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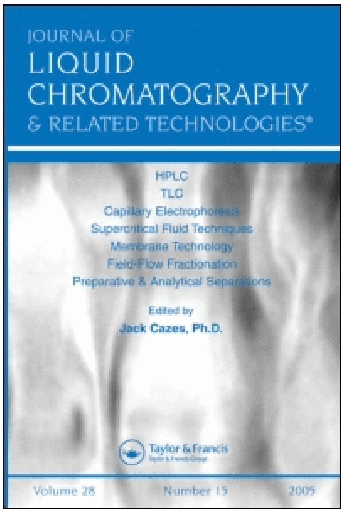

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CHARACTERIZATION OF HYDROCARBON WAXES BY GEL PERMEATION CHROMATOGRAPHY AND DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

An integral part of many elastomer compounding recipes is the wax since it contributes significantly to the performance characteristics of the vulcanizate. Frequently the only quality control tests applied by the user are a simple melting point range and a percent insolubles. This work demonstrates two analytical techniques that can provide much improved quality control monitoring of waxes. Differential scanning calorimetry and gel permeation give not only data on the melting characteristics but also supply information on the chemical structure and size distribution of the waxes. Using these methods replacement waxes can be selected on a technically sound basis.

BACKGROUND

A few years ago the commercial supplier of a number of waxes which BFGoodrich used in rather high volume announced that the waxes would no longer be available. We were therefore faced with the necessity of finding suitable replacement waxes at a reasonable price. Our needs were made known to other commercial suppliers and as a result we were faced with the prospect of evaluating some thirty odd waxes as possible replacements for the five being withdrawn from the market. The problem then became one of how to evaluate the waxes analytically in a reasonable period of time with minimal cost and come up with the best replacements.

Robinson and Johnson (1) had reviewed methods for analysis of waxes and concluded that probably a combination of column chromatography (LC), gas chromatography (GC) and infrared spectroscopy (IR) was the best for complete analysis. Levy (2) had demonstrated it was possible to quantitatively determine normal, iso, cyclohexyl and cyclopentyl hydrocarbons up to C_{33} with gas chromatography-mass spectrometry. Ludwig (3,4) had applied high resolution GC to the examination of hydrocarbon and ester waxes and was able to elute hydrocarbons up to C_{68}. The upper range of usefulness of GC for linear hydrocarbons is generally considered to be about C_{63}. Most waxes cover the range of C_{15} to C_{100} with microcrystalline waxes extending to even higher carbon numbers. Obviously then, GC cannot be used to separate and characterize all hydrocarbon waxes. Hillman (5) had reported on the use of gel permeation chromatography (GPC) to characterize and analyze waxes. Actually in his work he employed GC, nuclear magnetic resonance (NMR), molecular sieve separation and GPC to obtain data on carbon number range and distribution, amount of polyethylene in microcrystalline waxes, and total branched hydrocarbon content.

We felt that melting range and molecular weight distribution would be the two properties having the most effect on dispersion and migration characteristics of the waxes. Therefore, we decided to use a melting point profile by differential scanning calorimetry (DSC) and a molecular size distribution profile by GPC as the basis for comparison and selection of the replacement waxes.

EXPERIMENTAL

The thermograms were obtained on the scanning calorimetry module of the Dupont 900 Differential Thermal Analyzer. The 5-10 milligram samples of wax were placed in crimped aluminum pans and scanned from room temperature to 100°C at 10°C per minute.

The size distribution curves were obtained using a Waters Associates Inc. Model 200 GPC instrument. Five "Styragel" columns (120 cm x 7.6 mm I.D.) were used with exclusion limits 60, 100, 100, 500 and 1,000 Å as rated by Waters Associates. The average plate count of the system was 717 plates per foot. The solvent was tetrahydrofuran (THF) at a temperature of 40°C and a flow rate of 1 cm^3 per minute. The sample concentration was 0.2% (w/v) and the sample size 2 cm^3 resulting in a 4 mg loading on the columns. The columns were calibrated using a series of straight chain hydrocarbons and two low molecular weight narrow size distribution polystyrenes. The calibration curve (Figure 1)

