



CHAPTER II

THEORETICAL REVIEW

2.1 Dewaxing of Lubricating Oil

All lube stocks, except those from a relatively few highly naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperatures. Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing.

There are two types of dewaxing processes in use today. One process uses a selective hydrocracking process to crack the wax molecules to light hydrocarbons. The other process uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil. There are two principal solvents used in solvent dewaxing processes, propane and ketones. The ketone processes use either a mixture of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK) or MEK with toluene. The solvent acts as a diluent for the high molecular weight oil fractions to reduce the viscosity of the mixture and provide sufficient liquid volume to permit pumping and filtering. The process operations for both solvent processes are similar but differ in the equipment used in the chilling and solvent recovery portions of the process. About 85% of the dewaxing installation use ketones as the solvent and the other 15% use propane. A dewaxing aid such as a naphthalene-chlorinated wax condensation product or a methacrylate polymer is frequently added to the waxy oil feed at a level of 0.05 to 0.2 liquid volume percent on feed to modify the wax crystal structure. [3]

2.2 Wax Deoiling

The wax from dewaxing operation is commonly known as slack wax, contains oil, and the processes employed for the production of waxes are aimed at deoiling the slack wax (petroleum wax concentrate).

Wax sweating process is used to separate wax fractions from the wax obtained from paraffin slack wax. In the early meltdown process, slack wax is crystallized. The crystallized wax is then sweated while simultaneously draining the liquid drippings from the sweating oven. The congealing point of the liquid drippings is monitored. When the congealing point of the liquid drippings reached the melting temperature of the desired wax product, sweating and drainage are stopped, and the remaining solid bed

the sweating oven is rapidly melted and subsequently upgraded. [4] However, wax sweating can be carried out only when the residual wax consists of large crystals that have spaces between them, through which the oil and lower melting waxes can percolate. It is therefore limited to wax obtained from light paraffin distillate. The intermediate and microcrystalline waxes cannot be sweated because the oil is held tightly in the crystal lattice and does not migrate to the surface.

Wax recrystallization, like wax sweating, separates slack wax into fractions, but instead of using the differences in melting points, it makes use of the different solubilities of the wax fractions in a solvent such as the ketone used in the dewaxing process. When a mixture of ketone and slack wax is heated, the slack wax usually dissolves completely, and if the solution is cooled slowly, a temperature is reached at which a crop of wax crystals is formed. These crystals will all be of the same melting point, and if they are removed by filtration, a wax fraction with a specific melting point is obtained. If the clear filtrate is further cooled, a second crop of wax crystals with a lower melting point is obtained. Thus, by alternating between cooling and filtration, the slack wax can be subdivided into a large number of wax fractions, each with different melting points. This method can be applied to the microcrystalline waxes obtained from intermediate and heavy paraffin distillates, which cannot be sweated. [5]

2.3 Solvent Selection

The requirements of an ideal solvent for the fractionation of microcrystalline wax from intermediate wax include the following characteristics :

- 1) Complete miscibility with oil and microcrystalline wax at the various separating temperatures.
- 2) Low solubility of paraffin wax in the solvent.
- 3) It must be non-reactive with the other components in the intermediate wax.
- 4) Solvent should be of low boiling point for easy recovery from microcrystalline wax.
- 5) Solvent should be inexpensive, non-corrosive, non-toxic and thermally stable.

Paraffin wax (melting point 56 °C) dissolved in Benzene, Toluene and Xylene at various temperatures is shown in Figure 2.1.

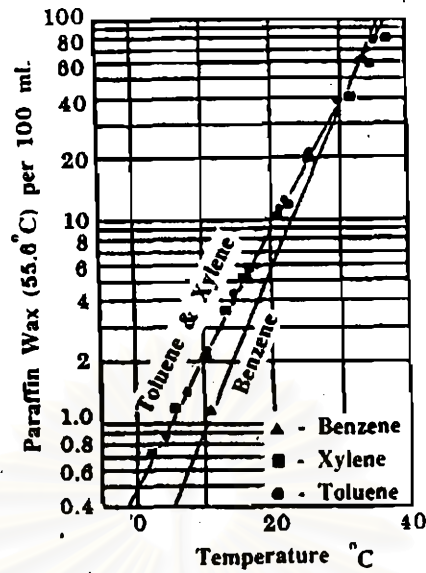


Figure 2.1 Solubility of paraffin wax in aromatic hydrocarbons

The use of MEK as solvent for paraffin wax solubility is shown in Figure 2.2.

