

## CHAPTER 2

### THEORETICAL CONSIDERATION

#### Waxes ( 1 )

Wax usually refers to a substance that is a plastic solid at ambient temperature and, on being subjected to moderately elevated temperatures, becomes a low viscosity liquid. Because it is plastic, wax usually deforms under pressure without the application of heat. The chemical composition of waxes is complex: they usually contain a broad variety of molecular weight species and reactive functional groups, although some classes of mineral and synthetic waxes are totally hydrocarbon compounds.

#### Classification of waxes

- A. Insect and animal waxes e.g., Beewax, Spermaceti
- B. Vegetable waxes e.g., Candelilla, Carnauba, Japan wax, Oiticury wax, Douglas - Fir Bark wax, Rice - Bran wax, Jojoba, Castor wax, Bayberry wax
- C. Mineral waxes e.g., Montan wax, Peat wax, Ozokerite and Ceresin wax, Petroleum wax
- D. Synthetic waxes e.g., Polyethylene wax, Fischer-Tropsch wax, Chemical Modified Hydrocarbon wax, Substituted Amide wax

## Petroleum waxes

Petroleum waxes, a term covering the wax-like materials derived from petroleum and related mineral oils ( e.g., shale oil ) are comprised essentially normal and branched-chain paraffins and solid-hydrocarbons of other saturated series ( 2 ) .

### Manufacture and classification of petroleum waxes ( 3 )

A schematic representation of the basic routes by which petroleum waxes are produced from crude oil is given in Fig . 2.1

These different routes by which separation is accomplished have given rise to three wax classifications namely, paraffin waxes, intermediate, and microcrystalline waxes.

Paraffin and intermediates are sometimes referred to collectively as 'distillate' waxes. Whilst serious and lengthy attempts have been made to define physical and chemical boundaries between these groups, none has succeeded.

#### A. Paraffin waxes

Paraffin waxes are mixture of saturated paraffinic hydrocarbons (alkanes), straight-chain or 'normal' alkanes being by far the major components of the mixtures, with varying proportions of paraffins having a degree of branching in their chains (iso-alkane) present, together with a small cycloalkane content .

The chain length of individual alkanes ranges from about 18 carbon atoms to about 45, the higher the proportion of iso-alkane likely to be present.

##### 1. Grades of paraffin wax ( 4 )

Paraffin wax is sold in various grades, with differ from one another chiefly in melting point. Generally, each grade covers a range of melting points of 2 ° C, for example 54-56 ° C. Melting points are given by either of two accepted standards: American melting point (AMP) and ASTM melting point, which is often called English melting point (EMP).

The most familiar types of paraffin wax on market are refined, and crude scale waxes.

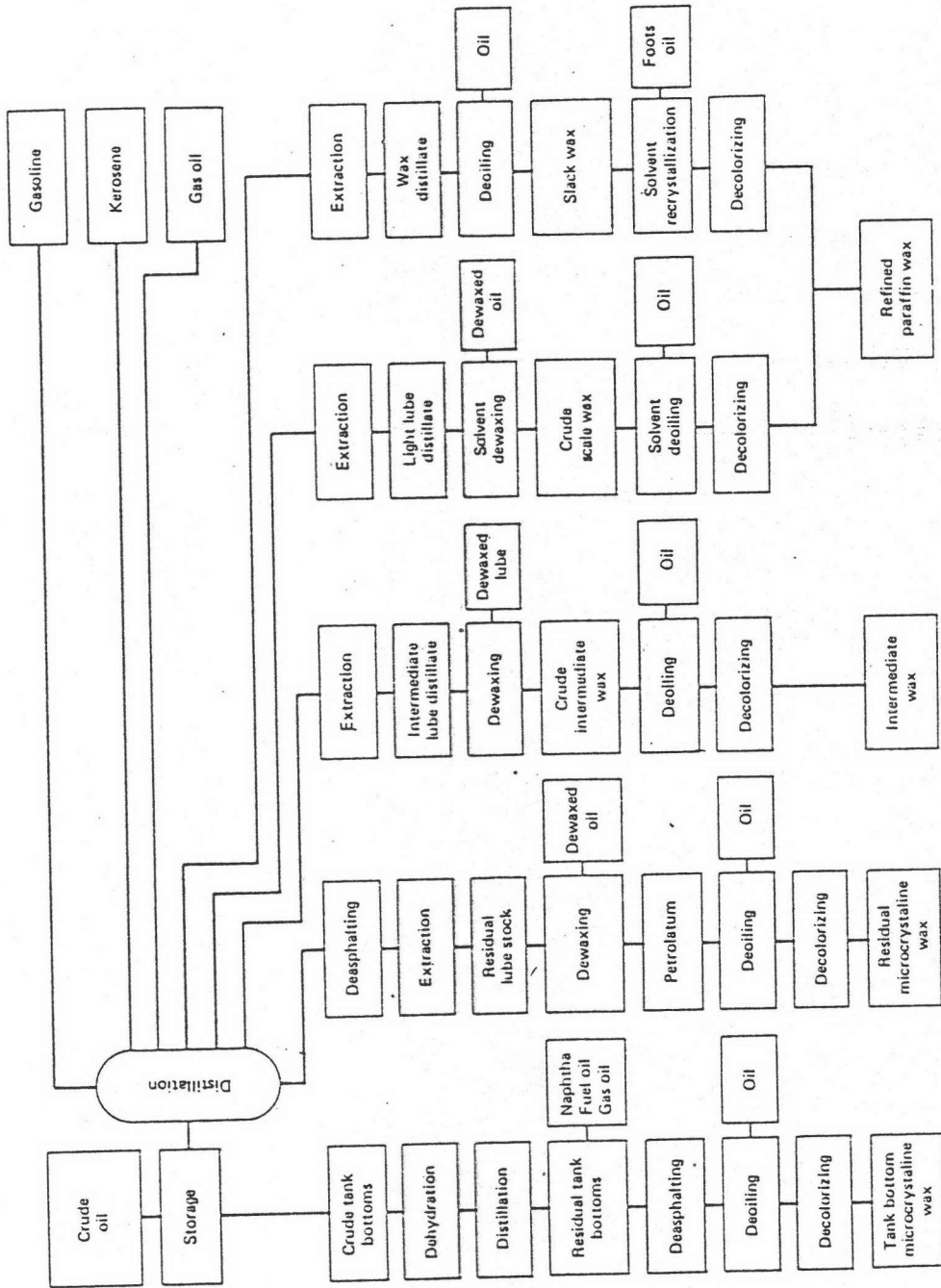


Figure 2.1 Refining of petroleum waxes. Courtesy of Petrolite Corporation.

a) Refined wax ( 5 )

Refined wax has a melting point range of 47-68 ° C, a color (Saybolt chromometer scale) +21 or lighter, and an oil content of 0.5 % or less. At ordinary temperatures, refined waxes are hard and frequently brittle, but when they become progressively softer and more plastic they finally melted to a thin clear liquid. The presence of small proportions of oil, due to insufficient refining, greatly affects certain properties. Such wax easily discolors when exposed to light. With as little as 0.5% oil content, the mechanical strength is much reduced and becomes mealy or is easily crushed to fine powder.

b) Crude scale wax

Crude scale wax has a melting point range of 47-57 ° C, a color darker than +21 on Saybolt chromometer scale, and an oil content of about 0.6-3%. It is not entirely stable in color even when bleached, nor it is not free from taste and odor ( 6 ).

The crude scale wax is sold in two forms: white and yellow. They are similar except for one step in refining procedure of bleaching the wax. Most of crude scale waxes sold in the market is the white type.

B. Intermediate waxes

Intermediate waxes are essentially hydrocarbon, with individual alkane chain lengths up to 60 carbon atoms. They have higher average molecular weights, with branch-chain components up to about 50 per cent of the whole.

The Intermediate waxes are not generally marketed as much paraffin and microcrystalline waxes .