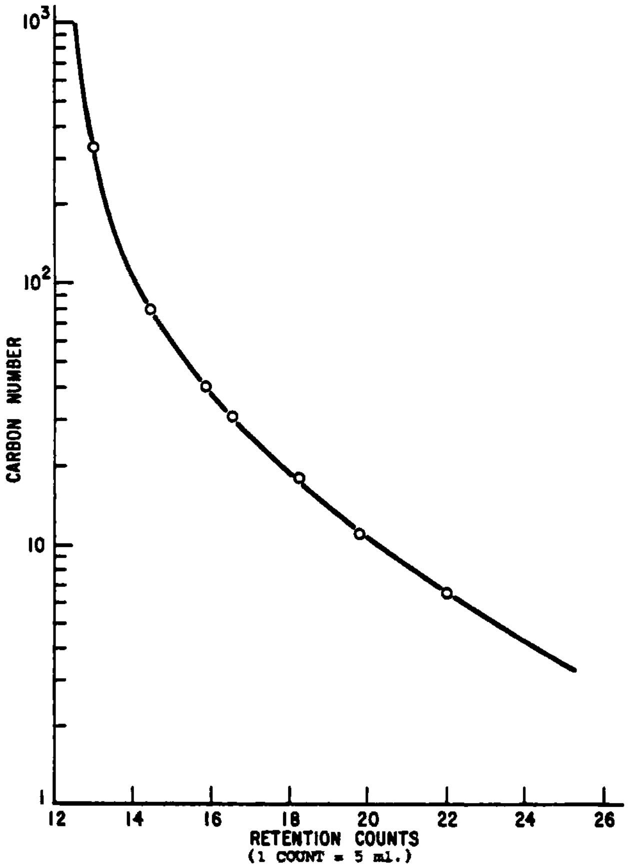


FIGURE 1
Carbon Number Versus Retention Count

was formed by plotting carbon number versus elution volume. It was felt that carbon number was an appropriate parameter since a large portion of most waxes is in the form of alkanes.

One of the suppliers who submitted waxes for consideration, also provided carbon number distribution data obtained by GC. These data were compared with that obtained by GPC.

RESULTS AND DISCUSSION

For those waxes on which GC data were available, a comparison was made between the carbon number of the peak of the GPC curve and the carbon number of the most abundant species from the gas chromatogram. The results are shown in Table I. Samples labeled A through E are the five waxes for which we needed to find replacements. Samples 1 through 6 are possible replacements. In all but one case, the agreement between the two sets of data is good. In the case of sample D, 59% of the wax was too large a molecular size to be resolved by the GC column and procedure employed. The highest carbon number reported in the GC data supplied was C_{46}.

TABLE I

Comparison of Carbon Number from GPC and GC Measurements

Sample	Carbon # GPC	Carbon # GC	ΔC#
A	30	29	1
B	35	33	2
D	44	33	11
1	30	29	1
2	49	>45	
4	29	26	3
5	25	25	0

A melting point versus carbon number curve (Figure 2) was constructed from data obtained from The Handbook of Chemistry and Physics, 49th Edition (6). Using this curve, melting points were obtained for each wax based on the carbon numbers of the peaks in the GPC chromatograms. Comparing these melting points with those obtained by DSC (Table 2) , good agreement was found for those waxes with narrow size distributions. For the broad distribution waxes agreement was not so good. For example, compare the melting points determined for the narrow distribution wax A with those determined for the broad distribution wax D. The main factor contributing to the poorer agreement for broad distribution waxes is the presence of more than one chemical structure in these waxes. Depending on the type of wax, there may be alkanes,

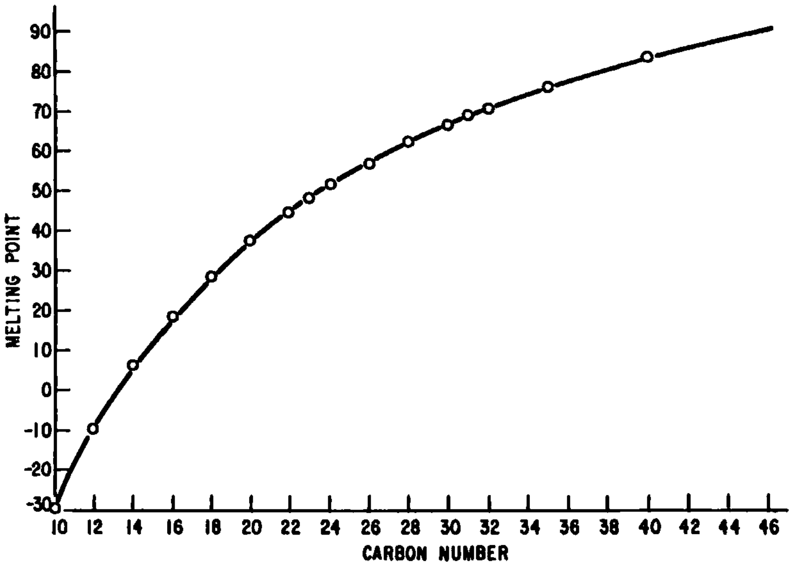


FIGURE 2
Melting Point Versus Carbon Number for Linear Hydorcarbons

TABLE 2

Comparison of Melting Points from GPC and DSC Measurements

Sample	Melting Point GPC	Melting Point DSC	Δmp
A	66.0	66.0	0.0
B	74.5	64.5[1]	10.0
C	78.0	69.0[1]	9.0
D	85.0	63.5[2]	21.5
E	57.0	56.5	0.5
1	66.0	64.0	2.0
2	83.0	56.0[3]	27.0
3	64.0	65.0	1.0
4	64.0	58.0	5.5
5	54.0	56.0	2.0
6	84.0	64.0[2]	20.0

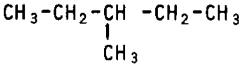
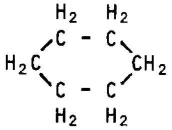
[1] isoparaffin, [2] cyclic, [3] dicyclic

noncondensed cycloalkanes, condensed cycloalkanes and in some cases benzenes and naphthalenes. Table 3 illustrates the effect that molecular structure can have on molar volume and melting point.

