CHAPTER II

THEORETICAL AND LITERATURE REVIEW

2.1 Waxes [1]

Wax usually refers to a substance that is a plastic solid at ambient temperature and, on being subjected to moderately elevated temperature, becomes a low viscosity liquid. Because of it plastic nature, 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

1. Insect and animal waxes
2. Vegetable waxes e.g., candelilla, carnauba, japan wax, Douglas-fir bark wax, rice bran wax, jojoba, castor wax, and bayberry wax.
3. Mineral waxes e.g., montan wax, peat waxes, ozokerite and ceresin waxes, and petroleum wax.
4. Synthetic waxes e.g., polyethylene waxes, Fischer-Tropsch waxes, Chemically modified hydrocarbon waxes, and substituted amide waxes.

2.2 Manufacture and classification of petroleum wax [2]

Petroleum waxes

Petroleum waxes, a term covering the wax-like materials derived from petroleum and related mineral oils are comprised essentially normal and branched chain paraffin and solid-hydrocarbon of other saturated series. [3]

Petroleum waxes are by-products of lubricating oils production. Petroleum waxes are removed from lubricating oils after distillation of crude oils, as shown in Figure 2.1.
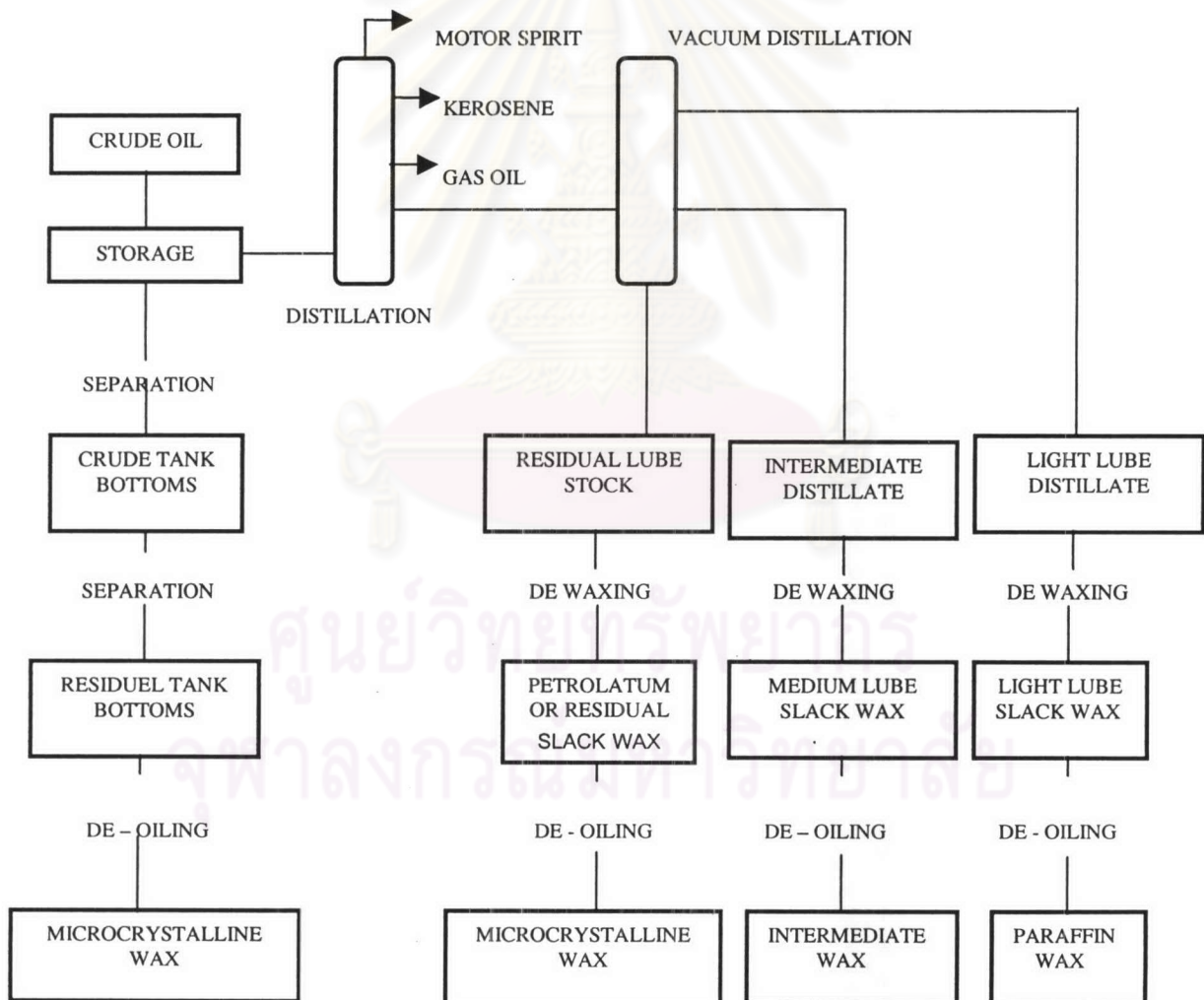