C. Microcrystalline waxes

Microcrystalline waxes also are mixtures of saturated alkanes, but with a much greater preponderance of branched-chain or cyclo molecules. The carbon atom content per molecule can vary from the mid thirties to well over eighty. The average molecular weight is much higher in the case of the distillate waxes. The complex branched-chain structure prevents any degree of close packing and macrocrystalline, giving rise to the original name

of 'amorphous' waxes, and later, rather more accurately, to current nomenclature of 'microcrystalline' waxes.

The microcrystalline waxes in 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. Usually a sticky wax of about 68-77 °C melting point, and a penetrometer value of more than 25 is implied. The waxes that are much harder, more oil-free, of higher melting point ( 82-90 °C ), and which have a penetrometer value of less than 25, are known as petroleum ceresins.

1. Petrolatum group

a) Petroleum jelly. Petroleum jelly has been defined as petrolatum, soft and salve-like, consisting of certain petroleum solid in admixture with oil. The molecular weight is usually over 480, and the melting points, which in any case are very ill defined, range from about 35-85 °C. It contains considerable quantities of saturated hydrocarbons other than n- paraffins.

b) Petrolatum wax. Petrolatum wax or crude petrolatum wax, as it is also called, contains more than 10 per cent of oil; it is obtained from the acid-treated petrolatum, stock, containing a fairly high percentage of wax, by treatment with naphtha and centrifugation of solution to remove excess oil.

2. Petroleum ceresin group

a) Petroleum ceresin wax. This is also wax of fine crystalline structure, which vary in color from dark brown to white. Unlike the petrolatum waxes, it is hard and brittle, and this constitutes the main difference between this two groups. Petroleum ceresins have molecular weights ranging from about 450-1000 and melting points from 70-105 °C.

### Crystal structure

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

Paraffin wax crystallizes in large, well form distinct crystals of plate and needle type. Paraffin waxes were originally called crystalline but now the term macrocrystalline is used. Microcrystalline wax crystals, as the name implied, are small and instinct; they were originally called amorphous but the term microcrystalline is more appropriate.

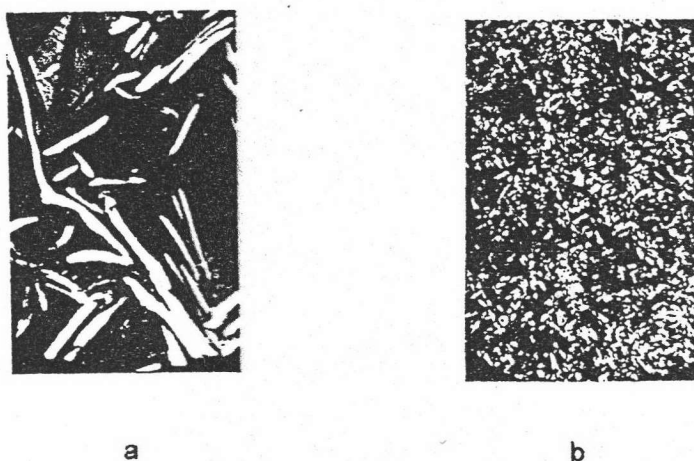


Figure. 2.2 Crystals of typical paraffin wax (a) compared with crystals of microcrystalline wax (b) under transmitted polarized light (50 x).

Although the division of waxes into paraffin (macrocrystalline) waxes and microcrystalline waxes on the basis of crystal size is valid to a great extent, there is no sharp line separating the paraffinic group from the microcrystalline group. Indeed there is a large group of waxes that could fall in either class and these waxes are sometimes referred to as semi-crystalline or semi-micro waxes.

A serious complication is found, however, in the fact that microcrystalline waxes can impress their own form and size on paraffin crystals, even when the percentages of microcrystalline wax in the mixture are too small to alter markedly other pertinent characteristics usually associated with paraffin wax. This illustrated by Fig. 2.3 ; using the same waxes shown in Fig. 2.2 only 5% of microcrystalline wax in paraffin results in crystals rather closely resembling those of microcrystalline wax itself. Classification by crystal size was therefore eliminated ( 7 ).

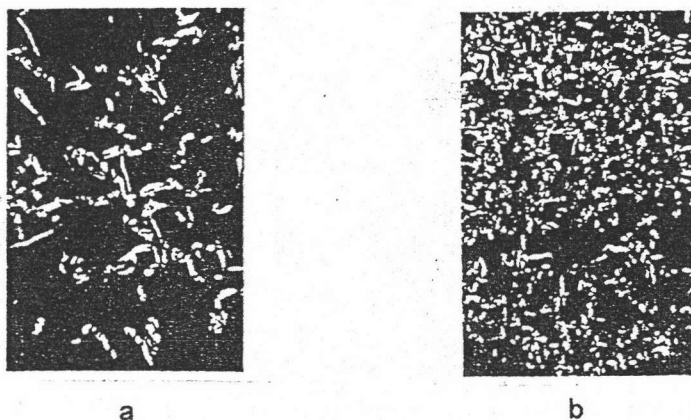


Figure 2.3 Blend of paraffin wax (99%) and microcrystalline wax (1%) (a) compared with blend of paraffin wax (95%) and microcrystalline wax (5%) (b) under transmitted polarized light (50 x).

### Production of petroleum waxes

#### A. Distillate or paraffin waxes

Since the bulk of paraffin wax present in crude oil boils over the same range as lube oil distillates, separation by distillation is not possible. Consequently the bulk of lube oil dewaxing is carried out by mean of crystallization from a suitable solvent system. Mixtures of toluene and methyl ethyl ketone are generally used, although other mixtures and some single systems such as methyl iso-butyl ketone, methyl n-butyl ketone, and propane are sometimes used.

The waxy oil feed is mixed with the appropriate solvent system and heated to a temperature sufficient to bring about complete solution of the wax. Cooling this solution causes the wax to separate, and when the mixture has reached the chosen low temperature it is passed to rotary vacuum filters where the solid is separated from the liquid in the form of a thin cake. This is washed with chilled solvent and then removed from the drum by being blown off the filter screen by inert gas. The solvent-containing filter cake is then either retreated with further mixed solvent in process of 'de-oiling', or transferred to the 'slack wax' storage by way of steam strippers, which effect solvent stripping and recovery. The solvent-free slack wax is then stored for sale or further processing.

The slack wax thus produced is generally brown in color and has an oil content of between 5 and 25 per cent.

Alternative solvent systems employing high specific gravity chlorinated hydrocarbons (the 'SN' process and the 'Bari-Sol' process), which allow separation of slurry to be carried out by centrifuging rather than by vacuum filtration were used in the past, but these have been largely superseded by MEK-toluene process.

A more recently technique using mixed ketone solvents, but achieving chilling by incremental dilution with cold solvent, claims much improved efficiency with subsequent ease and lower cost of further de-oiling. This process called the Dilchill dewaxing process, was adopted at several refineries in the USA in the 1970s.

The dewaxing operation remove a relatively small proportion of wax components from a large proportion of oil to produce slack wax. The next stage, de-oiling, removes oil from a large amount of wax, to give waxes of low oil content and commercially acceptable specification. Two methods are currently in use:

1. Solvent de-oiling

This is much the most widely used method. The normal solvent system again is methyl ethyl ketone-toluene ( 8 - 10 ).



Others solvents used for deoiling such as methyl ethyl ketone ( 11-13 ), ethylene dichloride ( 14 ), methyl isobutyl ketone ( 15-18 ), dimethyl formamide ( 19-20 ) etc. There are many solvents used for deoiling. N.V.AI' perovich et. al. evaluated the solvent selectivity in dewaxing and deoiling and found that the efficiency in removing paraffin wax by crystallization was determined by the solvency and selectivity of the solvents ( 21 ).

As in dewaxing, the feed is diluted with solvent in suitable ratio and dissolved by heating. On being cooled, as before, to predetermined temperatures, the wax separates and is filtered. Cooling further to lower temperatures gives further wax separation, the average molecular weight and melting point of this and any subsequent fractions being lower.

Each wax cake thus produced is remixed with further cold solvent, filtered and solvent washed, the solvent at all times being separated and recycled.

The ultimate oil content of fully refined paraffin wax should be less than 0.5 per cent.