The general relationship of melting point to structure is shown graphically in Figure 3. Using Figure 3 to correlate the carbon number from the GPC chromatogram and the melting point from the DSC trace, some indication of the chemical inhomogeniety of a wax can be obtained. For example, wax D and wax 6 (Figure 6) have GPC curves showing peaks at carbon numbers 44 and 43 that correspond to linear hydrocarbon melting points of 85° and 84° respectively. Their melting points by DSC are 63.5 and 64.0 respectively. Referring to Figure 3, we would expect these waxes to contain a great deal of cyclic structure. Both waxes are microcrystalline and contain 40 and 54% of cyclic and dicyclic structure. Likewise waxes B and C with GPC carbon numbers of 35 and 38 have DSC melting points of 64.5 and 69.0°C instead of

TABLE 3

Relationship of Structure, Size, and Melting Points of Hydrocarbon Waxes

	Molar* Volume	Elution* Volume	Melting Point
1. n-paraffin $CH_3-(CH_2)_4-CH_3$	152	172.2	-95.0
2. iso-paraffin  $CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{\mid}}{CH}-CH_2-CH_3$	149	173.5	-154.0
3. noncondensed cycloalkane 	124	181.1	6.5

* data from Cazes and Gaskill(7).

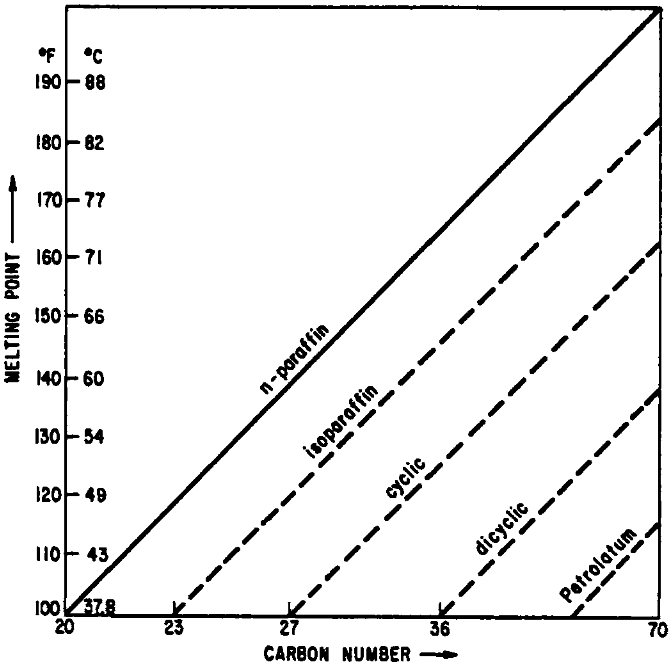


FIGURE 3
Melting Point Versus Carbon Number for Various Hydrocarbon Structures

74.5 and 78.0°C as expected for linear hydrocarbons. These would be suspected of having branched structure (isoparaffin).

Figures 4-7 show the GPC and DSC traces of the waxes for which replacements were required and the curves of the waxes

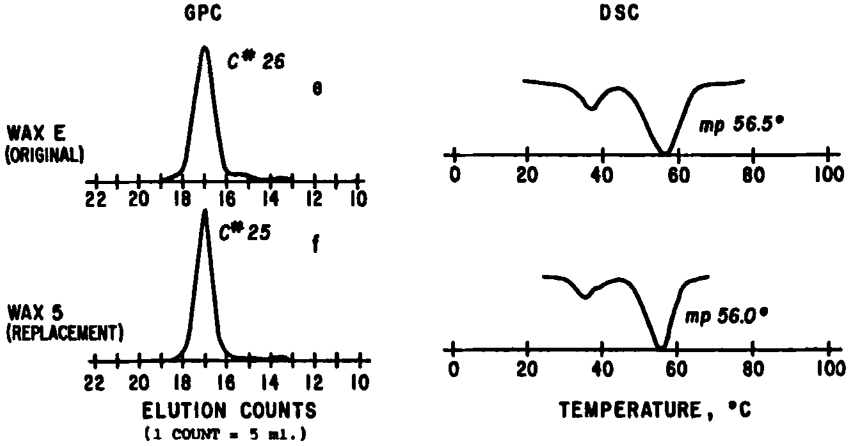


FIGURE 4
Size and Melting Point Profiles of Original (E) and Replacement (5) Waxes.

