Chapter

Introductory Chapter: Petroleum Paraffins

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1. Introductory

Waxes separated from petroleum are defined as the waxes present naturally in various fractions of crude petroleum [1]. Petroleum waxes are complex mixtures of hydrocarbons, amongst which are n-paraffin, branched chain paraffins and cyclo-paraffins in the range of C_{18}–C_{70} [2–4]. The quality and quantity of waxes manufactured from crude oils depend on the crude source and the degree of refining to which it has been subjected prior to wax separation [5, 6].

Paraffin waxes constitute the major bulk of such waxes, the other two types; produced in comparative quantities; also command a good market because of their certain specific end uses [2]. The paraffin waxes are solid hydrocarbons at room temperature.

Slack wax is a refinery term for the crude paraffin wax separated from the solvent dewaxing of base stocks. Slack wax contains varying amounts of oil (ranging from 20 to 50 wt.%) and must be removed to produce hard or finished waxes [1, 7]. If the slack wax separated from residual oil fractions, the oil-bearing slack is frequently called petrolatum [8].

Petrolatum is a general name applied to a slightly oiled crude microcrystalline wax. It is semi-solid, jelly-like materials. Petrolatum is obtained from a certain type of heavy petroleum distillates or residues.

Ozokerite wax is naturally occurring mineral wax. It is also a microcrystalline wax. Ceresin is a microcrystalline wax; it is the name formerly given to the hard white wax obtained from fully refined ozokerite. Petroleum ceresin is a similar microcrystalline wax but separated from petroleum. Ceresin and petroleum ceresins appear to have the same composition, structure, physical and chemical properties [1].

1.1 Composition of petroleum waxes

Petroleum waxes are substance, which is solid at normal temperatures. Paraffin and microcrystalline waxes in their pure form consist only solid saturated hydrocarbons. Petrolatum, in contrast to the other two waxes, contains both solid and liquid hydrocarbons. Petrolatum is semi-solid at normal temperatures and is quite soft as compared to the other two waxes.

Paraffin wax is a solid and crystalline mixture of hydrocarbons; it is usually obtained in the form of large crystals. It consists generally of normal paraffin ranging from C_{16} to C_{30} and may be higher. Proportions of slightly branched chain paraffin ranging from C_{18} to C_{36} and naphthenes; especially alkyl-substituted derivatives of cyclopentane and cyclohexane; are also present [1, 5, 8–10].

The average molecular weight of these paraffin waxes is about 360–420 [9, 11]. A paraffin wax melting at 53.5°C showed a space lattice having C—C bond length of 1.52°A, a C—C—C bond angle of 110°A, a C—H bond length of 1.17°A and an H—C—H bond angle of 105°A [12].

Microcrystalline waxes are obtained from the vacuum residue. The source for the production of microcrystalline wax is petrolatum or bright stock [13].

Microcrystalline waxes consist of highly branched chain paraffin; in contrast to the macrocrystalline; cycloparaffins and small amounts of n-paraffins and alkylated aromatics [1, 5, 9]. The actual chain length of the n-alkanes is approximately C_{34}–C_{50}. Long-chain, branched iso-alkanes predominantly contain chain lengths up to C_{70} [13].

The branched-chain structures of the composition C_nH_{2n+2} are found. Branched mono-methyl alkane, 2-methyl alkanes being found. As the position of the methyl group moves farther from the end of the chain, the amount of the corresponding alkane becomes smaller. The branched chains in the microcrystalline waxes are presented at random along the carbon chain, meanwhile in paraffin wax, they are located at the end of the chain [14].

The cyclo-alkanes, however, consist mainly of monocyclic systems. Monocyclopentyl, monocyclohexyl, dicyclohexyl paraffin and polycyclo paraffin are also found. Some microcrystalline waxes are mainly composed of multiple-branched isoparaffins and monocycloparaffins [1]. Moreover, non-hydrogenated micro waxes also mainly contain mono-cyclic and heterocyclic aromatic compounds [13].

Microcrystalline waxes have higher molecular weights (600–800), densities and refractive indices than paraffin waxes [1, 5, 6, 9].