Figure 2.1 Petroleum waxes refining

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

2.2.1 Paraffin waxes.

Paraffin waxes are mixture of saturated paraffin 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, to gether with a small cycloalkane content. The chain length of the individual alkanes ranges from about 18 carbon atoms to about 45, the higher the average molecular weight of the alkane mixtures, the higher the proportion or iso-alkane likely to be present

Grades of paraffin wax [4]

Paraffin wax is solid 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, semirefined, and crude scale waxes.

a) Refined wax

Refined wax has a melting point range of 50-51 °C, a color (Saybolt chromometer scale) 25-30, and oil content of 0.5% or less. At ordinary temperature, 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 strengths much reduced and become 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 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.

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

c) Semirefined wax

Semirefined wax is between refined waxes and crude scale waxes. It has a melting point range of 49-57 °C, and an oil content of about 0.6-3%. The important properties of paraffin wax are shown in Table 2.1.

Table 2.1 Properties of paraffin wax [5]

Properties	Values
Molecular Weight	300-500
Melting point, °C	47-68
Needle Penetration, at 25 °C	10-20
Oil content, % wt	< 0.5
Viscosity, at 98.9 °C (i) cSt	2.4-5.7
(ii) sus	35-45
Flash Point, °C	175-235
Specific gravity, at 100 °C	About 0.75-0.80
Refractive index, at 100 °C	1.430 – 1.433
Contraction from 5 °C above to 25 °C below M.P., %	13.5 -14.5
Flexibility at low temperature	Zero
Adhesion or laminating strength	Zero
Properties when mixed with petroleum oil	
(i) Ductility	Low
(ii) Staining or bleeding	High

2.2.2 Intermediate waxes

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

2.2.3. Microcrystalline waxes

Microcrystalline waxes also are mixture of saturated alkanes, but with much greater preponderance of branched-chain or cyclomolecules. 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 microcrystalline, 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 are 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 know as petroleum ceresins.

A. Petroleum 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) Petroleum wax. Petroleum wax or crude petroleum 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 a fairly high percentage of wax, by treatment with naphtha and centrifugation of solution to remove excess oil.

B. Petroleum cerasin group

a) Petroleum cerasin wax. This is also wax of fine crystalline structure, which varies in color from dark brown to white. Unlike the petrolatum waxes, it is hard and brittle, and these constitute the main difference between these two groups. Petroleum ceresins have molecular weights ranging from about 450-1,000 and melting points from 70-105 °C. The important properties of microcrystalline wax are shown in Table 2.2.