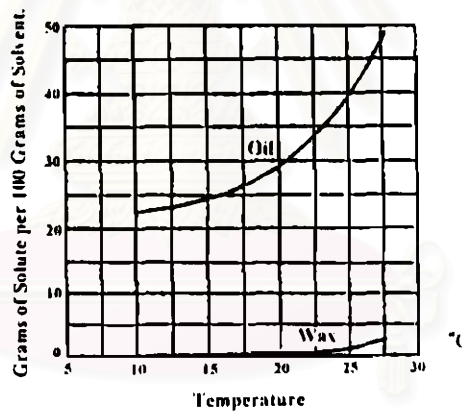


Figure 2.2 Temperature-solubility curves for paraffin wax and mineral oil in MEK

The solubility of paraffin wax in toluene increases more rapidly at higher temperature but the solubility of paraffin wax in MEK increases slowly at higher temperature. [6]

Intermediate wax consists of normal and non-normal paraffins (i.e. iso-paraffins, cyclo-paraffins and some of aromatic hydrocarbons.). Non-normal paraffins have similar structure to lubricating oil but the lubricating oil has more solubility in toluene and MEK.

2.4 Solubility of Paraffin Wax

Data on solubility are valuable in separating waxes from other substances, because a solvent may be available which will preferentially dissolve one component.

The solubility of higher molecular weight solvent increases with a rise in temperature more rapidly. The solubility a particular solvent is inversely proportional to the melting point of the paraffin wax, and for a particular paraffin wax, the solubility decreases with increasing density of the solvent. Benzene, of 0.677 density, dissolves about ten times as much paraffin wax as does machine oil, of 0.908 density. The solubility of paraffin wax in various organic solvents is as shown in Figure 2.3.

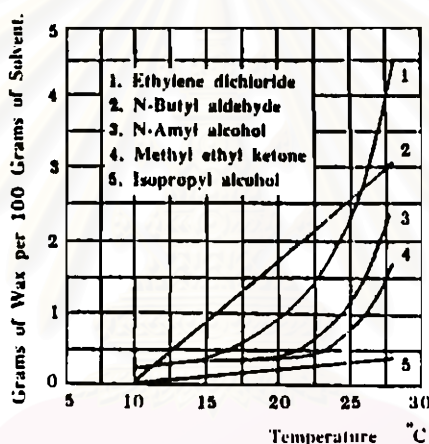


Figure 2.3 Temperature-solubility curves for paraffin wax in various organic solvents

The solubility of the paraffins increases more rapidly at higher temperature, a given lowering of temperature will cause the deposition of more paraffin wax at a high temperature than at a low temperature. The difference between the temperature at which paraffins first separate when a solution is cooled and the solidifying point of the paraffins varies inversely with the temperature of deposition, that is, the lower the concentration of the solution.

The solubility of paraffin wax in petroleum solvent is as shown in Figure 2.4. The chart shows that 100 ml. of a distillate, boiling at 190 °C, will dissolve 5 g. of paraffin wax when the melting point of the wax is 60 °C and the temperature of the solution is 23 °C.