## 2. De-oiling by sweating ( 22-25 )

The feedstock chosen as suitable for a sweating process is first melted to produce a homogeneous liquid, then cooled under conditions calculated to give a wax cake of coarse crystal structure. The temperature of cake is raised slowly in controlled manner in equipment designed to allow liquid components to drain away while retaining the higher melting solid residue of the cake.

The process thus removes not only the liquid oil, but also reduces the content of the iso-paraffins, which are of lower melting point than the normal alkanes of corresponding molecular weight, and it thus achieves a measure of fractionation at the same time as de-oiling.

The structure of wax cake in sweating process must be coarsely crystalline otherwise the oil is retained by capillary forces. Slack waxes containing too high an iso-alkane content give a relatively fine crystalline structure, thus cannot be de-oiled by this method.

Sweating has largely been replaced by solvent process, but more recent developments suggest that the operation will continue in small unit of high efficiency and low running cost.

Another de-oiling process consists in emulsifying the molten wax in liquid which does not dissolve paraffin wax and then cooling. The wax then separates as a solid, relatively oil-free mass and can be centrifuged off, while the bulk of oil remains in emulsion (26). As Irwin et. al. de-oiled wax by apparatus for wax de-oiling that they designed ( 27 ).

#### B. Intermediate and Microcrystalline wax

Separation of these waxes from the intermediate lube distillate, the residual lube stock, and the tank bottom, follows an essentially similar series of solvent extraction steps as for the distillate waxes. It is not possible to refine either type by traditional sweating techniques, nor can the measured oil contents of the microcrystalline range be reduced to such low levels as is standard with the paraffin waxes.

A problem in de-oiling process of microcrystalline wax is filtration but it may be solved by adding polar modifiers ( 28 ), nonpolar modifiers ( 29 ), organometallic surfactants ( 30 ), or calcium alkyl phenolate ( 31 ).

The final stage of refining all types of petroleum waxes to remove odour, taste, and colour, and thus to purify the wax to a standard complying with the various regulations covering usage in, or in contact with foodstuffs, is referred to as 'finishing'.

A variety of processes is in current use, percolation through activated clay or bauxite still being used for all types of petroleum wax ( 32-34 ).

There are other decolorizing processes such as Arthur T. Polishuk : using alkanol and aromatic hydrocarbon ( 35 ), Joseph F Pauloson : decolorizing wax by dialysis ( 36 ) and Robert J. Convery : treating wax with zinc chloride ( 37 ).

A more modern and versatile finishing treatment is the technique of hydrogenation, known as hydrofinishing, where wax, in its final form or as slack wax, is treated with hydrogen in the presence of catalyst at high temperature and pressure. Various hydrofinishing processes employ different catalysts operating under different conditions, with pressure ranging from 10 through a typical 85 to 200 atmospheres, and temperatures from 200 to 400 °C. The process is one of the chemical saturation, with virtually complete sulphur removal, optimum conditions producing a white odourless wax meeting high purity standards, and requiring no further finishing treatments ( 38-50 ).

Paraffin waxes may also be treated by the so-called 'acid-earth' process where agitation of the molten wax with a few per cent of sulphuric acid is followed by separation of acid sludge, and a treatment with neutralizing lime and activated earth. This process is not possible for microcrystalline waxes, because of the difficulties in separation of the acid sludge produced, and is now not widely used. Almost all refineries have adopted hydrofinishing processes.

#### Compositions of petroleum waxes

##### A. Paraffin and Intermediate Waxes

The chemical composition of petroleum waxes, to which reference has already been made, has much become very clear in recent years.

The first attempts to elucidate the constitution of simpler distillate waxes were by combinations of distillation and repeated fractional crystallizations to effect separations of individual or groups of components, and give a superficial picture of their constitution.

A step further in distillate wax analysis, urea is capable of giving crystalline adducts with normal alkane, where the urea molecules form a hexagonal prism enclosing an internal channel in which the linear portion of the hydrocarbon can fit. However, iso-alkanes with short side chains will also be adducted, provided that the branches are near the ends of the chains.

The development of high-temperature mass spectrometry was a major step forward in unravelling the detailed structure of paraffin waxes, but undoubtedly the technique which has done most to elucidate the composition of the light and intermediate distillation waxes has been high-temperature gas-liquid chromatography (glc).

The use of liquid phases capable of operating to 400 ° C and above allows normal alkanes of up to 60 carbon atoms to be detected and quantified. By the use of pure internal standards in combination with a standard analytical run, the normal content of a distillate wax may be estimated, and information obtained on the non-normals distribution. The chromatographic analysis of paraffin waxes is now established as a routine operation and good precision.

Figures 2.4 to 2.6 are the glc traces obtained on three typical distillate waxes, showing the carbon distribution of the alkane components of the waxes. The small peaks immediately before the main normal alkane peaks are those of the 2-methyl alkanes, whilst the unresolved area below the trace is proportional to the amount of more heavily branched non-normal hydrocarbons present in the wax.

The actual branched or 'non-normal' content of petroleum waxes can be determined quantitatively by adsorption of the normal alkanes using type 5 A Linde molecular sieve.

This synthetic zeolite is crystalline calcium alumino silicate having a crystal pore diameter of 5 ångströms ( Å ) into which straight-chain hydrocarbons molecules with critical diameter of less than 5 Å are adsorbed. Branched-chain hydrocarbons are not adsorbed. Thus there is provided the basic for a highly selective and quantitative separation technique. When used in conjunction with glc to monitor the progress of several extractions which may be necessary in the case of the higher non-normal content intermediates, the sieve analysis-glc technique provides detailed quantitative information on wax composition.

The figures recorded for non-normal contents of a wax are always higher than for those recorded on the same wax by urea adduction, for reasons stated earlier.

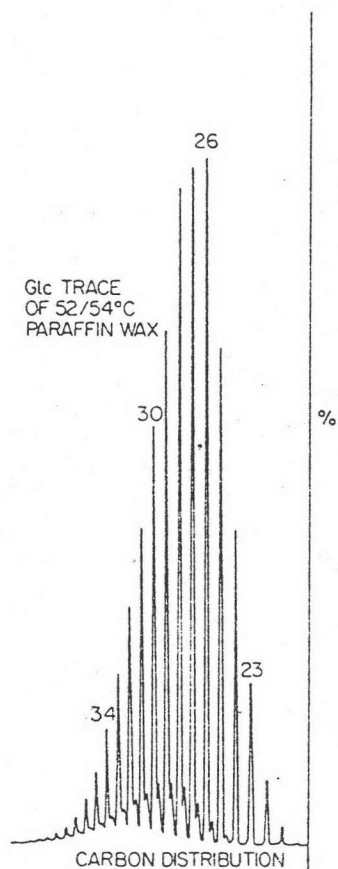


Figure 2.4 Carbon distribution of paraffin wax ( mp. 52-54 ° C ).

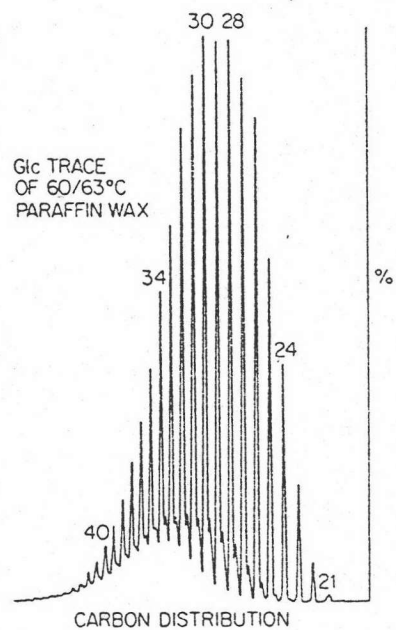


Figure 2.5 Carbon distribution of paraffin wax ( mp. 60-63 ° C ).

