# Petroleum wax as a hot-melt-adhesive modifier

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*ABSTRACT: Petroleum wax specifications are often not sufficiently descriptive of HMA performance requirements. Modern analytical tests provide more meaningful criteria to select waxes. A solid-phase structural model of wax can explain the role of such test data in predicting performance. The model illustrates the impact of wax refining and feedstock selection. Therefore, the adhesive compounder can completely identify purchasing requirements by including the petroleum wax source with common specifications.*

*KEYWORDS: Adhesives, hot melts, models, modifiers, paraffin wax, specifications, structural analysis, test methods.*

Petroleum waxes are used to enhance hot-melt-adhesive (HMA) performance in some applications. HMA properties—including open temperature, viscosity, set time, and compatibility, as well as cost—are determined to a large degree by the wax component (*1—4*). Knowing which wax to use in a particular application is valuable information for both the adhesive compounder and the end user.

Many types of petroleum wax are commercially available, including the broad classes of paraffin and microcrystalline. The test data in **Table I** show that wax selection is not arbitrary with respect to the effect upon performance (*5*). In fact, typical specifications sometimes are not adequate to predict the performance of HMAs and other end uses of wax.

What wax properties should you look for? Probably the specifications now used are adequate, although another variable, the wax source, should be considered more carefully. While modern analytical tests provide the detailed information required to discriminate one wax from another and are useful in troubleshooting product quality complaints, such extensive testing is not required on a batch-to-batch basis.

## Wax refining and quality control

Petroleum waxes are a plentiful and reliable source of low cost raw materials for the HMA industry, with almost 600,000 metric tons of finished products produced in the United States (*6, 7*). The typical refining process makes several grades of wax, corresponding to the lubricating oil grades produced, as illustrated in **Fig. 1.** Basically, special high-yield crudes are selected and then physical refining methods are employed to generate a wax of low oil content and other characteristics required in commercial applications.

The most common product quality specifications include melting point, oil content, and color. For some wax applications, these tests are not adequate by themselves to make a reliable performance judgment. This is the niche of the analytical chemist. However, the analytical test data do not provide a direct explanation of performance. An intermediate step, the material structure definition, has not been described in recent discussions on this topic.

## A material structure model

Pure compound studies are often useful when analyzing the behavior of complex systems. For petroleum wax, an *n*-alkane having a melting point similar to that of the product under study is sometimes evaluated, since commercial waxes are predominantly comprised of *n*-alkanes. **Table II** provides a list of such pure compounds and shows how *n*-alkanes of equivalent effective carbon chain length are selected.

In industry, any commercial wax contains a variety of pure compounds. A typical carbon chain length distribution is shown in **Fig. 2,** which is derived from gas chromatography data. This is only part of the deviation from the ideal case. Commercial products also contain branched chain structures and chains having closed ends. Such complexity is exemplified by the analysis results in **Table III,** which compares the special types found in two petro-

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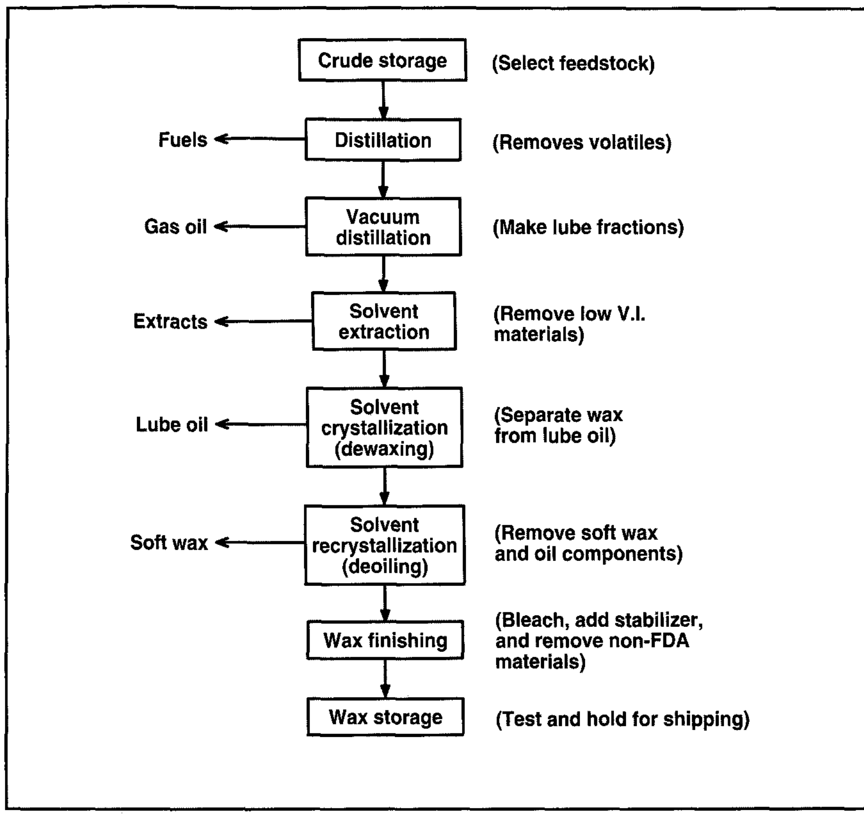
I. The role of wax in hot melt adhesive properties