**Table 2.2** Properties of Microcrystalline waxes [5]

Properties	Values
Molecular Weight	500-800
Melting point, °C	60-96
Needle Penetration, at 25 °C	5-50
Oil content, % wt	2-15
Viscosity, at 98 – 9 °C (i) cSt	9-25
(ii) sus	50-100
Flash Point, °C	230-315
Specific gravity, at 100 °C	About 0.80-0.90
Refractive index, at 100 °C	1.435-1.445
Contraction from 5 °C above to 25 °C below M.P. ,%	
Flexibility at low temperature	Zero
Adhesion or laminating strength	Zero
Properties when mixed with petroleum oil	
(i) Ductility	Low
(ii) Staining or bleeding	High

2.3 Wax Crystal [4]

Then types of crystals, which were formed when these pure waxes were crystallized from a solvent, were carefully studied. Three different types were found. Most of these waxes formed plate-type crystals; another group crystallized as needles, and the remainder assumed forms that could not be identified. The last group was called "malcrystalline," for lack of a better name. 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.

Storage of wax that contains small crystals may result in the growth of large crystals, but it can never cause a change in their type. This can be accomplished only be 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 constituted the basic fraction of paraffin waxes. The needle and malcrystalline type 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. Types of wax crystals are shown in Figure 2.2.

Plate   Needle   Malcrystalline   Microcrystalline
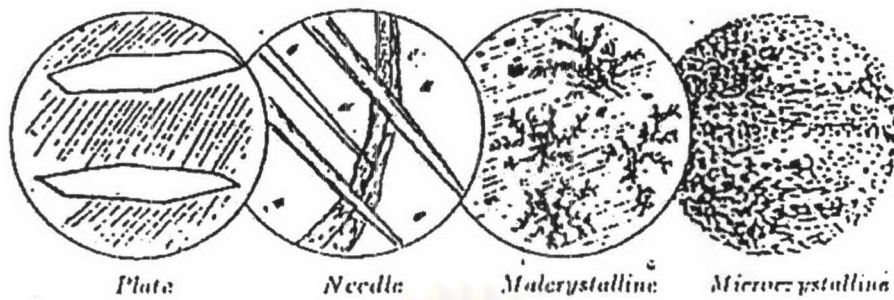
Figure 2.2 Type of Wax Crystal [6]

2.4 Solubility of Wax

2.4.1 Solubility of paraffin wax [4]

The solubility of higher molecular weight solvent increases with a rise in temperature more rapidly. The solubility of 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. The solubility of the paraffin 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 temperatures at 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.

2.4.2 Solubility of Microcrystalline waxes [6]

Microcrystalline waxes have a low order of solubility in polar solvents, and are soluble to an appreciable extent in non-polar solvents at ordinary room temperature, and extremely soluble at advanced temperatures (e.g. 66 °C). They are ordinarily rate as insoluble in methanol, ethanol, isopropanol, butanols, and amly alcohol at room temperature; like wise in isopropyl acetate, ethylene dichloride, nitrobenzene, furfural, phneol, cellosolve, and "Chlorex". They are soluble in Chlorofrom, carbon tetrachloride, benzene, toluene, xylene, and turpentine; and slightly soluble in naphtha, solventand kerosene.

The higher-melting microcrystalline waxes (e.g., 88/91 °C) are less soluble in solvents than the lower-melting waxes (e.g., 77/79 °C).

2.5 Production of waxes

2.5.1. Dewaxing [7]

All lube stocks, except those from a relatively few highly naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperature. Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing. There are two types of processes in use today. One 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. The other uses a selective hydrocracking process to crack the wax molecules to light hydrocarbons.

A. Solvent dewaxing

There are two principal solvents used in the United States in solvent dewaxing process, propane and ketones. Dichloroethane-methylene is also used in some other countries. The ketone-processes use either a mixture of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK) or MEK with toluene. The solvents act 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 portion of the process. About 80% of the dewaxing installations use ketones as the solvent and the other 20% use propane. The comparative advantages of disadvantages of the processes are:

Propane:

1. Readily available, less expensive and easier to recover

2. Direct chilling can be accomplished by vaporization of the solvent thus reducing the capital and maintenance costs of scraped-surface chillers

3. High filtration rates can be obtained because of its low viscosity at very low temperatures

4. Rejects asphaltenes and resins in the feed

5. Large differences between filtration temperatures and pour point of finished oikls (15 to 25 °C, 25 to 45 °F)

6. Requires use of a dewaxing did

Ketone:

