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# DISTINGUISHING HYDROCARBON AND POLYALKYLENE WAXES BY GAS CHROMATOGRAPHY AND DIFFERENTIAL SCANNING CALORIMETRY

SUSAN M. DYSZEL and BRUCE C. PETTITT

*U.S. Customs Service, 1301 Constitution Ave., NW., Washington, DC 20229 (U.S.A.)*

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## ABSTRACT

Polyalkylene and hydrocarbon waxes are classified under different tariff categories in the Harmonized System of Tariffs which is being developed for world-wide use. Two analytical techniques were applied to a collection of waxes with number average molecular weight between 450 and 2000. While gas chromatography clearly differentiates the polyethylene waxes from the other types, it is limited by the molecular weight range of the waxes. Analysis by differential scanning calorimetry along with the application of numeric parameters from the melting profiles successfully differentiated the polyalkylene waxes from the hydrocarbon waxes.

## INTRODUCTION

The U.S. Customs Service is interested in distinguishing between polyalkylene waxes and hydrocarbon waxes as separate articles of commerce. In the work reported here, wax samples obtained from the Customs Co-Operations Council were examined analytically to develop a set of distinguishing characteristics.

The wax collection consisted of twenty samples which included paraffinic, microcrystalline, Fischer–Tropsch and polyethylenic waxes (Table 1). The number average molecular weight for these waxes ranged from 450 to 2000. After an initial survey by infrared spectroscopy, gas chromatography (GC) and differential scanning calorimetry (DSC) were applied.

## GC ANALYSIS

The gas chromatographic column and analysis conditions are shown in Table 2. Figure 1 shows the resulting chromatogram from a polyethylene wax with its distinctive even-numbered carbon pattern. The presence of branched hydrocarbons (peak clusters between the major straight chains) in

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TABLE 1

Waxes

| ID | Type | ID | Type |
|---|---|---|---|
| 1245 Paraffin | paraffin | Petrac 165 | degraded polyethylene |
| 1236 Paraffin | paraffin | Poly Wax 500 | polyethylene |
| | | Weissen T-40 | polyethylene |
| Microsere 5819 | microcrystalline | Epolene C-18 | polyethylene |
| HI-MIC-1080 | microcrystalline | Epolene C-10 | polyethylene |
| Microsere 5714 | microcrystalline | A-C Polyethylene 6A | polyethylene |
| Be Square 195 | microcrystalline | Poly Wax 1000 | polyethylene |
| | | Poly Wax 2000 | polyethylene |
| Pt-White Wax 0602 | Fischer–Tropsch | | |
| FT-150 | Fischer–Tropsch | Epolene N-15 | degraded polyethylene |
| FT-180 | Fischer–Tropsch | Epolene N-10 | degraded polyethylene |
| | | Epolene N-12 | degraded polyethylene |

Petrac 165 (Fig. 2) is due to its method of manufacture. Petrac 165 is made by thermal degradation of a very high-molecular weight polyethylene. Figure 3 shows the chromatogram from a Fischer–Tropsch wax. GC does less well in distinguishing between the paraffin and microcrystalline waxes as seen from Fig. 4. This is not surprising as they are closely related petroleum products. Even here, it is our opinion that careful quantitation would show that the microcrystalline waxes have a higher percentage of branched hydrocarbons than do the paraffins. In any event, the real limitation of gas chromatography has to do with the molecular weight of the samples. With the conditions noted, we were able to analyze out to C-54 (MW 758). While this range could be extended somewhat, it is clear that there is an upper molecular weight limit which many samples will exceed.