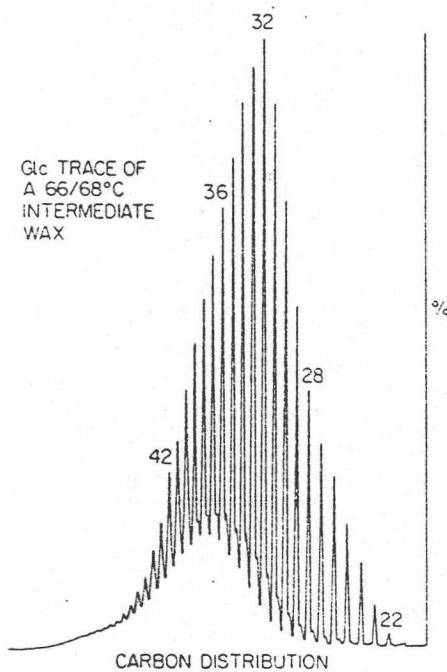


Figure 2.6 Carbon distribution paraffin wax ( mp. 66-68 ° C ).

The thermoanalytical technique of Differential Scanning Calorimetry (DSC) is another aid to the investigation of petroleum wax properties and composition, providing a highly characteristic record of melting and crystallization behaviour of a wax, measuring directly energies associated with solid-liquid transitions ( 51 ).

#### B. Residual and Microcrystalline Waxes

Knowledge of the composition of microcrystalline waxes is much less advanced than for distillate waxes, because the high molecular weight of this type of wax makes it less susceptible to analysis. In particular, whilst the vast number of isomer of any given carbon number renders resolution by glc impossible, and the determination of the small normal content difficult, the excessive temperatures and times needed to clear the columns of retained hydrocarbon makes the attempt highly undesirable.

Some of most detailed analytical work has been carried out on Middle East and Venezuelan crudes, and confirms that the microcrystalline waxes from these materials are composed mainly of multiple-branched iso-paraffins and monocycloparaffins. The analytical separations in this work were base on pyrolysis, hydrogenation, and gas-liquid chromatography.

#### C. Petrolatum

The mixture of microcrystalline waxes and higher molecular weight oil produced by dewaxing a de-asphalted vacuum distillation residue from a crude oil is usually termed a 'residual slack wax' , but equally , it may be thought of as a crude petrolatum.

Refining without further de-oiling, by using the same techniques as for microcrystalline waxes can produce a Pharmacopoeia grade petrolatum or petroleum jelly.

## Physical properties of petroleum waxes

### A. Distillate Waxes

Since straight-chain alkanes are the major component of these waxes, it is natural that many detailed studies on pure normal alkanes which have been made should be used as reference criteria in the investigations into the physical properties of the waxes themselves.

The straight-chain alkanes in the range from 20 to 36 carbon atoms are known to show transition points in the solid phase ( 52 ). This means that at least two modifications are known, stable at different temperatures and with different crystal habits, and numerous workers have investigated these crystalline forms of the pure or purified alkanes ( 53,54 ).

Mazee ( 55 ) investigated binary mixtures of alkanes of adjoining or near adjoining carbon numbers, and found a continuous series of mixed crystals, the equilibria between the two solid phases showing pronounced maxima in the transition range. However, if the alkanes differ by many units in chain length no mixed crystals are formed, but a normal eutectic is observed, and, as expected, in paraffin waxes the same phenomenon is recorded.

This endothermic transition from the onset of the solid-solid transition to the completion of melting can be followed easily and in a quantifiable manner by differential scanning calorimetry, and rather more laboriously by plotting the cooling curve, illustrated schematically in Fig. 2.7.

The wax is liquid at A, and as the temperature falls through the plateau melting point B-C (the first-order transition point), the material changes from liquid to a solid having a hexagonal crystalline structure. As the temperature continues to fall the crystalline structure changes exothermally from hexagonal to orthorhombic at D, the second order transition point.

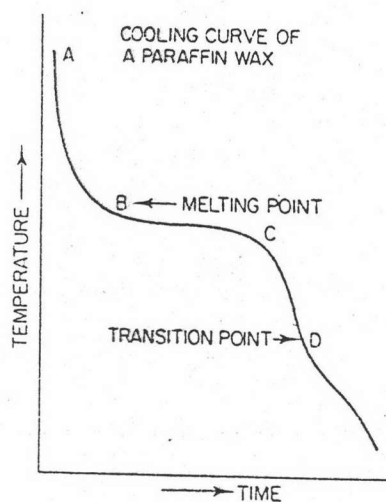


Figure 2.7 Cooling curve of paraffin wax.

The DSC scan of the same type of paraffin wax produces a more easily recognized second order transition, together with a sharp melting peak.

These phenomena are readily observed with the lower melting point waxes previously referred to, i.e. where the mass of carbon chains are of low carbon number, but as the average chain length increases, the temperature range in which the hexagonal lattice is stable becomes narrower, the second order transition moving nearer and nearer to the melting point.

With a substantial proportion of 30 and more carbon atoms per molecule present in the wax the hexagonal lattice is not clearly defined, and with increasing average chain length there is a direct crystallization from the liquid into the orthorhombic, and the transition is not seen ( 56 ). This can be seen in Fig. 2.8 and 2.9.

Figure 2.8 shows the DSC scans recorded on four low melting point paraffin waxes produced from the same light lube slack wax, the same weight of wax being used in each case, the scan zero being displaced vertically for each of comparison. It will be noted that the lowest melting point wax shows two solid-solid transition.



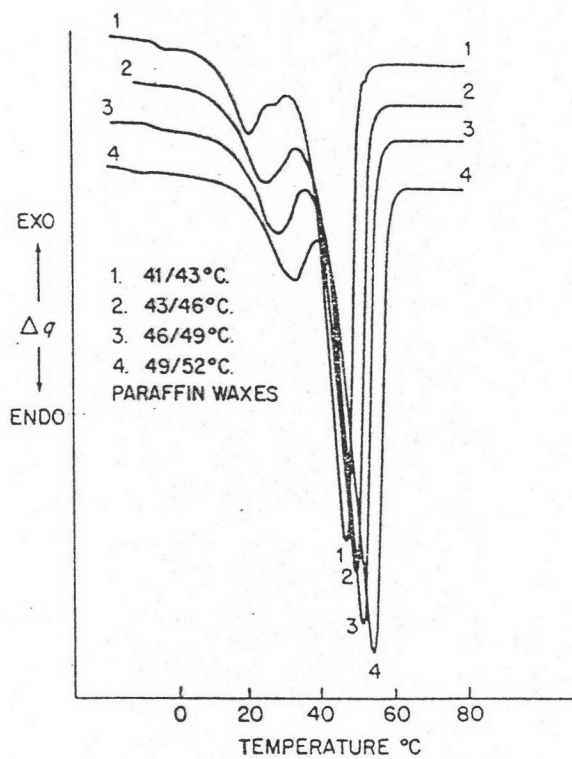


Figure 2.8 DSC of paraffin waxes ( mp. 41-52 ° C ).

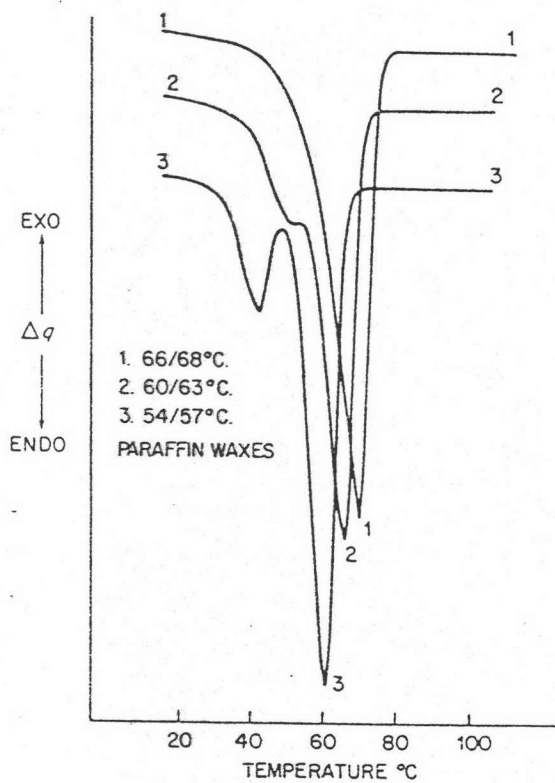


Figure 2.9 DSC of paraffin waxes ( mp.57-68 ° C ).