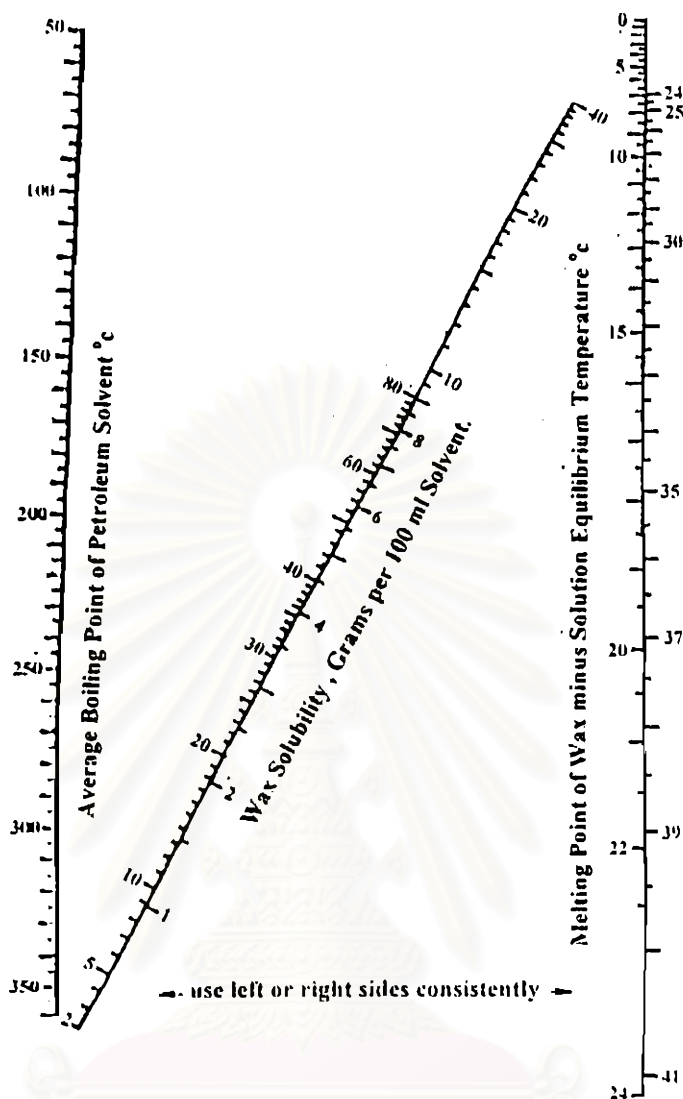


Figure 2.4 Solubility of paraffin wax in petroleum solvents.

The melting point of wax has a profound effect on its solubility in any given solvent. The higher melting waxes are less soluble than those of lower melting point. [6]

2.5 Wax Crystal

It has also been observed that paraffin wax crystallizes in both plates and needles, depending on the conditions of crystallization. One theory explained this as being due to differences in viscosity of the medium and also to the rate of cooling. This explanation discounted the idea that differences in composition had any bearing on the type of crystals formed. Buchler and Graves attributed the differences in the crystal system entirely to the presence of the impurity, which they called "soft wax". It is now generally recognized that the rate of cooling affects merely the size of the crystals formed and not

their type. Storage of wax that contains small crystals may result in the growth of larger crystals, but it can never cause a change in their type. This can be accomplished only by removing from the wax, or adding to it, an impurity which is capable of impressing its form on the basic type. It was concluded that the plate-type crystals represent straight-chain hydrocarbons and constitute the basic fraction of paraffin waxes. The needle malcrystalline types of crystals were probably the "soft wax," of Buchler and Graves, and these were assumed to be branched chain hydrocarbons. Microcrystalline waxes are composed largely of these types, although high-melting paraffin waxes will sometimes be found to contain small amounts of needles, but the crystals are of extremely small or microscopic size. [6] Types of wax crystals are shown in Figure 2.5.

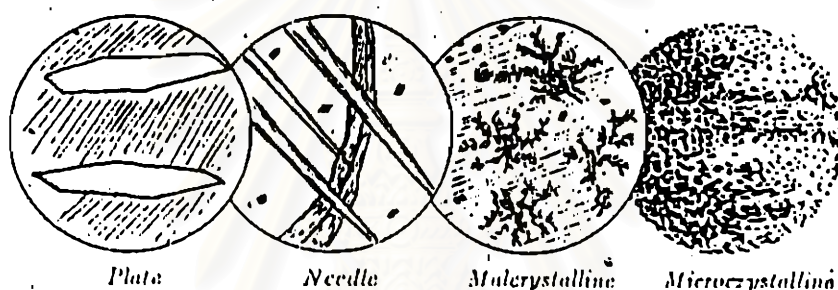


Figure 2.5 Types of wax crystals [7]

Needle type waxes are much more soluble in various solvents than plate-type waxes of the same molecular weight, the malcrystalline type was intermediate between the two. For waxes of the same melting point, regardless of type, have about the same degree of solubility. Mixtures of the plate, needle and malcrystalline types, each having the same melting point, were prepared and their behavior in crystallization was noted. It was found that the needle type was strong enough to impress its form on the plates if both types were allowed to crystallize simultaneously from the same solution. However, if crystallization was such that the needle type was kept in solution, either by high temperature or by excess of solvent, the plate type formed its characteristic crystals.