TABLE 2

GC conditions

| | |
|---|---|
| Column | 12-m, fused-silica coated with a bonded methylsilicone phase (DB-1) at a film thickness of 0.1 $\mu$m |
| Carrier gas | He at $\bar{u} = 47$ cm $s^{-1}$ |
| Temperature program | 120–350°C at 5° $min^{-1}$ |
| Injector | 325°C |
| FID detector | 380°C |
| Sample | 0.050 g wax in 10 ml xylene |
| Injection size | 0.5 $\mu$l |
| Split | 200 : 1 |

Note: sample solution heated to effect dissolution

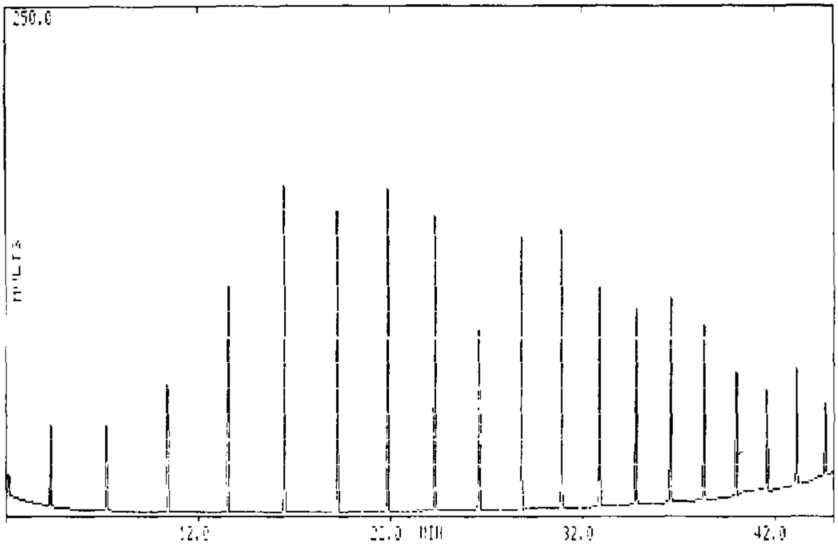

Fig. 1. Poly Wax 500, polyethylene wax.

## DSC ANALYSIS

Differential scanning calorimetry was chosen to characterize the shape of the melting endotherm, to identify the peak melting temperature and to calculate the heat of fusion per gram of wax. The instrumental and experimental conditions are given in Table 3. The DSC curves were plotted and the percent melted at various temperatures is shown numerically and graphically.

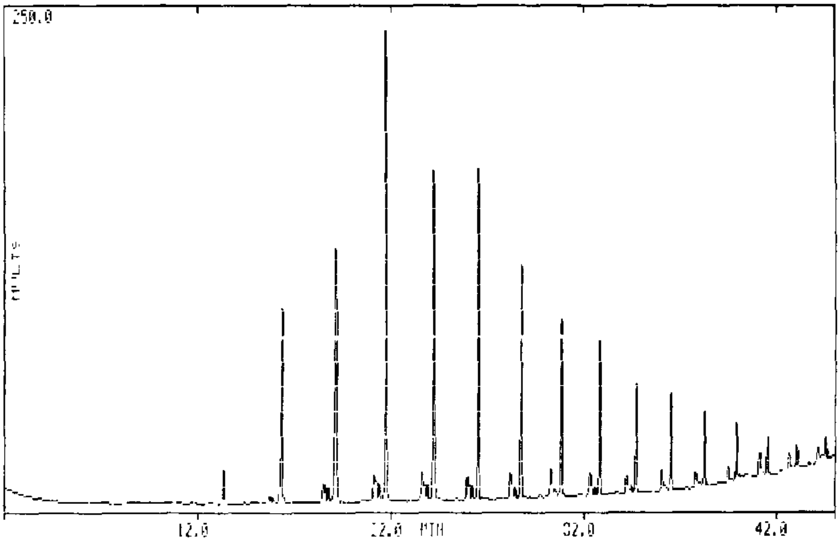

Fig. 2. Petrac 165, polyethylene wax.