Figure 2.9, the wax with melting point of 54-57 ° C has the solid-solid transition, while the wax melting point of 60-63 ° C has the small solid-solid transition. The wax with melting point of 66-68 ° C shows no the solid-solid transition because increasing average chain length and melting point cause the disappearance of the solid-solid transition.

#### B. Microcrystalline waxes

Since wax with carbon more than 36 atoms even normal alkanes crystallize directly from the melt into the orthorhombic state, it is to be expected that microcrystalline waxes, containing much higher molecular weight hydrocarbons with high non-normal contents, will fail to show second-order transition points. Furthermore, the non-normal content hinders the formation and growth of orthorhombic crystals so that under a microscope the crystal structure of such a wax is extremely fine, generally appearing needle-like with many mal-crystalline masses. As the amount of softer amorphous highly branched hydrocarbon increases with increasing average molecular weight of microwax, so the melting point decreases and softness, viscosity, and ductility increase.

Several of the valuable analytical techniques applied to distillate waxes, such as glc and mass spectrometry, are unable to resolve the complexities of the higher microcrystalline waxes, but both of gel permeation chromatography (gpc) ( 57 ), and, to a greater extent, DSC, continue to provide useful information and records of the melting point distribution of the component hydrocarbons, and thus the overall performance characteristics of the specific microcrystalline wax.

Hardness, rigidity, brittleness, and low viscosity in a petroleum wax are associated primarily with its degree of crystallinity. Thus a microcrystalline wax with an appreciable content of normal alkanes of the highest molecular weight is hard, of medium viscosity, and of high melting point. Those with much higher non-normal contents are more viscous and softer, whilst those consisting almost wholly of iso-alkanes and cyclo-alkanes have appreciable flexibility, ductility, adhesiveness, and the higher viscosity of any of the petroleum waxes.

The melting point of all petroleum waxes is thus governed by the proportions and molecular weights of the various normal alkanes present. Melting point increases with the average molecular weight of normal alkanes present, and side-chain branching tends to lower the overall melting point.

#### Methods of testing petroleum waxes

Many routine methods exist for testing wax properties and assessing petroleum waxes. Most of these methods are more suitable for checking the constant quality of wax output in refineries, or on receipt at a user, than for true identification or characterization purposes. Several of these methods are equally appreciable to blended product, i.e. where two or more waxes of different properties, or where additive such as polymer, resin, oils, etc. are mixed in wax, but care should be taken to ensure that the particular test method is then really appropriate.

#### A. The most commonly used tests are as follows :

##### 1. Melting point and setting point

##### a) IP 55, ASTM D 87, ISO 3841

Molten wax is allowed to cool in a specified apparatus while the temperature is recorded at frequent intervals, the point at which the temperature remains within a range of  $0.1^{\circ}\text{C}$  for one minute being taken as setting point. This is the 'cooling curve' method as depicted in Fig. 2.7. This method is not suitable for microcrystalline or intermediate waxes, or blends of paraffin waxes with these or any additive.

##### b) IP 76, ASTM D 938, ISO 2207

The congealing point of petroleum wax or petrolatum is determined by applying a drop of molten wax to a thermometer bulb, and noting the temperature at which it congeals when the thermometer is rotated under standard cooling conditions. This method is suitable for all waxes and blends. Some anomalous results can be obtained when materials of widely differing viscosities and melting or setting points are mixed.

c) IP 33, ASTM D 127, ISO 6244

The drop melting point of wax or petrolatum is determined by recording the temperature at which a drop of the sample falls from the bulb of a thermometer when heated under standard conditions. Anomalous results are obtained on blends when materials of widely differing melting or setting points or viscosities are mixed.

2. Viscosity ( IP 71, ASTM D 445, ISO 3140 )

The viscosity of molten petroleum wax is a measure of its normal-non-normal composition, and is important in many packaging applications. The classical U-tube kinematic viscosity method is described by this method, and is suitable for all waxes and low-viscosity blends.

For much higher viscosity blends of petroleum waxes with polymeric and resinous additives, some mechanical rotational method such as described by ASTM D 2669 is desirable.

3. Oil content ( IP 158, ASTM D 721, ISO 2908 )

This standard test method is based on dissolving the oil-containing wax in a specified solvent and cooling to an arbitrarily chosen low temperature at which the insoluble material is defined as ' wax ', and the soluble portion as ' oil '. Thus ' oil ' is defined only by method used, and in particular by the arbitrarily chosen temperature at which separation of solid and liquid is effected.

There is a good deal to say for employing this test at temperature or temperatures higher than the stipulated minus 32 ° C, since the proportion of components of a petroleum wax which are liquid or semi-solid at ambient or near ambient temperatures has a considerable bearing on the characteristics and applications of that wax.

In a distillate wax, too high an ' oil ' content will give a greasy texture to the wax surface, impair its tensile strength, scuff resistance, seal strength potential, staining propensity, color stability.

In microcrystalline waxes, an increase in 'oil' content may bring about an increase in flexibility, but too high an 'oil' content softens the wax unduly, gives poor temperature stability, and impairs the tensile strength and sealing potential.

Whilst the IP 158 type test remains the standard test for waxes of unknown oil content, wide line nuclear magnetic resonance (NMR) techniques calibrated by IP 158 are being used increasingly for routine control of specific refinery wax streams.

#### 4. Penetration (ASTM D 1321, ISO 3992, IP in preparation)

The needle penetration of petroleum waxes is the distance in units of 0.1 mm to which a standard needle penetrates into the sample under fixed conditions of load, time, and temperature. It is an indication of the hardness of the wax, but the doubtful value in the case of very hard waxes where the precision of the method approaches the level of the readings obtained.

If the test is carried out over a temperature range, from 15 to 50 °C for example, a temperature against penetration curve can be plotted which can be a valuable guide to the staining ( 'bleeding' ) potential of the wax or wax blend, to its temperature resistance, and hence to its performance in heat-seal and packaging application.

The penetration of petrolatum, IP 179, ASTM D 937, ISO in preparation, is determined in a similar manner to the measurement on waxes, but a metal cone is used instead of a needle.

If the petrolatum is subjected to 'working', i.e. shearing, pumping, or trowelling, the structure of the product breaks down to some extent and the product softens, giving on measurement a higher penetration figure. The original penetration will not be regained unless the petrolatum is remelted and allowed to cool. A specific test, determining the worked penetration of grease (IP 50) may be used on a petrolatum, and subjects the sample to a standard shear treatment, whereupon the penetration is the re-measure of resistance of the petrolatum to shear, and is a vitally important characteristic in many industrial applications.

In general, for a given hardness of starting material, the higher the non-normal content of the petrolatum the smaller will be the difference between worked and unworkm penetrations, and thus the greater the resistance to shear.

5. Color ( IP 196, ASTM D 1500, IP 17, ASTM D 156 )

Several methods are available for measuring colour, some of which are listed above. All are based on comparing in the molten state, by transmitted light, the colored glasses of varying intensity and hue. All such measurements are subjective, and values obtained by the different methods cannot be correlated exactly, though approximate conversion are possible.

6. Odour and taste

The detection and measurement of these properties is highly subjective.

Waxes to be used in the food packaging industry must be free form any odour or taste which could transfer itself to the foodstuff to a degree detectable by the consumer, and whilst there is a standard odour test for petroleum waxes ( IP 185, ASTM D 1833 ), there is no recognized test for taste.

Most users of wax in the food packaging industries use their own highly specific odour and taste tests employing panels of skilled operators.

7. Refractive index ( ASTM D 1747 )

This standard test, carried out using light of a particular wavelength and wax at a specified temperature, usually 80 ° C or 100 ° C , is a useful method of checking variation in composition or quality of petroleum waxes. The RI of a hydrocarbon or mixture of hydrocarbons is dependent on the degree of crystallinity of the sample ; thus a sample alkane or a low average molecular weight paraffin wax gives alow RI figure, e.g. 1.4190 at 100 ° C, where as a substantially normal-alkane-free microcrystalline wax gives much higher figure, e.g. 1.4420 at 100 ° C.

