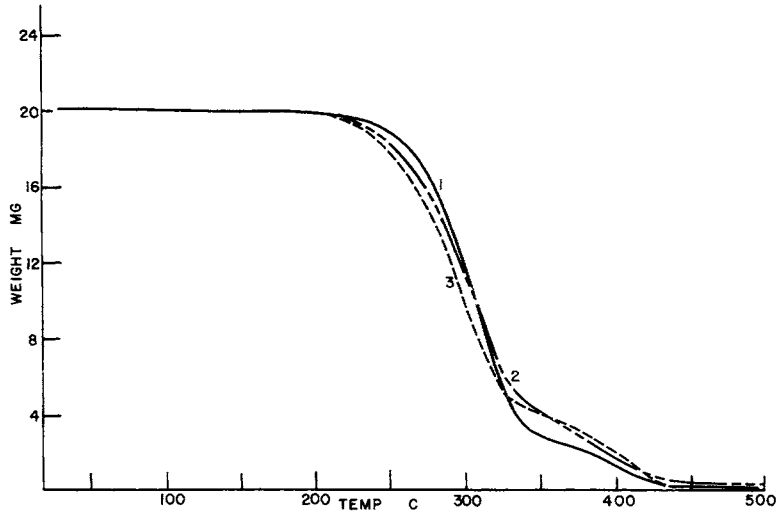

FIG 2.—Thermogravimetric curves for dental inlay waxes. 1, Kerr hard; 2, Kerr regular; 3, Peck's Purple hard.

TABLE 2
PERCENTAGE OF CARNAUBA WAX IN DENTAL INLAY WAXES

Sample	Carnauba (%)
Kerr Blue Inlay Casting Wax—hard	17.0, 17.8 → 17.4
Kerr Blue Inlay Casting Wax—regular	23.8, 26.0 → 24.9
Dr. Peck's Inlay Wax—Purple hard	24.0, 24.6 → 24.3

Figure 3. The order of the waxes with respect to the temperature where loss of weight started was paraffin, ceresin, polyethylene wax, litene, and barnsdahl. The weight vs temperature curves for ceresin and polyethylene wax had slopes that were less steep than the other three waxes. Litene and barnsdahl waxes could be heated to considerably higher temperatures before weight loss occurred than could the other

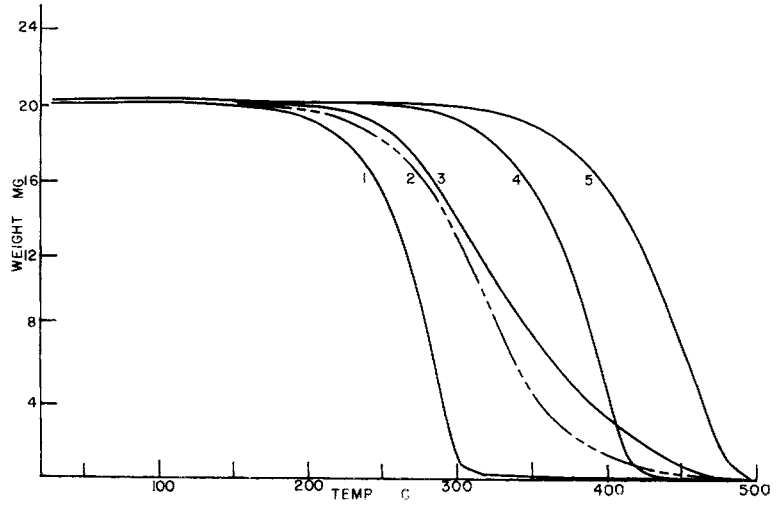

FIG 3.—Thermogravimetric curves for hydrocarbon waxes. 1, paraffin wax; 2, ceresin wax; 3, polyethylene wax; 4, litene wax; 5, barnsdahl wax.

three waxes. None of these waxes had any measurable residue at 485 C.