    1. Small difference between filtration temperature and pour point of dewaxed oil

      (5 to 10°C, 9 to 18°F)

      a. Lower pour point capability

      b. Greater recovery of heat-by-heat exchange

      c. Lower refrigeration requirements

    2. Fats chilling rate. Snock chilling con be used to improcess operations.

    3. Good filtration rates but lower than for propane.

B. Selective hydrocracking.

There are two types of selective hydrocracking processes for dewaxing oil, one use a single catalyst for pour point reduction only and the other uses two catalysts to reduce the pour point and improve the oxygen stability of the product.

2.5.2 Deoiling [2]

The dewaxing operation removes 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

    2. De-oiling by sweating

2.5.2.1 Solvent de-oiling

This is the most widely used method. There are many solvents used for deoiling such as methyl ethyl ketone, methyl ethyl ketone-toluene, ethylene dichloride, methyl isobuthyl ketone, dimethyl formamide etc. As in dewaxing, the feed is diluted with solvent in suitable ratio and dissolved by heating. On being cooled, as before, to predermined temperature, the wax separates and is filtered. Cooling further to lower temperatures gives further wax separation, the average 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 percent.

2.5.2.2 De-Oiling by sweating

The feedstock chosen as suitable for a sweating process is first melted to produce a homogeneous liquid, and 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.

2.6 Wax Sweating Process

The solid wax was slowly heated in a sweating oven during sweating; the temperature of the wax in the oven was slowly raised to liquefy part of the wax. As the oven, the wax began to melt. The first liquid fraction to drained from the bed through the over pan. The liquid drippings was collected in the bottom of the oven and drained into pan. As each range of temperature become full, the wax in the pan was tested for its drop melting point, congealing point, oil content and the other physical properties. The sweating process continuous until ill of the wax in the oven had been melted and collected in the pan.

2.7 Oxidized Hydrocarbon waxes [6]

Hydrocarbon waxes, such as paraffin and microcrystalline waxes, which have been artificially oxidized to produce an appreciable amount of fatty acids, or saponifiable matter, are known as oxidized waxes. The object of oxidizing hydrocarbon waxes is to make them more or less saponifiable. The oxidation is accomplished by blowing air through the wax for a prescribed period of time at a controlled temperature. In carrying out the oxidation of paraffin waxes (M.P. 52-57 °C) the temperature should range between 150 and 180 °C; the application of increased pressure speeds up the

reaction when air is used as the oxidizing agent. By withdrawing the partially oxidized wax and adding fresh wax to the reaction zone the darkening of the oxidized product can be avoided.

The wax acids produced in the oxidation process of both fatty and hydroxy acids as well as their anhydrides,lactones,and lactides,give oxidized waxes their peculiar characteristics. The hydroxy acids are in the range C_{13-17} $H_{26-34}OHCOOH$. Catalysts of manganese, nickle, chromium, and cobalt can be resorted to, when it is desired to obtain a higher yield of acids in the oxidized wax.

2.8 Industrial application of petroleum waxes [2]

Petroleum waxes find extensive use in many 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 fide 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 with 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 loss in the USA of up to a third of the then existing wax market. A further setback came in 1970s with a change to the polyethylene bagging of bread from the traditional waxed wrapper, although this change has 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 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, polyisobutenes, 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 calendared paper is carried out to reduce water and water vapor 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 though 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 elimination, 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 pass through heated finishing rolls which force the wax into pores of the paper in a process call "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 vapor 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 knows as hot-melt

coatings, and is 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 vapor, gases, and odors. 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 of petroleum wax based Adhesives to produced 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 vapor 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 though" 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, seafood, 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 creates 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 meters per minute under a falling thin curtain of molten wax blend, which deposits a continuous film on the board's surface. Boat 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 vapor 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 to percent, 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 ensue 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 labeling.

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 fiber 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 proportion 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 form these classes are used as technical grade petroleum jellies in the production of modeling clays; molding compounds anticorrosive coatings, electric insurants, etc.