For known components in blend, the technique can be used to give a quantitative assessment of the composition.

B. Testing of wax and wax products ( 58 )

Properties of petroleum waxes such as oil content, melting point, hardness, viscosity, density, colour, etc., serve to characterize the various grades of wax, and can be determined by standard tests.

These tests do not measure the performance of wax in many of its applications, and functional tests in which the conditions of the application are stimulated are in common use, although few of them have yet been standardized. Some of the more important are listed below.

Tensile strength is defined as the longitudinal stress required to break a test specimen of specified dimensions in a standard ASTM D 1320

The rigidity modulus is the ratio of stress to strain in a material subjected to a shearing force. It gives an indication of the force required to shear the material, and in the case of paraffin wax provides a better correlation with product quality for certain applications than do other less precisely defined properties such as hardness or penetration or even the above-mentioned tensile strength.

Some food wrappers are sealed by pressing the portion to be sealed successively between heated and cooled plates. The force required to pull apart two strips of standard paper, coated with wax to be tested, and sealed together in this way, is a measure of the suitability of the wax for this application.

Waxed papers tend to stick together, which is undesirable. This tendency is measured by a ' blocking test ' in which sheets of waxed paper are laid on one another, pressed together by a weight, and kept successively at a range of temperatures; the temperature at which sticking first occurs is the blocking point. This test has been standardized by the ASTM D 1465.

When wax cartons are bent or deformed, as in closing and opening, the wax coating should not flake and allow particles of wax to drop into the contents. This quality is assessed either by flexing tests or by dropping a weight on to wax-coated board.

When waxed paper is passed between rollers in the course of waterproofing, the wax should not 'scuff' off the paper and build up on the roller. This quality is assessed by passing a waxed paper strip between two rollers, one of which is loaded, and determining the loss in weight of strip.

The glossiness of waxed paper and its retention of gloss on storage are important characteristics in relation to customer reaction. Visual inspection is highly subjective and is liable to variable ratings, and a more objective test is used in which the reflected light is measured by special instruments.

Permeability to water vapor is measured by sealing a moisture-absorbing salt such as calcium chloride in a waxed container, storing the container in a humid atmosphere under standard conditions, and measuring the increase in weight of the salt.

#### Toxicity of petroleum waxes

In recent years legislation has been introduced in most countries to protect consumers against health hazards arising from chemical substances, including petroleum products, coming into contact with food stuffs.

Various polycyclic aromatic hydrocarbons ( PCAHs ) have been shown to be carcinogenic in biological laboratory tests; hence legislation in most countries now requires that hydrocarbon waxes used in, or coming into contact with foodstuffs, shall conform to specific purity requirements, and shall be shown to be substantially free of polycyclic aromatic hydrocarbons.

In an extensive testing programme on a very large number of petroleum waxes, Shubik et.al.( 59 ) showed by animal feeding trials that no health hazard is present if the waxes met certain purity requirements. Based on this work, and using the same waxes Howard et. al. ( 60 ) developed a screening test for the control of polycyclic aromatic hydrocarbons which was adopted as the standard control procedure in the US ( F and DA Regulations, Section 172.886 ).



The method is based on an extraction of any PCAHs by dimethyl sulphoxide and, after some intermediate operations, the measurement of the ultra-violet absorption of these extracts. This method has been widely adopted, although some countries use alternative techniques for PCAH control. Germany, for example, has adopted the F and DA paragraph 172.886 test for microcrystalline waxes, but on paraffin uses an alternative nitromethane extraction / paper chromatography test, with visual comparison against a known concentration of a recognized PCAH as control.

#### Industrial application of petroleum waxes

Petroleum waxes find extensive use in many different branches of industry. Well over a hundred different applications are listed in the references, and these by no means exhaust the range of these versatile materials.

It is increasingly difficult to obtain reliable statistics regarding total worldwide wax usage, and even more difficult to find such figures broken down into end-use data. Until 1972 the American Petroleum Institute publish such data for application tonnages within the USA, but since then only very general production statistics have been available through such organizations as the Institute of Petroleum within the UK, and from the Bureau of Mines in the USA until 1978, when the Department of Energy's Information Administration take over this function.

It is valuable, therefore, to have an authoritative survey of output at the end of the USA and an estimate of end-use markets as they then existed. This and other surveys showed a consumption of wax within North America estimated in excess of 1 million tons.

The largest market is in the paper converting industry, but on the whole this is showing little growth, increases in certain areas being balanced by a slow decline in other areas. In Europe, for example, flexible packaging still represents the largest usage within the paper converting field, although in USA this has been overtaken by the growth of the wax impregnated corrugated industry.

From time to time there have been dramatic setbacks in wax usage, such as for example in the 1960s when the replacement of wax coated milk cartons by polyethylene coatings resulted in loss in the USA of up to a third of the then existing wax market. A further setback came in the 1970s with a change to the polyethylene bagging of bread from the traditional waxed wrapper, although this change has been complete than was at first predicted.

These setbacks have, in time, been offset by new applications within the paper converting industry and by the expansion of other markets.

Probably the biggest boost to the increase in petroleum wax consumption within the packaging and converting industries came in the early 1960s with the introduction of the hydrocarbon compatible ethylene-vinyl acetate copolymers (EVAs). Their ability to increase heat-sealing characteristics, flexibility and toughness of petroleum waxes quite significantly, was the foundation for the growth in heat-sealable coating and the development of the hot-melt adhesive industry.

Whilst unmodified petroleum waxes still find varied and large scale applications, there are vastly more end uses where the requirements can only be met by modifying the physical properties of the wax through blending with other materials.

The EVAs have already been mentioned, but there are very many other polymers, including vinyl acrylate copolymers, butyl rubbers, poly isobutenes, polyethylenes of widely differing molecular weight, polypropylene, EP and EPDM rubbers, and several thermoplastic rubbers which enhance the valuable characteristics of petroleum waxes in particular applications and outlets. Many types of resins and rosins enhance adhesion, tack, and other desirable properties of wax-based products.

Since the packaging and converting industry continues to account for perhaps 50 per cent of total refined wax output, some of the major operations responsible for this tonnage will be considered in greater detail.

## A. Packing industry

### 1. Waxed paper

The waxing of paper or calendered paper is carried out to reduce water and water vapour permeability, and to prevent to some extent the loss of strength which paper experiences when coming into contact with water.

Waxing can be carried out using many different configurations of coating machinery, but essentially the paper web is passed in a continuous strip through a bath of molten wax or wax blend, or it is allowed to pass over a roll which itself dips and revolves in a wax bath. In either case, by a system of doctoring bars or squeeze rolls, excess wax is eliminated, and the weight of applied wax controlled.

When it is desirable to have little wax on the surface of the paper, for example in paper used for wrapping foodstuffs, etc., the paper web is passed through heated finishing rolls which force the wax into the pores of the paper in a process called 'drying-waxing', the resultant paper surface being dry and apparently wax-free.

When, on the other hand, the wax is retained largely on the surface of the paper, the operation is called 'wet waxing', and this is achieved by rapidly chilling the wax film from a double-sided coating or total immersion. Maximum rate of cooling occurs when the waxed paper is passed at speed through a chilled water bath whilst the wax coating is still molten.

The minimum size of wax crystal resulting from this treatment produces maximum gloss, which together with maximum moisture vapour resistance resulting from a continuous and uniform film of wax, gives coated paper which are used for biscuit, chocolate, and sweet outer wraps, bread wraps, carton liners, shelf paper, etc. The waxes used for these operations are of low viscosity, rarely of more than 15 cp at operating temperatures, and are blends of paraffin waxes with additions of low molecular weight polyethylenes, EVAs, microcrystalline wax, and occasionally resins.

## 2. Coated containers

An extension of the above techniques to thicker paper substrates, or to thin solid paper-board, leads to production of containers for cold drinks, ice-cream, fruit juices, cheese, etc. and to very important product range of folded cartons. These are of solid paper-board, and are supplied by paper converters to consumers in the form of flat blanks, already printed and wax coated. The cartons are then filled, folded and sealed by customer, usually a large scale food processor or packer, the contents being typically frozen foods, ice-cream, butter, bacon, pies, etc.