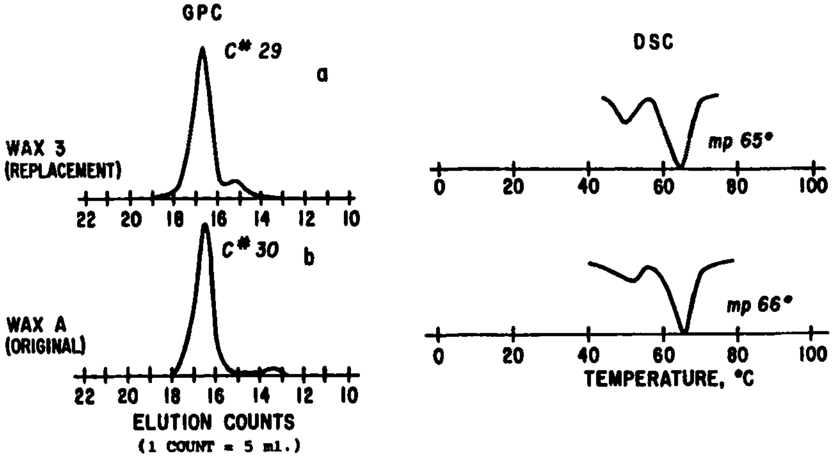


FIGURE 5
Size and Melting Point Profiles of Original (A) and Replacement (3) Waxes

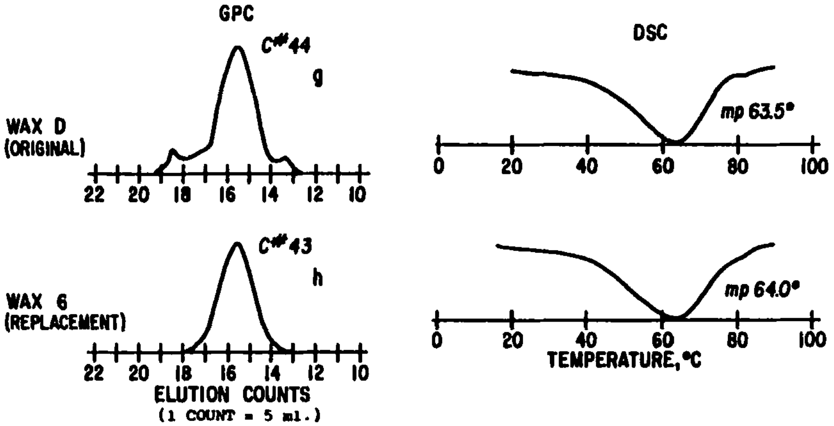


FIGURE 6
Size and Melting Point Profiles of Original (D) and Replacement (6) Waxes

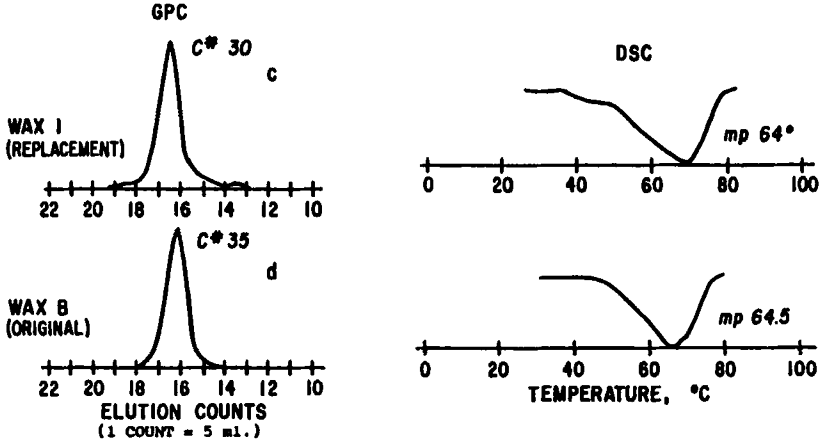


FIGURE 7
Size and Melting Point Profiles of Original (B) and Replacement (1) Waxes

selected to replace them. No good match was found for one of the five. Of the four shown, three are excellent matches and the fourth, while not identical is generally similar. Subsequent use of the selected replacement waxes in actual rubber compounds has proven the correctness of these selections.

CONCLUSIONS

GPC and DSC are two relatively fast and inexpensive tests for quality control of waxes. Either is to be preferred over a simple melting point and insolubles test. By combining the two tests, not only can information be obtained on melting profile and molecular size distribution but also on the chemical homogeniety of the wax. Using these tests, replacement waxes can be selected on a sound basis.

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