| Test | Paraffin Blend Result[a] | Microwax Blend Result[b] |
|---|---|---|
| Elastic modulus, kPa | 69M | 52M |
| Elongation, % | 450 | 450 |
| Viscosity, cP, 150°C | 25M | 40M |

Source: "ELVAX" Resins Formulating Guide, E.I. Dupont and Co., Technical Bulletin.

[a]Blend comprised of "ELVAX" 260 (40%), "NIREZ" 1135 (30%), "SHELLWAX" 200 (30%).
[b]Blend comprised of "ELVAX" 260 (40%), "NIREZ" 1135 (30%), "BE SQUARE" 190/195 (30%).

1. Typical petroleum wax refining steps




leum waxes (*8*). Many wax properties are sensitive to these nonidealities.

Crystal form identification is a case in which the pure compound analogy has been useful. Pure compound studies indicate the types of crystals and species arrangement to look for in commercial waxes, as shown in **Fig. 3** (*9–11*). Also, much similarity is found between the pure $n$-alkanes and commercial waxes regarding phase transition properties (*12*). Differential Scanning Calorimetry analyses confirm that the two transition characteristics found in $n$-alkanes of similar molecular weight are also observed in commercial waxes, as shown in **Fig. 4.** A representation of species arrangement in wax crystals is provided in **Fig. 5** (*10, 13*). The intermolecular forces present are of the dispersive van der Waal's type.

In reality, petroleum wax in the solid phase is not a simple mixture of crystals wedged together, which is the familiar case for metals and many other systems. The structural model is completed by adding an amorphous, liquid-like phase which acts to bind the crystals together. Therefore, the crystalline phase is actually dispersed in a continuous phase comprised of the more highly branched and low molecular weight species, which tend to be liquid at use conditions, as depicted in **Fig. 6.**

## Applying the model

The material structure model of petroleum wax explains performance differences between various products. The contribution of the amorphous phase to strength properties is especially important. A useful analogy is that of asphalt concrete, in which the amount as well as integrity of the asphalt binder is key to optimum mechanical stability of the pavement mix (*11*).

The role of the continuous phase upon wax strength is demonstrated in **Fig. 7.** The graph plots needle penetration against the amount of oil added to a resin-modified paraffin. Since penetration units are the inverse of hardness, the figure shows that even small additions of soluble liquid to the continuous phase produce a dramatic softening trend. The trend becomes rational by considering that the oil content of fully-refined paraffin (FRP) is within the domain of oil additions tested. That is, seemingly small additions to the wax are much greater in magnitude relative to the existing amorphous component. Similar observations have been made in the literature on the topic (*14*).

Like the case of a pavement mix stated above, the mechanical integrity of the amorphous wax component is also important. Polymeric materials within a certain molecular weight range are known to be compatible with the species found in the amorphous part, and so to selectively influence properties (*15*). The results of a wax-polymer blend study are shown in **Fig. 8.** The blend viscosities indicate the effect of polymer molecular weight, using commercial microcrystalline wax, petroleum hydrocarbon resin, and two polyethylene resins added to FRP.