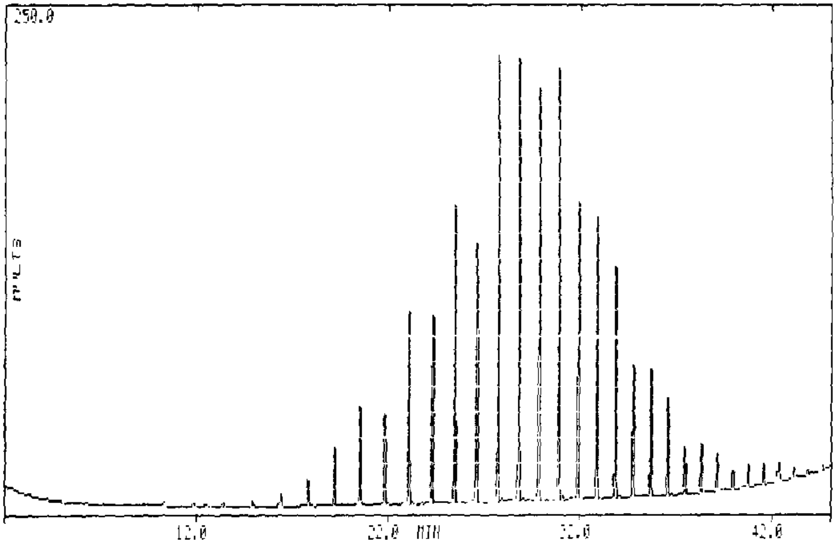

Fig. 3. Pt-White Wax, Fischer-Tropsch wax.

The resulting DSC curves were first visually compared. Several observations were made. (1) The two paraffin samples had similar melt profiles, featuring a solid–solid transition prior to the solid–liquid transition. An example of a paraffin endotherm is shown as Fig. 5. (2) Most of the polyethylene waxes had melt profiles similar to each other (Fig. 6) and different from the paraffins. (3) The degraded polyethylene waxes had melt profiles (Fig. 7) similar to each other and different from the paraffins.

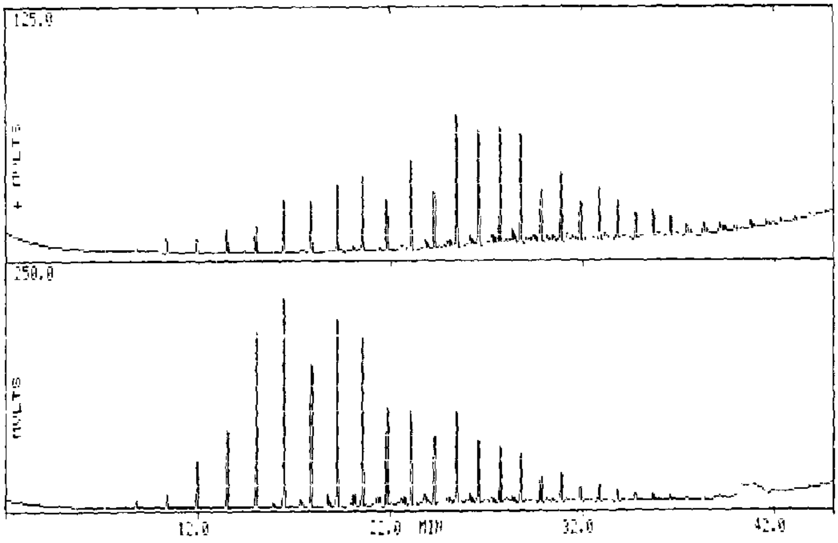

Fig. 4. Microcrystalline wax compared with paraffin wax.

TABLE 3

DSC experimental conditions

| | |
|---|---|
| Instrument | PE DSC-2 with TADS |
| Sample size | 2–10 mg |
| Encapsulation | aluminum pans |
| Atmosphere | nitrogen |
| Heating rate | 10° min$^{-1}$ |
| Temperature range | 275–400 K (0–125°C) or until melt |
| Cooling rate | 50° min$^{-1}$ |
| Program | heat, cool, heat |
| Output | melt endotherm normalized to calories per gram of sample |

(4) The microcrystalline waxes had melt profiles (Fig. 8) which were also different from the paraffins. (5) There were enough "oddballs" to require data handling techniques beyond visual inspection.