Similar work showed that the malcrystalline wax is even more powerful than the needle type in impressing its form on plates and on mixtures of plates and needles. Thus, any blends with the malcrystalline type will yield malcrystalline formations, unless this impurity is kept from the sphere of activity by higher solubility.

One practical utilization of these differences in crystallization is found in the manufacture of paraffin wax by the sweating process. It is well known that a wax

distillate with good pressing characteristics contains plate-type crystals, and that a slack wax with good sweating characteristics will crystallize as large interlacing needles. [6]

2.6 Characterization of Waxes

Petroleum wax is a mixture of many hydrocarbons, each of carbon number contains many type of structures. The evaluation was carried out using the chemical method, differential scanning calorimetry (DSC), mass spectrometry and gas chromatography. The chemical method is based on the reaction of non-normal paraffins with antimony pentachloride. In carbon tetrachloride solution the reacted hydrocarbons form an insoluble tarlike sludge so as to leave a clear phase of the normals and excess antimony chloride. The chloride is removed by extraction with 8N HCl and the normal paraffins are measured from the specific gravity of the carbon tetrachloride solution. This method has been successfully applied in the C_{16} - C_{36} range. Normal paraffins above C_{36} dissolve in carbon tetrachloride to a much lesser degree so that an alternative method must be used. [8]

Gas chromatography determined the carbon number distribution and concentration of normal and non-normal paraffins. When waxes containing n-paraffins (C_8 - C_{40}) are charged to a temperature programmed GC packed column of a suitable substrate, the normal paraffins emerge as symmetrical resolved peaks. If compounds others than n-paraffins are present, these will appear as intermediate peaks and also as a broad background, as shown in Figure 2.6.

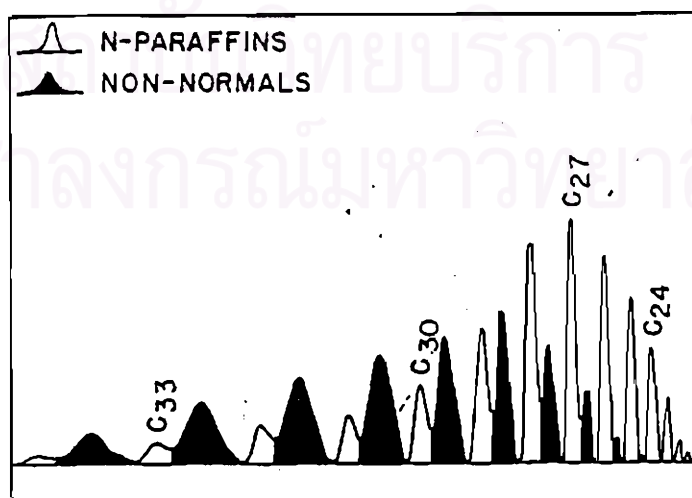


Figure 2.6 Chromatogram of GC packed column

A temperature programmed chromatograph and a column of microcrystalline wax bottoms on microbeads was prepared with chemical and mass spectrometric analyses. Individual n-paraffins compared favorably with the mass spectrometer although there appeared to be a tendency for GC to give high values for lower carbon numbered hydrocarbons and low results in the higher molecular weight range. [8]

The standard test method for analysis of petroleum waxes by GC, following ASTM D 5442-93, covers the quantitative determination of the carbon number distribution in the range from n-C₁₇ through n-C₄₄, as shown in Figure 2.7.