**II.** Melting points of hydrocarbons

| Name | Carbons in molecule | Melt point, °C |
|---|---|---|
| Methane | 1 | -183 |
| *n*-Octane | 8 | -57 |
| *n*-Octadecane | 18 | +28 |
| Low M.P. paraffin | 26* | +54 |
| High M.P. paraffin | 31* | +63 |

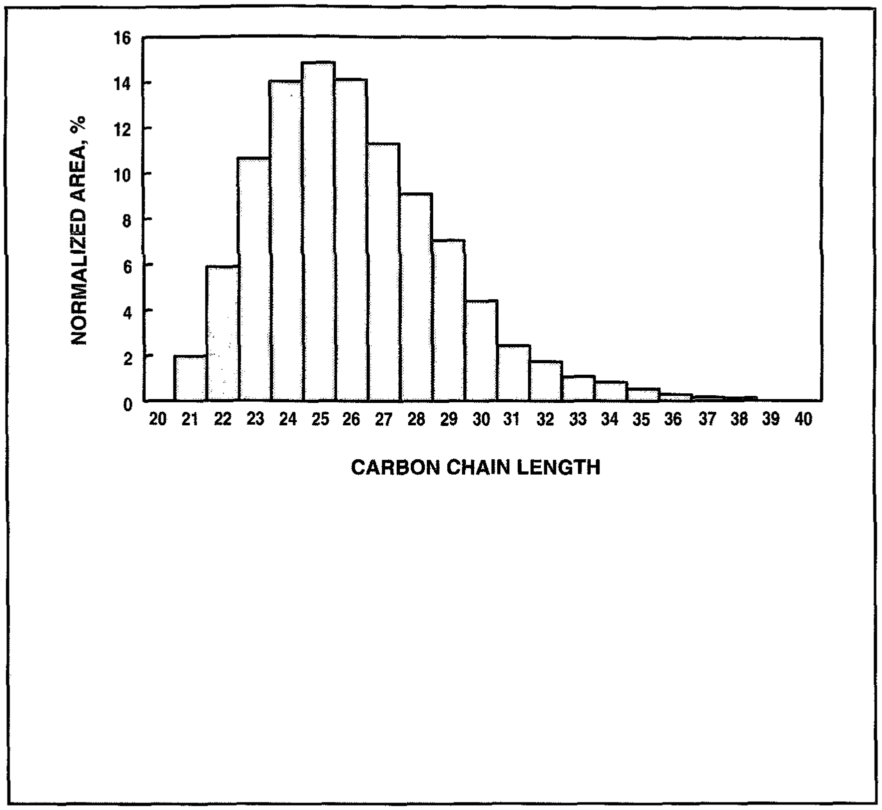
*Weight-average of species present

**III.** Chemical species in commercial paraffin waxes

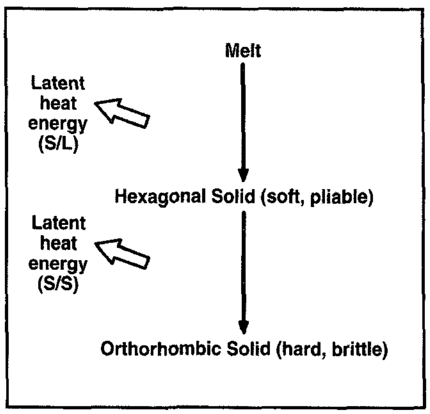
| Type of compounds | Wax "A" | Wax "B" |
|---|---|---|
| *n*-alkanes | 75.5 | 66.5 |
| Branched alkanes | 13.5 | 17.9 |
| Monocyclo alkanes | 10.2 | 13.4 |
| Polycyclo alkanes | 0.6 | 1.9 |
| Aromatics (total) | 0.2 | 0.3 |
| (Melting point, °C) | (52) | (63) |

Source: Edwards, Ind. Eng. Chem. 47(12): 2555(1955).

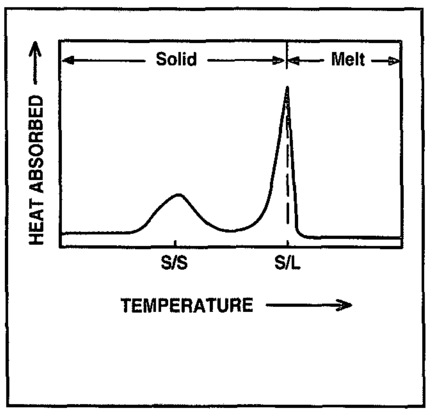
**2.** *n*-alkane distribution (commercial 54° M.P. FRP).