Numeric parameters were created against which a wax sample endotherm could be compared. These parameters were established for the hydrocarbon waxes, namely, paraffin, microcrystalline and Fischer–Tropsch waxes. These parameters and their underlying definitions are given in Tables 4 and 5, respectively.

The first parameter chosen for examination was $T_{max}$. Only three of the eleven polyethylene waxes had a $T_{max}$ value which fell within the range of

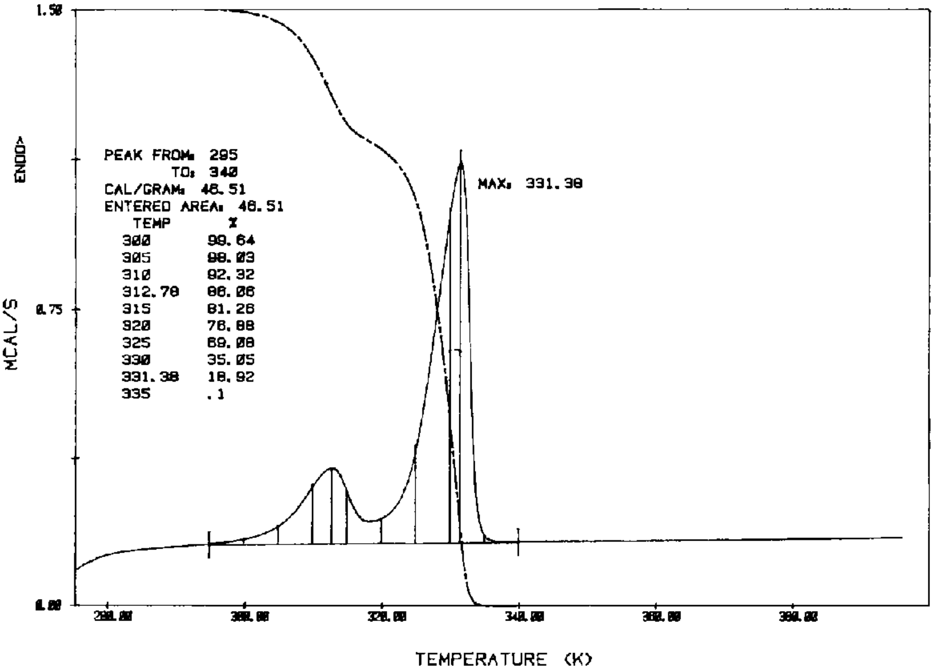

Fig. 5. 1245, paraffin wax. (———) Melting curve; (- - - - -)% solid.