It general in this type of application for the additive content of the to be considerably higher than previously described, with EVA copolymers, polyolefines, and ' hot tack ' resins being the most commonly used.

The ever-increasing proportions of polymeric additives give higher and higher viscosities to the wax coatings, and much more sophisticated machinery is necessary to apply them at speed and in controlled thickness. Although there is no agreed viscosity demarcation line, higher viscosity wax-polymer blends have become known as hot-melt coatings, and are designed to have good adhesion to almost any substrate. They can be tailored to heat-sealable, and to provide excellent barriers to grease, water, water vapour, gases, and odours. They are able to withstand deep-freeze conditions, and have good gloss, gloss stability, and a high degree of scuff resistance.

## 3. Laminated carton

A further extension of carton production is the use of petroleum wax based adhesives to produce laminated cartons, two substrates being sealed together by the setting wax. Here the waxes, predominantly microcrystalline in type, are blended with tack including polymers such as butyl rubber, polyisobutene, EPDM, polypropylene, etc., to give high-viscosity products which do not soak into the substrates at laminating temperatures.

The operation of laminating gives further increased water and water vapour barrier properties, increased strength or rigidity, and / or a more economic package, and typical of the contents so packaged are hygroscopic detergents and soap powders.

#### 4. Miscellaneous laminations

It will be obvious that since laminating grade petroleum waxes or wax blends can be designed to adhere to virtually any surface, the scope for design of different laminates for specific end uses is unlimited.

Since examples are the aluminium foil-hot-melt coated paper composite for wrapping soap tablets, foil-grease proof paper lamination for butter wrapping, and the ' strike through ' laminates of aluminium foil to tissue paper which utilize low-viscosity laminating grade microcrystalline waxes, capable of soaking through the tissue on application of heat to form a seal with another surface.

#### 5. Wax-treated corrugated board

Probably the greatest increase in wax usage in the packaging field over the past fifteen years has been in the production of wax-treated corrugated boxes.

The considerable increase in strength, water resistance, ease of stacking, and the cost savings compared with heavier gauge board, wood or plastic, are the reasons for this substantial growth. Particularly in North America considerable tonnages of fruit, vegetables, poultry, sea-food, and meat, are conveyed in wax corrugated boxes. There is also a growing market in bulk containers, pallets, etc., and a significant replacement of timber in crates and cases by wax-treated boxes.

The wax treatment can be performed in three ways, by the curtain coating, partial impregnation, or saturation coating, using different qualities of wax blends, and achieving different standards of performance.

##### a) Curtain coating.

In curtain coating, the corrugated board passes at speeds of up to 150 metres per minute under a falling thin curtain of molten wax blend which deposits a continuous film on the board's surface. Both sides can be coated by running the board

through the coater again.

Wax blends used here contain appreciable amount of polymer and resinous additives, and in coating the board surface give greatly increased moisture vapour and water resistance.

Impregnation of the corrugated board does not take place, so the basic board strength is not increased.

b) Partial impregnation

A control amount of wax, usually about 10 per cent, is used to impregnate the board in the corrugator. A higher degree of impregnation is not possible without interfering with the effectiveness of the water-based adhesive used to bond flute the liner. Some increase in board compression strength, water resistance, and performance at high humidity is realized by this technique, but a true wet service performance is not obtained.

However, following partial impregnation on the corrugator by curtain coating as previously described, a good wet-service container can be produced.

Low-viscosity paraffin wax based blends are normally used in this can be produced.

c) Saturation waxing

This operation involves impregnating the fluting and outer liners with wax, and there are currently three techniques in use for achieving this end. In the first the wax is sprayed into the fluting during the passage of the board along the corrugator, whilst in the second the finished board is dipped into the molten wax, and in the third the board is passed vertically beneath free-flowing cascades or weirs of molten wax. All three methods attempt to remove surplus wax and ensure uniform distribution, but there is little doubt that the immersion method is the most difficult to control and lead to erratic wax weights. The cascade process appears to be the most successful, giving a high degree of process control and a large throughput.

The waxes used are generally paraffin waxes modified with small percentages of low molecular weight polyethylenes, the wax pick-up being about 45 per cent of the board weight. However, refinements in operating conditions are tending to reduce this figure to a more cost effective 30-40 per cent figure.

#### 6. Hot-melt adhesives

As previously indicated, the transition from a low-viscosity wax, the simplest thermoplastic, to an entirely polymeric thermoplastic system is, in terms of available blends, gradual one.

The title of hot-melt adhesives, as distinct from heat-sealable hot-melt coatings, implies that the polymer and resin components are in the major phase, petroleum wax being in the minor, and in many cases, very much the minor phase.

In this type of product petroleum wax may be regarded as a high melting solvent for the resin and polymer components, acting to reduce the viscosity, and modify the softening point, blocking temperature and 'open time' of the adhesive.

The petroleum waxes used in hot-melt adhesives generally high melting point microcrystalline or intermediate waxes, or blend thereof, and the main outlets for the wax containing hot-melt adhesives are in book-binding, carton and case sealing, paper spiral tube winding, carpet backing, footwear, and labelling.

#### B. Petrolatum

Mention has already been made of the production of residual slack waxes by the dewaxing of de-asphalted vacuum distillation residues of crude oil, and their subsequent refining to produce petrolatum or petroleum jelly. Such products are mixtures of microcrystalline waxes and oil, and represent high viscosity, high shear resistance materials of long fibre and substantial texture

Petrolatum is also often produced by blending residual slack wax or microcrystalline waxes with distillate wax or distillate slack waxes and mineral oils to produce lower viscosity products of lower shear resistance, i.e. which spread more easily and have smoother salve-like consistencies.

With still higher proportions of paraffin or intermediate waxes present, stiffer pastes are formed which readily break down under mild shear conditions to produce fluid or semi-fluid films, ideal as bases of ointments for burn dressings, etc.

Unrefined or semi-refined products from these classes are used as technical grade petroleum jellies in the production of modelling clays, moulding compounds, anticorrosive coatings, electric insulants, etc.

Refining of these grades produces appropriate petrolatums, varying in colour from white to yellow, complying with Pharmacopoeia requirements or national food regulations, and hence finding use in pharmaceutical and food contacting applications.

Blends of residual slack waxes with heavy extract or naphthenic oils produce high-viscosity 'green' petrolatums, widely used in heavy industrial applications such as capable impregnants, anticorrosive coating, greases, and insulants.

### C. Rubber compounding

Petroleum waxes are used extensively in the rubber industry to reduce or prevent ozone cracking of stressed double-bonded rubber components such as tyres, belting, hose, etc.

They operate by dissolving in the rubber at vulcanization temperatures, but become insoluble and incompatible as the rubber cools, where upon the individual hydrocarbons migrate in highly temperature dependent manner through the rubber mass to form a mobile film at the rubber surface. This acts as a protective physical barrier to ozone present in air which would otherwise attack any double-bonded stressed polymer, producing the characteristic cracking and crazing of the compound.

Paraffin and intermediate waxes are the only effective agents in this application, although residual slack waxes are sometimes used processing aids.

The amount of wax used varies with the end use and type of compound, but is usually between 0.1 and 3 per cent of the total weight of compound.



#### D. Candlemaking

The candle industry continues to be a large user of petroleum wax, with many hundreds of thousands of tons of paraffin wax being supplied annually for this application. The Third World countries consume a large proportion of the total, but all countries share in production of utilitarian, decorative, and religious candles.

Stearic acid, high melting point microcrystalline and synthetic waxes, low molecular weight polyethylenes, and beeswax are commonly used additives, the candles being produced by dipping or moulding, but more often nowadays by compression moulding or extrusion.

The paraffin candle has grown greatly in favor because of its greater illuminating power and the absence of the pungent and disagreeable odour that characterizes the old stearin candle when it is blown out. A high degree of luster combined with translucency, and ready adaptability to ornament in shape and color are other desirable qualities of paraffin. Addition of stearic acid or other substances minimizes the chief objection to paraffin candles, which is their inability to support their own weight in warm weather ( 61 ).