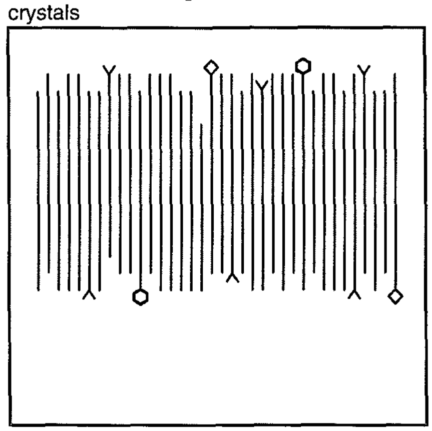

**3.** Crystal forms in petroleum waxes




**4.** D.S.C. thermal fingerprint of paraffin




**5.** Molecular arrangement in petroleum wax crystals



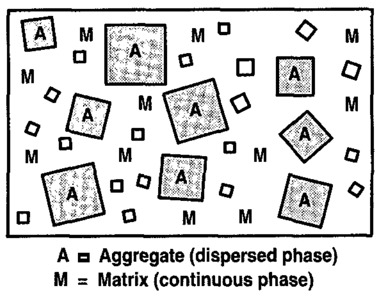
The response of needle penetration to resin additions is substantial and more pronounced than one would suppose without considering the small amount of amorphous material present. The base wax is shown to set apart from the trend line for the blends. The base wax outlier supports the idea that the polymer selectively interacts with the continuous, as opposed to the dispersed, solid phase and thereby adds to the mechanical integrity. Other supporting data are available (*8, 16*).

## Add source to specifications

No two waxes from different sources are exactly alike. The degree to which the differences are important is decided by the wax user, who compares one product alternative against others. Analytical methods can be used to better understand the chemistry of waxes and, through the material structure model, how the chemistry affects performance.

Although useful, the modern analytical techniques are not a requirement to the specifications issue. Such tests as well as actual performance measures are best employed in product demonstration studies, not for routine inspection. Petroleum refineries

**6.** Solid phase representation of petroleum wax



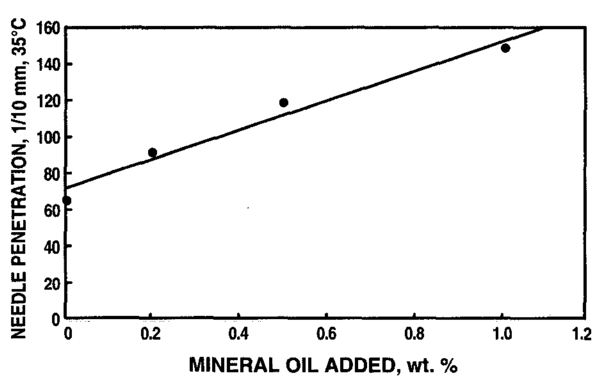

**IV.** Performance differences between two commercial paraffins of similar specification

| *Test* | *Wax "A"* | *Wax "B"* |
|---|---|---|
| Melting point, °C* | 58 | 58 |
| Oil content, wt%* | < 0.5 | < 0.5 |
| Color, Saybolt* | >28 | >28 |
| Viscosity, cSt, 100°C | 3.80 | 3.69 |
| S/S Transition point, °C | 42 | 34 |
| Heat capacity maximum, J/g/°C | 30 | 19 |
| Heat of fusion, J/g | 221 | 221 |
| Needle penetration, 1/10 mm, 100 g/5 s, | | |
| at 25°C | 13 | 14 |
| at 35°C | 107 | 115 |

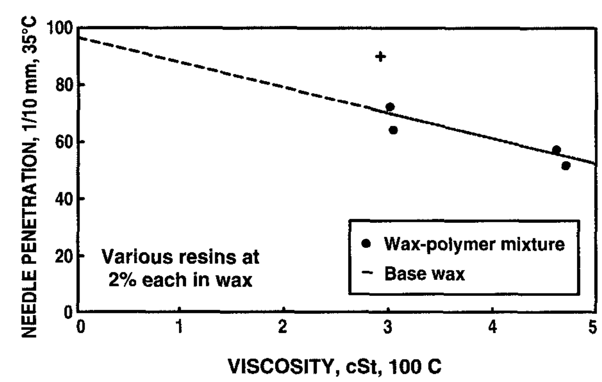
*Product specification tests

Note:
Wax "A" derived from straight run refinery stream.
Wax "B" derived by blending two straight run waxes.

**7.** Oil effect on hardness (mineral oil added to 54° M.P. FRP)




**8.** Resins versus hardness (resins added to 54° M.P. FRP)




produce consistent products, and the only real variable to the user is that of the source.

An example of the need for source control is given in **Table IV.** Here a blended product is compared to a narrow melting point range paraffin of similar specifications. The outstanding difference is that of the solid–solid transition point, indicating probable cold flow differences. On the other hand, stress cracks are more likely to develop in the narrow range product (*17*). ■

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