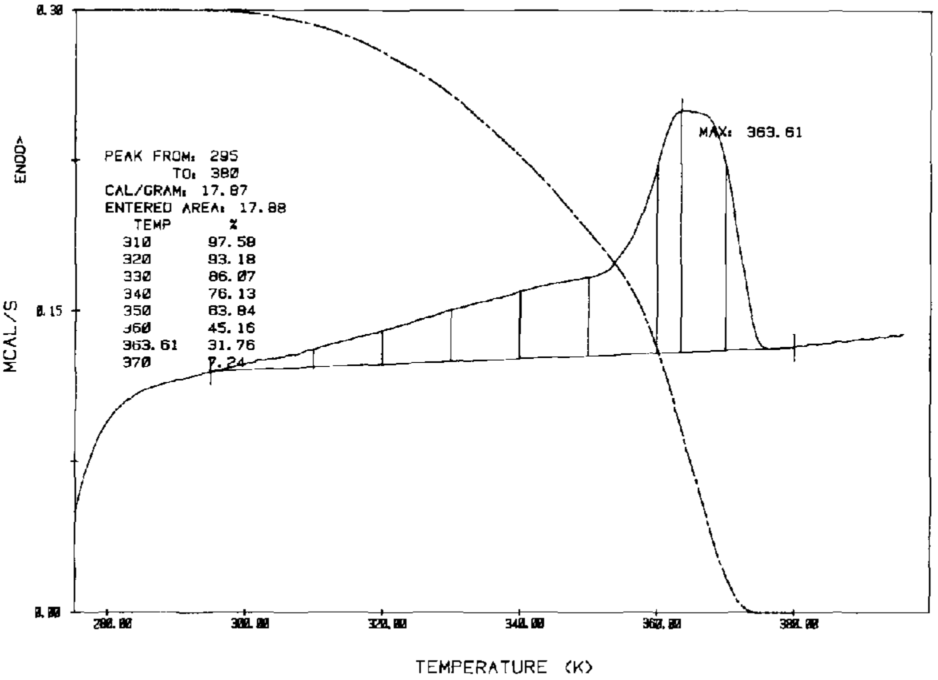

Fig. 6. Epolene C-18, polyethylene wax. (———) Melting curve; (- - - - -)% solid.

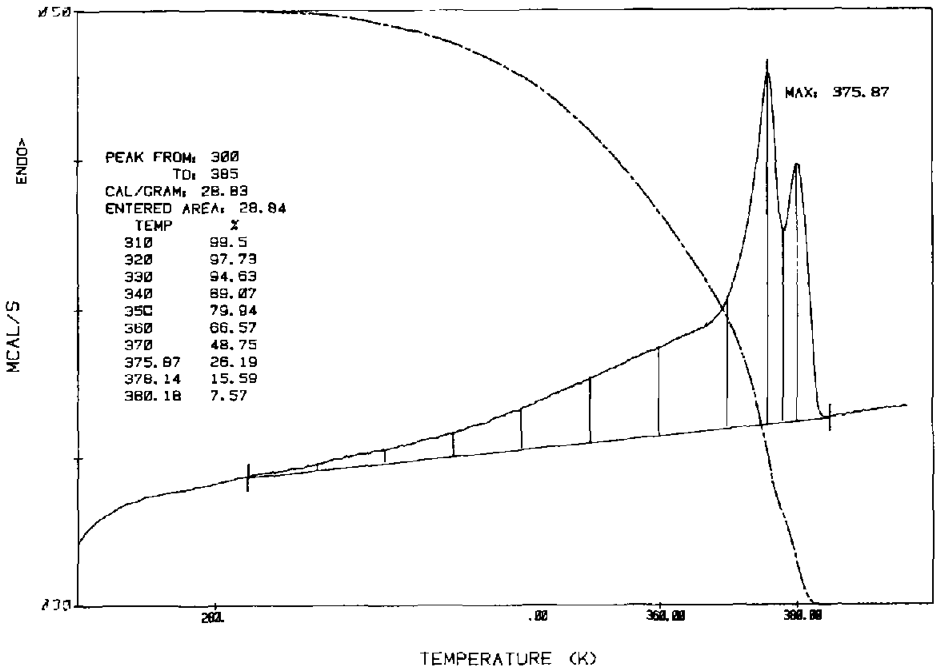

Fig. 7. Epolene N-10, degraded polyethylene wax. (———) Melting curve; (- - - -)% solid.

