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Raising the efficiency of petrolatum deoiling process by using non-polar modifier concentrates separated from paraffin wastes to produce different petroleum products

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Abstract

Deoiling of crude petrolatum was intensified by addition of 1 wt.% of non-polar modifier concentrates separated from slack wax waste and compared with pure *n*-alkane mixtures; (C_{20}+C_{22}) and (C_{24}+C_{26}). Data revealed that, 1 wt.% of the separated (C_{20}+C_{22}) *n*-alkane mixture is selected as the preferable modifier to intensify and improve the deoiling process of crude petrolatum. X-ray diffraction patterns and SEM photographs observed that, the addition of 1 wt.% of non-polar modifier concentrates gave hard waxes having somewhat crystal growing and higher crystal sizes and possess more holes than the hard waxes separated without using a modifier. Different petroleum products were produced by using both the products of petrolatum deoiling process; the microcrystalline wax and the slop wax. Various grades of hardened ceresin were formulated by addition of low density poly ethylene with the separated microcrystalline wax. Fourteen formulated blends of petrolatum were prepared based on the microcrystalline wax and slop wax saturate with heavy and light paraffin oils, respectively. According to the standard specifications of US Pharmacopoeia and National Formulary of petrolatum and Ultra Chemical Inc. of liquid petrolatum, the blend formulations (3-8) are classified as technical petrolatums. Meanwhile, two of them (7 & 8) are classified also as liquid petrolatums. The blend formulations (9-14) are classified as white pharmaceutical petrolatums. Meanwhile, three of them (12-14) are also within the limits of standard specifications of ultrapure liquid petrolatums.

Key Words: Deoiling process; non-polar modifier concentrates; pure n-alkane mixtures; microcrystalline wax; ceresin; petrolatum

1. Introduction

Petroleum waxes are broadly defined as the waxes naturally present in various fractions of crude petroleum. Originally, they were considered as by products in the dewaxing of lubricating and gas oils, but, today they are valuable products for many industrial applications [1].

Petroleum waxes in their various fields of application require many different specifications. These can only partly be satisfied by a suitable choice of feedstock and the manufacturing processes, or even by some modifications of these processes. Petroleum waxes are based in a wide variety of applications. They are used in paper, match, rubber, ink, electrical, dental and cosmetics industries and in household chemicals, building construction and manufacture of metals and ceramics.

As the consumption of wax products in the world market increases, the increase of profitability of wax production will lie on the improvement and modification techniques of macro- and microcrystalline waxes as base materials as well as the development of other wax products [2-4].

Microcrystalline waxes are microcrystalline products, solid at room temperature, their melting points are ranged from 60-93^{o}C and usually produced from heavy petroleum distillates or residues or tank bottoms. Petrolatum is a general term applied to a crude microcrystalline wax containing some oil. It is semi-solid, jelly-like materials. It is a base material for the manufacturing of medicinal petroleum jelly or medicinal petrolatum. Slop wax is a microcrystalline wax or semi-microcrystalline wax, its melting point is lower than the microcrystalline one. It is the remainder wax obtained from petrolatum deoiling process after the separation of the microcrystalline wax. Ceresin is a hard microcrystalline wax having higher melting point than the microcrystalline wax itself [1].

In the processes of manufacture and refining of petroleum waxes; solvent dewaxing and deoiling, respectively; crystallization takes place from solution. The precipitation of wax crystals during cooling is a function of two important processes, crystal nucleation and crystal growth. The greatest difficulties for dewaxing and deoiling petrolatum are related to the stage of filtering slurries of solid hydrocarbons that tend to form an inter-crystalline structure [5].

The formation of large, multilayer, aggregated crystals requires the choice of modifiers that will rearrange the structural formations of paraffinic hydrocarbons in the required direction. Many organic additives, pour-point depressants, certain organometallic compounds and all possible macromolecular substances with a polymeric structure had been tested in the laboratory as modifiers for structural conversions of the solid phase. Many of these additives, while they have a strong modifying effect, will lose this property when the medium is moistening [6].