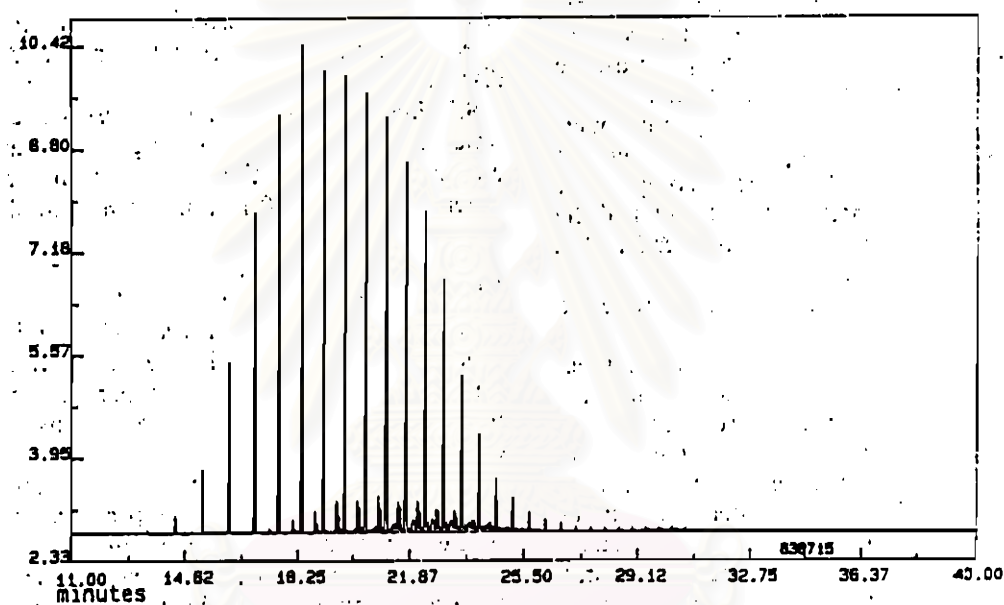


Figure 2.7 GC chromatogram of wax analysis following ASTM D 5442-93

In addition, the content of normal and non-normal hydrocarbons for each carbon number is also determined. A WCOT column with a stationary phase coating of methyl siloxane or 5% phenyl methyl siloxane have been successfully used. Waxes with a carbon number above n-C₄₄ is determined by difference from 100 mass percentage and reported as C₄₅⁺. [9]

Recent advances in column technology have extended the upper working temperatures of capillary columns to nearly 500°C. A gas chromatograph containing an injector and detector system compatible with oven temperature of 500°C, with programmable injector. A gas chromatographic containing a programmable injector and high temperature FID, system compatible with oven temperature of 500°C, was employed to screen a wax residue obtained from a petroleum refinery. [10] The GC

chromatogram of wax which analyzed by High Temperature GC (HT GC) is shown in Figure 2.8.

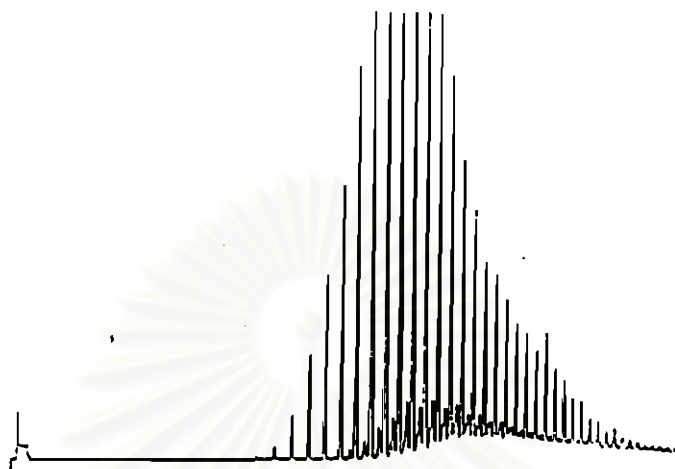


Figure 2.8 Chromatogram of wax analysis by HT GC

2.7 Previous Works Concerned

As mentioned previously, paraffin wax is derived from the wax-distillate fraction of crude petroleum and is separated from other lower-melting waxes lost in foots oil and sweater oil. In addition, higher-melting waxes, which are sold as microcrystalline or petrolatum waxes, are derived from heavier lubricating-oil fractions or tank bottom sludge of crude oils. The microcrystalline waxes offered in the market are often designated by their method of preparation and physical properties. For example, the name petrolatum wax applies to a microcrystalline wax refined from petrolatum stock or the microcrystalline wax in the petrolatum stock can be separated by recrystallizations and settling from naphtha solution at reduced temperatures.

2.7.1 Production of Microcrystalline Waxes

Agrawal, K.M., et al, [11] studied about a production of microcrystalline waxes from crude oil tank sludges. In oil fields and refineries during the storage of crude oil, some solid components along with water, residual oil, asphaltenes etc. settle down at the bottom of the storage tanks. These deposits commonly called as "Tank bottom sludges" are quite rich in microcrystalline waxes. An improved technology considered of feed preparation by acid-clay treatment, additional recovery of wax from clay and solvent

treatment for production of microcrystalline wax (m.p. 95-96 °C) from tank bottom sludges.