Refining of these grades produces appropriate petrolatum, varying in color form 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" petrolatum, 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 ton 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. Candle making

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 beewax are commonly used additives, the candles being produced by dipping or molding, but more often nowadays by compression molding of extrusion.

The paraffin candle has grown greatly in favor because of its greater illuminating power and the absence of the pungent and disagreeable odor that characterizes the old stearin candle when it is blown out. A high degree of luster combined with translucency, ready adaptability to orament 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 there in ability to support their own weight in warm weather.

E. Polishes

Polish for wood, leather, linoleum, and automobile bodies, etc., have traditionally contained a mixture of animal and vegetable waxes as beeswax or carnauba, with proportion s 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 dispersion 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 blend with compatible emulsions or modifiers such as polymers, resins, rosins, etc.

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

The applications listed above represent the major outlets for petroleum wax in industry, but significant tonnage 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.

2.9 Previous Works Concerned

2.9.1 Sweating Process

Armstrong, A.D., et al., [8] improved apparatus for sweating the wax. In which the body of wax is much thicker than six inches. The improved apparatus permits thick wax to be rapidly and efficiently sweated with higher percentage of white paraffin wax than that yielded by any other known sweating apparatus. It produced the quality of paraffin wax, tasteless, odorless wax of stable color in a single operation.

Iwin, R.E., et al., [9] improved the method and apparatus, which separate lower melting point constituents (generally oil and isoparaffins) of a slack wax. The apparatus provides a low cost installation and yield comparable to those accomplished in a solvent deoiling process.

Roeff, R.M., [10] improved method of wax sweating which was effective, efficient, and economic. It reduced the time required to sweat wax and improve product quality and yield. It also allowed refineries and other manufactures to accurately produce the type of wax products they wanted and increase wax production

Sangarun, C., [11] separated of microcrystalline wax, paraffin wax and oil fractions from intermediate waxes, type 500SW and 600SW slack waxes, using solvent extraction and fractionational crystallization techniques. This investigation tried to study the effect of the temperature and solvent (MEK and toluene) on these slack-waxes fractionations. It was found that the MEK was better than toluene. The MEK fractionational extraction was performed form 20 to 60 °C. Paraffin waxes, which contain large amount of straight chain hydrocarbons, were preferentially separated at extraction temperature of 60 °C. Microcrystalline waxes, which contain large amount of branched-chain hydrocarbons, showed better separation at 30, 40 and 50 °C. The fractionation crystallization using MEK was performed at 10, 0, -10 and -20 °C. Both microcrystalline waxes, which were separated at 10 and 0°C, and fractionated oils, which were separated at -10 and -20 °C, contain large amount of naphthenic hydrocarbons.

2.9.2 Oxidation of microcrystalline waxes

Hicks-Bruun, M.M., [12] oxidized paraffin for the production of fatty acids which comprised mixing the paraffin to be oxidized with 1% of a cobalt salt of an organic acid, heated the mixture at 110 °C and passed oxygen into the mixture at the rate of 1.1 liters per minute. Product had a ratio of saponification number to acid number not greater than 1.9.

Annable, W.G., et al, [13] oxidized microcrystalline wax which had an oil content below 0.7% by weight using catalytic oxidation in liquid phase at temperatures between about 138-166° c until the wax attained a saponification number of at least 40 and an acid number of at least 10. The oxidized wax was precipitated and extracted by cooling the oxidized wax -solvent mixture to a temperature between about -12 °C and -23 °C.

Haines, R.M., et al, [14] improved a process for the preparation of hard, oxidized microcrystalline wax. The wax of very low oil content was oxidized in the liquid phase, used oxygen or air and a suitable oxidation catalyst. The oxidized wax mixture was then subjected to extraction with a deoiling solvent, and removed the acidic and ester oxidation products. The deoiled wax mixture was then saponified with aqueous alkali and separated from mixed soap solution, washed with water and filtered. The wax was dried and followed by nitrogen stripping. The final wax product produced in this process was a very hard wax having a very low penetration.