1.2 Properties of petroleum waxes

1.2.1 Physical properties

Almost all, the physical properties of petroleum waxes are affected by the length of hydrocarbon chain, distribution of their individual components and degree of branching [10, 15].

Paraffin waxes are composed of 40–90 wt.% normal paraffins of about 22–30 carbon atoms and possibly higher, accordingly, they differ very little in physical and chemical properties. The remainder is C_{18}–C_{36} isoalkanes and cycloalkanes [5, 16]. Straight chain alkanes in the range from 20 up to 36 carbon atoms show transition points in the solid phase. Thus two modifications, stable at different temperatures and different crystal habits, are known [1].

Microcrystalline waxes contain substantial proportions of highly branched or cyclic hydrocarbons in the range from 30 to 75 carbon atoms [5, 6, 17].

Paraffin waxes, relatively simple mixtures, usually have a narrow melting range and are generally lower in melting point than microcrystalline waxes. They usually melt between 46 and 68°C. The melting point of paraffin waxes increases in parallel with molecular weight. The branching of the carbon chain, at identical molecular weights, results in a decrease in the melting point. Paraffin waxes can be classified according to the melting point to soft (lower m.p.) and hard (higher m.p.) paraffin waxes.

Microcrystalline waxes are more complicated so it melts over a much wider temperature range. They usually melt between 60–93°C and 38–60°C, respectively [6, 9, 10].

Oil content is a fingerprint of the quality of the wax. The method of determination depends upon the differential solubility of oil and wax in a given solvent.

Paraffin wax, microcrystalline wax and petrolatum have a different degree of affinity for oil content. Paraffin wax has little affinity for oil content. It may be taken as a degree of refinement. Fully refined wax usually has an oil content of <0.5%.

Microcrystalline waxes have a higher affinity for oil than paraffin waxes because of their smaller crystal structure. The oil content of microcrystalline wax is 1–4 wt.%, depending on the grade of wax [9].

1.2.2 Mechanical properties

The hardness and crystallization behavior of macrocrystalline paraffin waxes are interfered distinctly by their distribution width, average chain length and n-alkane content [18].

Hardness is the resistance against the penetration of a body (needle, cone or plunger rod) under a defined load, this body is made of a harder material than the substance being tested. To measure the hardness of paraffin waxes, penetration tests are widely accepted. It is a common feature of strength and hardness tests that the test specimens are subjected to short-time stresses [10].

The penetration test is the most widespread technique for determining the hardness and the thermal sensitivity of petroleum waxes. Macrocrystalline waxes change to a greater extent with temperature than that of microcrystalline waxes. An increase in oil content results in an increase in penetration values of both macro- and microcrystalline waxes [1].

1.2.3 Food grade properties

These properties concern waxes and petrolatums for food grade. Their potential toxicity could be attributed to aromatic residues. The latter are characterized directly by using UV spectra in the spectral zone corresponding to aromatics.

Each country has adopted its own code governing waxes, which come in contact with food and non-food grade [19, 20].

1.3 Crystal structure of petroleum waxes

The class of organic crystals represents a broad range of geometries, including needles, plates, cubes, rods, prisms, pentagons, octagons, hexagons, rhomboids and pyramids. Each of these forms results from crystallization from a solution. The geometry of the crystals formed is determined by the solute/solvent interaction and the physical conditions of the system (e.g., temperature, pressure and mechanical mixing).

One interesting characteristic of crystals is that they can form a variety of shapes, which are due to the environmental conditions under which they form. They can be large or small, extend long distances or short, be well-defined or diffuse; in short, they can display an impressive array of forms. It is this variety of form upon which crystal modifiers are intended to take advantage [21].

All petroleum waxes are crystalline in some degree and it is possible to classify waxes in terms of the type of crystals formed, when the wax crystallizes out of solution.

1.3.1 Macrocrystalline waxes (paraffin waxes)

The paraffin crystals appear in three different forms: plates, needles and mal shapes; the latter are small size, undeveloped crystals, which often agglomerates. The conditions for the formation of these shapes have been studied by many researchers. They have come to the following conclusions:

1. The three crystal forms of paraffin waxes depend on both the conditions of the crystallization process and the chemical composition of the wax.