Additives with various functional actions; surfactants; were tested as polar modifiers in the process of deoiling petrolatums. Not all of the modifiers that are effective for the modification of solid hydrocarbon crystal structure in the production of high-melting microcrystalline waxes. The improvement in the phase separation rate in filtering the solid hydrocarbon slurry and the decrease in the oil content in the microcrystalline wax depend on the length of the radical and the polarity of the modifier molecule [7]. Aqueous sodium chloride was tested as ionic modifier for deoiling petrolatum. It increases the selectivity of the highest-melting hydrocarbons but it is not affect the filtration rate [8].

The addition of non-polar modifiers, especially individual n-alkanes with an even number of carbon atoms in the molecule (C_{20}–C_{24}) to the wax deoiling solvent to improve the crystallization of solid hydrocarbons during the deoiling of petrolatum to produce microcrystalline wax was studied. The filtration rate was greatly increased and the resulting microcrystalline wax contained < 0.5 wt.% oil. These modifiers are highly effective in the range of 0.5 - 1 wt.% [5, 9-11]. However, application of these modifiers in industrial deoiling installations is not economic because of the high cost of pure n-alkanes. On the other hand, these hydrocarbons occur as petroleum by-products during lubricating oils manufacture. Thus, our work aims to raise the efficiency of petrolatum deoiling process by improving the crystallization of solid hydrocarbons and accelerating the filtration rate to produce different petroleum products by using non-polar modifier concentrates; (C_{20}+C_{22}) and (C_{24}+C_{26}) *n*-alkane mixtures; separated from slack wax waste.

2. Materials and Methods

2.1. Materials

One appropriate crude petrolatum (petroleum waxy by-product) obtained from Alexandria Petroleum Company is used and evaluated in this study for deoiling process and production of different petroleum products. Its physical and molecular type composition characteristics are represented in Table 1. Also, the deoiling process of crude petrolatum and its final products are explained and presented in Scheme 1.

Table 1: Physical characteristics and molecular type composition of Alexandria crude petrolatum

Scheme 1: Schematic diagram of crude petrolatum deoiling and its final products

2.2. Deoiling process

Alexandria crude petrolatum was subjected to one stage fractional crystallization (deoiling process) [12-14] using butyl acetate (BA) solvent at fixed solvent feed ratio of 8:1 for dilution and 2:1 (S/F, by weight) for washing and at ambient fractionating temperature of 20^{o}C. In this technique, the high melting components of the wax (hard wax) got precipitated while the low melting ones (soft or slop wax) remained in the solution.

2.2.1. One stage fractional crystallization technique

A known weight of crude petrolatum was dissolved in the corresponding amount of solvent in a beaker and heated till the mixture becomes homogeneous. The non-polar modifier was added to the homogeneous mixture after 10 min to avoid the dissolution of the non-polar modifier crystals in the solution before starting crystallization. Then the mixture was cooled gradually at room temperature for two hours. The beaker and the buchner funnel were transferred to a controlled temperature unit and gradually cooled to the desired temperature (20^{o}C) for 12 hours to prevent direct cooling which make quenching leading to form small crystals left in the mixture. The beaker contents were

transferred to the funnel and filtered through a Whatman filter paper No.43 by using controlled suction (8.6 Psi). The wax cake was washed with an additional solvent at the same temperature and added at small increments. Solvents were removed from the wax cake and the filtrate by distillation.

The non-polar modifier concentrates which were prepared from light slack wax waste and added to the petrolatum deoiling solvent mixture are as follow:

(a) 0.5 to 1.5 wt.% of the non-polar modifier concentrate of low carbon number atoms (C_{20}+C_{22}) of the light slack wax after its adduction.

(b) 1 wt.% of the non-polar modifier concentrate of low carbon number atoms (C_{20}+C_{22}) of the paraffins (saturates) separated from light slack wax with liquid-solid chromatography technique followed by its adduction.

(c) 1 wt.% of the non-polar modifier concentrate of high carbon number atoms (C_{24}+C_{26}) of the hard wax separated from light slack wax after deoiling at 30^{o}C followed by its adduction [15].