Bednarski, O., et al, [12] studied about a manufacture of petrolatum. Petrolatum is prepared by melting mixture of 65-92 wt.% paraffin slack wax and 10-35 wt.% hydrocarbon oil (obtained from a selectively refined vacuum distillation b.p. 360-560 °C from a sulfurous paraffinic-asphaltic petroleum) at 70-135 °C and subsequent adsorption refining by using 10-35 wt.% activated earth and ≤ 5 wt.% activated carbon at 100-135 °C. Optionally, low-molecular weight polyethylene is added to the oil-slack wax mixture. The resulting product is suitable for corrosion protection of metal parts (e.g., machinery, engines) during storage and for cosmetics and pharmaceuticals after high refining. The resulting white odorless product had prop point of 47-48 °C and contained 8-12 wt.% aromatic hydrocarbons.

Moskal, M., et al, [13] studied about a manufacture of microcrystalline waxes. Microcrystalline waxes (drop point 60-85 °C) are prepared from slack wax resulting from solvent dewaxing of deasphalted heavy fractions of paraffinic or paraffinic-asphaltic petroleum. The slack wax is deoiled by using solvents at 10-35 °C and refined by adding 5-20 wt.% bleaching clay at 110-115 °C. Optionally, the slack wax is mixed with a slack wax resulting from solvent dewaxing of an oil fraction (480-570 °C) at 100 °C, and refined by using the bleaching clay.

Bahl, J.S., et al, [14] studied about a FDA grade microcrystalline waxes through bauxite percolation alone. Finishing of microcrystalline wax using bauxite percolation to obtain food grade quality product with acceptable color and stability has been studied. Deoiled microcrystalline wax percolated over an activated bauxite at a temperature of 110-130 °C and flow rate 0.2-0.7 bbl/ton-h has been found to be comparable in quality requirements.

2.7.2 Fractionation of Waxes

Katayama, Y. [15] studied about a separation of waxes by solvent extraction. Petroleum paraffin waxes or oligomeric polyolefin waxes, produced in the Ziegler-catalyzed polymerizations, are separated into fractions with different melting point by extraction with solvents at a temperature lower than the melting point of the waxes and evaporation. Thus, extracting polyolefin waxes (m.p. 86 °C, average C no. 48.1) with

toluene at 10, 20, 30, 40 and 50 °C, respectively, gave fractions with m.p. 17.1, 27.5, 50.3, 58.6 and 73.3 °C and having average C no. 17.9, 22.0, 24.7, 29.2 and 34.3 respectively.

Cadenhouse-Beaty, P.J. and De Beer, S.W. [16] studied about a process for the purification and fractionation of petroleum wax. Oil containing wax feed material, e.g., slack wax, is de-oiled by dissolving the wax in a solvent at a first temperature, cooling the solution to a temperature below the first temperature to induce separation of the solution into a solid wax fraction and a liquid fraction, and centrifugally separating the two fractions.

Moskal, M. and Piecuch, J. [17] studied about a fractionation of mixture of solid petroleum hydrocarbons. Fractionation of mixtures of petroleum hydrocarbons crystallizing from oil fractions b.p. 280-560 °C and from deasphalted residual oil fractions b.p. 560-620 °C is done in deoiling chambers at temperature higher by 2-3 °C than the solidification temperature of the required fractions. The procedure is suitable for production of hydrocarbon waxes with a solidification temperature of 45-82 °C. The products are suitable for manufacturing of cosmetics, pharmaceuticals, and paper.

Jone, R.L. et al. [18] studied about a fractionation process for petroleum wax. Heavy intermediate petroleum wax is separated into two fractions in a wiped film evaporator to provide a lower boiling fraction of narrow melting range particularly suitable for use in hot melt adhesive formulations.

2.7.3 Wax Analysis

Zhac, T., et al. [19] determined the contents of normal and isomeric paraffins and their carbon number distributions in paraffin wax and microcrystalline wax using high temperature GC with on-column injector was reported. The total contents of n- and i-paraffins under each carbon number are obtained by now base integral model, and the contents of n-paraffin under each carbon number. The results were compared with that obtained by the method of molecular sieve adsorption and they showed a good agreement with each other. The method is simple, fast and accurate and is widely applicable.