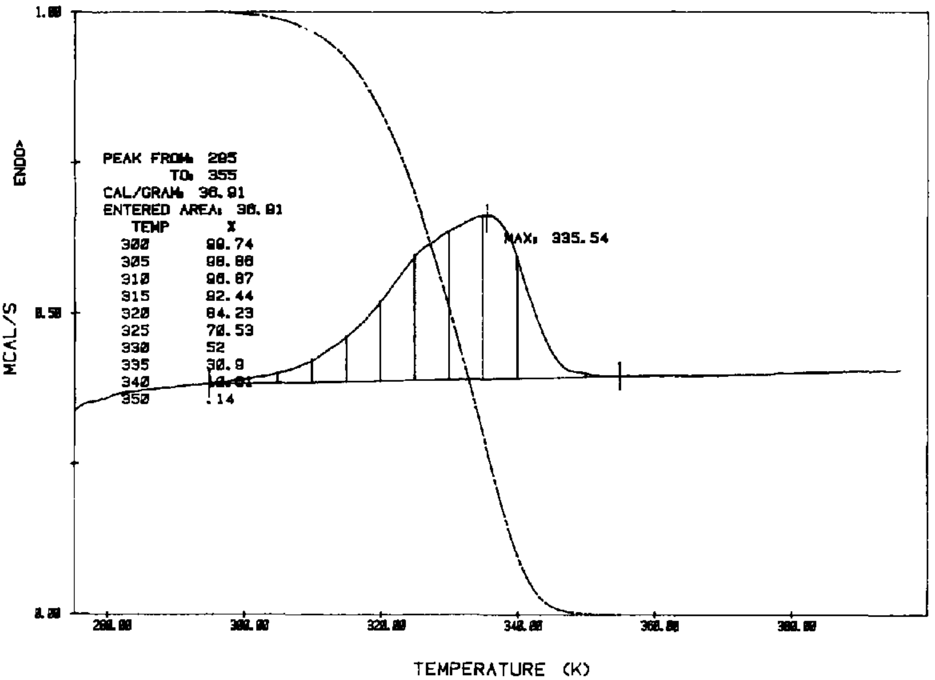

Fig. 8. Microsere 5714, microcrystalline wax. (———) Melting curve; (- - - - -)% solid.

the hydrocarbon waxes. These three waxes were then compared against the remaining parameters to see if they too could be excluded. Table 6 lists these three waxes with the parameter which excluded them from the hydrocarbon waxes.

TABLE 4

Parameter table for hydrocarbon waxes

| | Paraffin | Microcrystalline | Fischer–Tropsch |
|---|---|---|---|
| $T_{max}$ (K) | $\leq 337$ | $\leq 357$ | $\leq 357$ |
| $T_{max} - T_0$ (K) | $\leq 27$ | $\leq 57$ | $\leq 43$ |
| $\Delta H/g$ | ~ 46 cal $g^{-1}$ | $34 < \Delta H/g < 44$ | $50 < \Delta H/g < 55$ |
| PS | $3 < PS < 4$ | $0.6 < PS < 4$ | $0.8 < PS < 8$ |
| $\Delta T_{1/2}$ (°) | $< 8$ | $22 < \Delta T_{1/2} > 47$ | $7 < \Delta T_{1/2} \leq 36$ |

TABLE 5

Definition of terms

| | |
|---|---|
| $T_{max}$ | temperature at maximum signal deflection |
| $T_0$ | temperature at which melt endotherm leaves the baseline |
| $\Delta H/g$ | heat of fusion per gram of sample |
| $T_e$ | temperature at which melt endotherm returns to baseline |
| PS | $(T_{max} - T_0)/(T_e - T_{max})$ measure of peak shape |
| $\Delta T_{1/2}$ | endotherm width in degrees at half height |

TABLE 6

Parameter analysis of three polyethylene waxes

| Wax | Reason for exclusion |
|---|---|
| Weissen T-40 | $(T_{max} - T_0)$ outside range for all hydrocarbon waxes |
| Poly Wax 500 | not paraffin—outside all parameters<br>not microcrystalline—outside $\Delta H/g$<br>not Fischer–Tropsch—outside $(T_{max} - T_0)$ |
| Petrac 165 | not paraffin—outside all parameters<br>not microcrystalline—outside $\Delta T_{1/2}$<br>not Fischer–Tropsch—outside $(T_{max} - T_0)$ |

## CONCLUSION

Two literature references [1,2] confirm that the melt endotherms observed for these waxes are illustrative of the class of materials. It has been demonstrated that differential scanning calorimetry and data analysis can be used to differentiate the polyalkylene waxes from the hydrocarbon waxes without the molecular weight limitations experienced by GC analysis.

## REFERENCES

1 A.P. Gray, Instrum. News, 17(1).
2 B. Flaherty, J. Appl. Chem. Biotechnol., 21 (1971) 144.