Isothermal runs were made of 2.5% carnauba and 98.5% paraffin wax in air and in oxygen at 50 C below the inception of weight loss indicated by the runs made at a heating rate of 15 C/minute. No detectable increase in weight was observed that might indicate oxidation. When oxygen was bubbled through samples of liquid wax for 24 hours and thermogravimetric curves were then determined at 15 C/minute, no detectable difference was observed on comparing these curves with those obtained on the original wax. Differential thermograms were obtained as described[1] on the waxes treated with oxygen, and no extra thermal peaks were observed.

Discussion

The thermogravimetric curves could be used for semiquantitative analysis of mixtures of binary waxes. The method was more successful for mixtures having components with melting and boiling points that were well separated. For example, it was easier to analyze carnauba (mp, 76 to 83 C) in paraffin wax (mp, 52 C) than beeswax (mp, 51 to 63 C) in paraffin wax. The analyses for 50% or more of beeswax in paraffin were inaccurate because of the indefiniteness of the break in the thermogravimetric curves.

The thermogravimetric curves for dental inlay waxes were interesting because Kerr hard wax apparently contained less carnauba wax than Kerr regular, and the hard wax contained a higher melting hydrocarbon wax (60 C) than the regular wax (57 C).[1] The Kerr regular had 0.2% of the original weight remaining at 485 C in nitrogen, which indicates the presence of resins not present in the Kerr hard wax. Peck's hard wax had about the same amount of carnauba wax as Kerr regular but contained a broader melting range hydrocarbon wax with a slightly higher melting point (58 C)[1] than the Kerr regular. The control of the properties of these waxes can be accomplished not only by the percentage of carnauba wax but also by the selection of the melting point and melting range of the hydrocarbon wax.

The slope of the thermogravimetric curves gives an indication of the molecular weight distribution of hydrocarbon waxes. The curves for paraffin, litene, and barnsdahl indicate a narrow molecular weight distribution with barnsdahl having the widest distribution. Polyethylene wax and ceresin had the broadest molecular weight distribution of the waxes, with polyethylene wax having the broadest. The curve for polyethylene wax indicates the higher molecular weight fraction is about 20%, whereas for ceresin wax the higher fraction amounts to only 6% of the total wax. This interpretation of these curves is consistent with differential thermal analysis of the same waxes.[1]

Thermogravimetric curves may or may not be related to differential thermal curves. The former represent weight loss as a function of temperature and the latter indicate thermal transitions or phase changes. If the phase change is accompanied by a weight loss, such as boiling, then a decrease in the thermogravimetric curve should approximate the thermal transition. The thermogravimetric curves for waxes showed that substantial weight loss did not occur until one of the components melted and it would level off once that component had been vaporized. However, thermal transitions (DTA) in paraffin wax involving a crystal structure change but melting was not indicated on the thermogravimetric curves.

It should be emphasized that other measurements such as DTA, gas chromatography, or other analytic techniques are usually necessary to identify the components being lost in thermogravimetric tests.

Conclusions

Thermogravimetric analysis was conducted on binary mixtures of paraffin wax and carnauba or beeswax; in addition, similar tests were performed on several dental inlay casting waxes and commercial hydrocarbon waxes. Semiquantitative analysis of carnauba in paraffin wax was possible at up to 75% carnauba wax; however, the analysis of beeswax in paraffin was satisfactory only at concentrations below 50%.

Thermogravimetric curves of dental inlay waxes allowed an estimation of the carnauba wax present and indicated the type of hydrocarbon wax used. The control of the properties of these waxes is accomplished by a combination of factors including the amount of carnauba wax, the melting range of the hydrocarbon wax, and the presence of resin.

The approximate percentage of the distribution of low and high molecular weight fractions of some hydrocarbon waxes was determined. The slope of the weight vs temperature curves indicated the distribution of molecular weights in the hydrocarbon waxes.

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