#### E. Polishes

Polish for wood, leather, linoleum, and automobile bodies, etc., have traditionally contained a mixture of animal and vegetable waxes such as beeswax or carnauba, with proportions of cheaper petroleum or oxidized petroleum waxes. For ease of spreading, the waxes are dispersed in either volatile organic solvents as liquid or paste polishes, or in aqueous dispersions as cream or emulsion polishes.

With the continuing growth of synthetic polymer-based polishes, this is a relatively small and declining wax market.

#### F. Wax emulsion

Where ease of application at low temperature is a requirement, petroleum waxes are supplied and used as dispersions in water. The standard production method is mix molten wax and hot water containing emulsifying wax, using controlled cooling and homogenization to control particle size and viscosity. At the point of manufacture a true

emulsion may be formed, but during cooling the wax droplets solidify; thus the final product is more correctly described as an aqueous dispersion.

The solid content commonly varies 30 to 65 per cent, of which 25 to 60 per cent may be wax. If required, other materials may be co-dispersed or emulsified, or the finished wax dispersion may be blended with compatible emulsions or modifiers such as polymers, resins, rosins, etc.

Wax dispersions find their main outlets in the particle board manufacturing industry, where their incorporation into the board improves the water repellency and dimensional stability dramatically. Other important applications are in paper and paper board production where water repellency and the qualities of clay coatings are improved, and in latex foam carpet backing formulations where surface tack is eliminated.

The applications listed above represent the major outlets for petroleum wax in industry, but significant tonnages of waxes are used in a wide variety of other applications, ranging from chewing gum and crayons, PVC lubricants and matches, pottery and ski coatings, to textiles and thermostats.

### Opportunities in petroleum waxes

Although, in the present, using of plastic can instead of petroleum waxes in some cases, tendency of petroleum waxes consumption increase in every years.

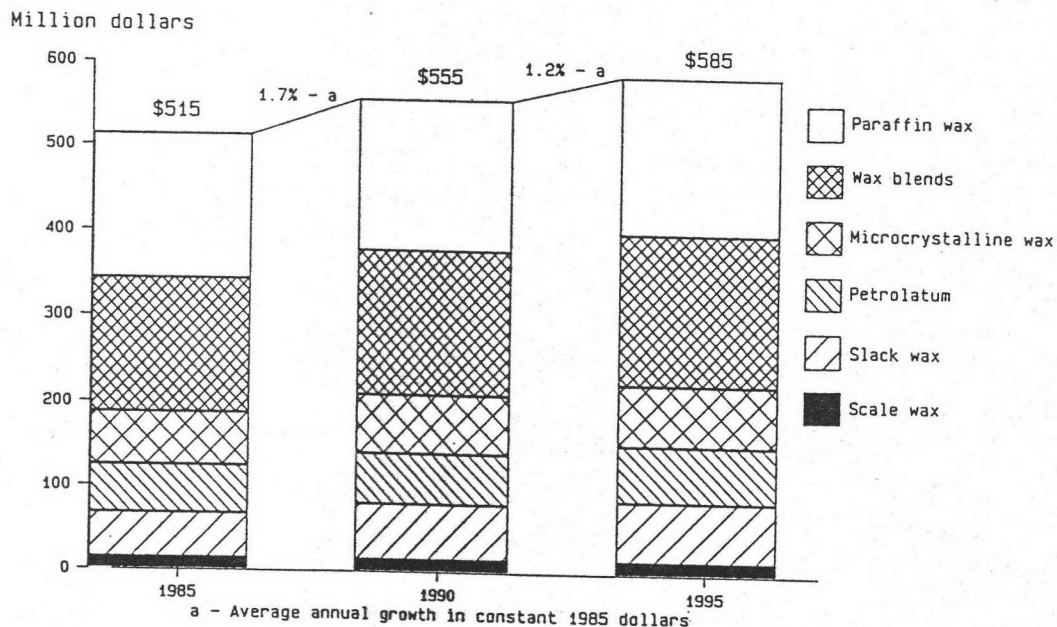
In 1978, USSR interested in a considerable improvement in the technology of petroleum wax production by improvement of the equipment used in de-oiling ( 62 ).

In 1983, the end-use consumption of USA for refined paraffin and microcrystalline wax was 1,343 millions of pounds ( 63 ).

In 1985, overall USA sale of petroleum waxes were forecasted to grow at 1.7% a year, reaching \$ 555 million in 1990. Sales were projected to continue to increase at 1.2% a year to 1995, based on survey.( Fig. 2.10 ) ( 64-66 ) Refined products, including paraffinic wax, microcrystalline wax and scale wax are expected to experience slightly better growth prospects than such unrefined products as slack wax and petrolatum. ( Fig. 2.11 ) ( 67-68 )

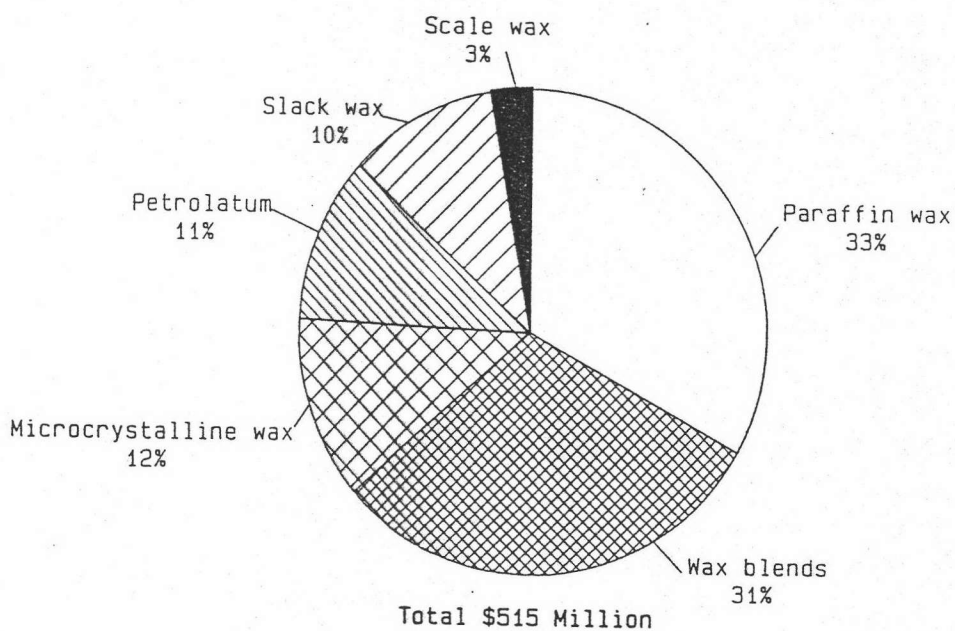
In 1987, Total, Institut Francais du Petrole ( IFP ) and French engineering firm technip had signed a contract with Chinese refining company Gao-Qiao to provide technology and engineering for a paraffin waxes hydrotreatment plant in Shanghai, according to Total ( 69-70 ).

In 1990, Venezuelan oil company Maraven, a subsidiary of state energy monopoly Petroleos de Venezuela S.A. ( PDVSA), is working on plans for a \$ 500-million ' industrial park ' for petrochemicals. Slated for 1995 startup, it will be sited alongside Maraven's Cardon refinery in western Venezuela. PDVSA declines to describe the planned Cardon venture as a ' petrochemical complex ' because it will not be based on naphtha or ethane crackers feeding derivatives units. Instead, the new plants will transform refinery streams into high-value substances through supplementary processing. An example of this value-adding process is the upgrading of paraffinic ' slack wax ' a by-product of lubricant base made at Cardon, that is the raw material for microcrystalline wax and white oils used to make medicinal oils ( 71 ).



SOURCE: Kline & Company, Inc.

Figure 2.10 Forecast U.S. consumption of Petroleum waxes 1985 to 1995.



SOURCE: Kline & Company, Inc.

Figure 2.11 U.S. sales of Petroleum waxes by product 1985 .