The previous non-polar modifier concentrates mentioned in (a, b & c) were compared with two mixtures of pure n-alkanes with an even number of carbon atoms of *n*-(C_{20}+C_{22}) and *n*-(C_{24}+C_{26}) in the percentage of 1 wt.% based on the feed. The percentages of C_{20}, C_{22}, C_{24} and C_{26} in the pure mixtures of (C_{20}+C_{22}) and (C_{24}+C_{26}) were taken as their percentages in the prepared non-polar modifier concentrates.

2.3. Production of petroleum products

Besides the production of microcrystalline waxes, different types of petroleum products were prepared for various industrial applications depending on the main product; microcrystalline wax; and the by-product; slop wax; of the deoiling process.

2.3.1. Ceresin formulation

Microcrystalline wax; obtained by deoiling the crude petrolatum by using 1 wt.% of a non-polar modifier concentrate of the even carbon number atoms (C_{20}+C_{22}); was blended with low density poly ethylene (LDPE) in the percentages ranging from 2 to 10 wt.% to obtain different grades of petroleum ceresin with different melting points.

2.3.2. Petrolatum formulations

The microcrystalline wax; obtained by deoiling the crude petrolatum by using 1 wt. % of a non-polar modifier concentrate (C_{20}+C_{22}); was blended with heavy paraffin oil (1-8 blends) in the percentages ranging from 20 to 90 wt.% to obtain different grades of technical petrolatums.

The slop wax; obtained by deoiling the crude petrolatum by using 1 wt.% of a non-polar modifier concentrate (C_{20}+C_{22}); was subjected to liquid-solid chromatography technique to separate its saturates. Then, the slop wax saturate was blended with light paraffin oil (9-14 blends) in the percentages ranging from 10 to 60 wt.% to obtain different grades of medicinal petrolatums.

All petrolatum blends were made in the molten state with vigorous stirring to secure homogenous blends on cooling to room temperature. The operating conditions were as follow: the blending temperature = 90^{o}C, time of blending = 30 min and stirring speed = 150 r.p.m.

2.4. Methods of analysis

The crude wax, the isolated hard and soft waxes and all produced petroleum products were physically characterized according to American Society for Testing and Materials (ASTM) standard methods [16]. The standard methods for analysis are, congealing point (ASTM D-938), kinematic viscosity (ASTM D-445), refractive index (ASTM D-1747), density (ASTM D-1418), mean molecular weight (ASTM D-2502), oil content (ASTM D-721), cone penetration (ASTM D-937), needle penetration (ASTM D-1321), color (ASTM D-1500) and sulfur content by using X-ray fluorescence sulfur meter (ASTM D-4294).

The filtration rate was calculated by using equation (1).

$$R = W_F / A.\ T \qquad (1)$$

Where R is filtration rate, W_F is the weight in Kg, A is the area of the funnel bottom in $m^2 = \pi r^2$ and T is the filtration rate in hour (h)

Where $\pi = 3.14$ and r = radius of funnel used in deoiling process. The subscript F refers to the filtrate produced through deoiling process.

The type of the isolated hard waxes was specified according to TAPPI-ASTM equation to classify the waxes as macro-crystalline (Paraffin), semi-microcrystalline and microcrystalline waxes. The distinction between these groups is made on the basis of viscosity. The proposal is as follows using equation (2).

$$n_D^{210^oF} = 0.0001943t+1.3994 \quad (2)$$

Where n_D is the refractive index calculated by the equation and t is the congealing point temperature in $^{\circ}$F. A paraffin wax is characterized by refractive index less than that obtained by the above equation and by a viscosity at 210°F of lower than 7.4 centistokes. A semi-microcrystalline wax is characterized by refractive index higher than that obtained by the above equation and by a viscosity at 210°F of lower than 10 centistokes. A microcrystalline wax is characterized by refractive index higher than that obtained by the above equation and by a viscosity at 210°F of 10 centistokes or higher [17, 18].