2. Plate crystals are obtained from lower boiling points paraffinic distillates, while the needle and mal-shaped crystals are obtained from the higher boiling points ones and from vacuum residues.

3. For a given molecular weight limit, the higher melting point constituents crystallize in plate type in which the crystals are hexagonal plate. The low-melting ones crystallize in needles while the medium-melting ones crystallize in mal shapes.

4. Normal paraffin crystallize in plates. Needle crystals contain both aliphatic and cyclic hydrocarbons, while mal-shaped crystals are characterized by their content of branched hydrocarbons.

5. Low-cooling rates during crystallization will result in large crystals for both plate and needle forms, while the crystal growth for mal-shaped crystals is very slight.

6. The solubility of paraffin in a solvent is inversely proportional to their melting points. In the presence of solvent, wax mixtures begin to crystallize at relatively low temperatures in the form of plates followed by mal-shaped crystals. However, the constituents crystallizing in needles are more soluble than those crystallizing in plates. Therefore, needles crystals will appear only at lower temperature and higher concentrations

7. Plate crystals can readily be transformed into needle and mal-shaped crystals. Under appropriate conditions, the needle crystals can be transformed into mal-shaped crystals [10].

Normal paraffin, C_{17}–C_{34}, may exist in three and possibly four crystal forms. Near the melting point, hexagonal crystals are the stable form. At somewhat lower temperatures, the odd-numbered from C_{19} to C_{29} are orthorhombic, even numbered ones from C_{18} to C_{26} is triclinic and those C_{28}–C_{36} is monoclinic [22, 23].

1.3.2 Microcrystalline waxes

Both n-paraffin and isoparaffins crystallize in needle forms; they differ in that the latter does so at all temperatures, while higher temperatures are required for the former. The needle form of the isoparaffins differs from that of ceresins or paraffin waxes containing ceresins, in that the crystals of former are large and loose, while those of the latter are extremely small and dense [14].

Microcrystalline waxes may contain substantial percentages up to 30% of paraffin which, when separated, crystallize well as high-melting macro crystalline or paraffin wax. The microcrystalline wax material interferes and imposes its crystallizing habit on the other material [16, 24].

Although the classification of petroleum waxes into macro crystalline and microcrystalline waxes on the basis of crystal size is valid to a great extent, there is no sharp line separating the two groups. Indeed, there is a large group of waxes that could fall in either classes and these waxes are called intermediate waxes, blended waxes, mal-crystalline waxes and semi-microcrystalline waxes. But semi-microcrystalline wax adopted [17].

1.4 Manufacture of petroleum waxes

The manufacture of petroleum waxes is closely related to the manufacture of lubricating oils. The raw paraffin distillates and residual oils contain wax and they are normally solid at ambient temperature. Removal of wax from these fractions is necessary to permit the manufacture of lubricating oil with a satisfactory low pour point. Manufacture of petroleum waxes includes the following technological processes:

- Production of slack waxes and petrolatums by dewaxing petroleum products.
- Refining of the wax products.
- Deoiling and fractional crystallization.
- Percolation process.
- Hydrofinishing process.
- Acid treatment.
- Adsorption process.

1.5 Applications of petroleum waxes

As the consumption of wax products in the world wax market increases; especially for food, pharmaceutical and cosmetic grades and specialty wax; the increase of profitability of wax production will lie on the improvement of blending and modification techniques for macro- and microcrystalline waxes as base materials as well as the development and applications of new wax products [25].

Petroleum waxes are based in a wide variety of applications. Some of its most important applications were used in industry such as, paper industry, household chemicals, cosmetics industry, dental industry, match industry, rubber industry, building constructions, electrical industry, inks industry and powder injection molding industry beside that of hydrogen production and energy storage applications [4, 10, 26–30].

2. Conclusion

Fractions of petroleum wax can be achieved to separate more than one type of paraffin wax such as macrocrystalline and microcrystalline waxes, the waxes characterization such as carbon number, hardness, crystal shape, composition and molecular weight depend on the condition of separating the wax, paraffin wax act like a joker in different industries such as inks, papers, cosmetics and ceramic fabricating using powder injection molding industry.

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