The aromatic and saturate contents of the crude petrolatum and the isolated hard and soft waxes were determined using liquid-solid column chromatography technique. A 1.3 cm diameter and height of 130 cm column packed with activated silica gel (60-200 mesh size) was used**.** The column was then moistened with 100 ml of n-heptane to dissipate the heat of adsorption. A 10 grams sample of the wax dissolved in few milliliters of n-heptane were transferred to the column. The column was then eluted with 300 ml of n-heptane followed by 200 ml benzene and finally 100 ml of a 1:1 mixture of absolute methanol and benzene [19]. Fractions of 25 ml were taken from the column, the solvent distilled off and the refractive index of each fraction was determined. According to the refractive index data at 20^{o}C, elutes were combined into saturates, mono-, di- and poly-aromatics. The saturate hydrocarbons have refractive indices not more than 1.48. The mono-cyclic, bi-cyclic and poly-cyclic aromatics have refractive indices from 1.48 to 1.53, 1.53 to 1.59 and higher than 1.59, respectively [20, 21].

Ultraviolet absorbance for the produced formulated blends (9-14) was determined at 290 nm by using UV/VIS/NIR- spectrophotometer, JASCO, V570, USA.

2.5. X-Ray diffraction

The X-ray diffraction patterns were run to study the crystal size of the hard waxes separated by using non-polar modifiers; pure and prepared mixtures of *n*-alkanes. They were recorded in the range $2\theta = 4–70^0$ with a step size (2θ) of 0.02 and scan step time (s) of 0.4, in a P Analytical-XPert Pro, (Netherland) with K-Alpha l radiation and equipped with a Cu source with K-alpha 1 wavelength of 1.54056 A^0. The instrument was operated at 40 kV and 40 mA.

The 2θ, Full Width at Half Maximum (FWHM) and d spacing were obtained. Wax crystal size was calculated according to Scherrer equation (3) [22]. It is as follows:

$$I = 0.9 \lambda / B \cdot \cos(2\theta/2) \quad (3)$$

Where I is the wax crystal size, $\lambda = 1.54^0$A and B is the peak width and equal to FWHM / 57.3.

2.6. *Scanning electron microscope (SEM)*

SEM was used to observe the surface, shape and crystal size of the hard waxes separated by using non-polar modifiers; pure and prepared mixtures of *n*-alkanes. The wax was coated with gold by K550X sputter coater, England then scanned by scanning electron microscope (SEM; Quanta 250 FEG, Netherland).

3. Result and Discussion

3.1. Effect of addition of prepared concentrates and pure mixtures non-polar modifiers on petrolatum deoiling process

The effect of addition of non-polar modifiers; the prepared concentrates and mixtures of pure *n*-alkanes; (C_{20}+C_{22}) & (C_{24}+C_{26}) on petrolatum deoiling process was studied at fractionating temperature of 20^{o}C, at solvent ratios of 8:1 and 2:1 by weight for dilution and washing, respectively and by using butyl acetate solvent. Data are represented in Tables 2 and 3, respectively.

Table 2: Effect of addition of the prepared non-polar modifier concentrates on the deoiling of crude petrolatum

Table 3: Effect of addition of 1 wt.% of non-polar modifiers; mixtures of pure n-alkanes; on the deoiling of crude petrolatum

Addition of the prepared non-polar modifier concentrates (C_{20}+C_{22}) & (C_{24}+C_{26}) during fractional crystallization process results in a higher filtration rate, congealing point and mean molecular weight and a lower yield, oil content and needle penetration of the hard waxes isolated from crude petrolatum than those separated without using a modifier. It is interest to note from the data in Table 2 that, increasing the non-polar modifier concentration; (C_{20}+C_{22}) *n*-alkanes prepared from the light slack wax after adduction; from 0.5 to 1 wt.% during fractional crystallization process leads to a slight increase of filtration rate, congealing point and mean molecular weight and a slight decrease of yield, oil content and needle penetration of the hard waxes isolated from crude petrolatum. On the other hand, no improvement was observed on increasing the modifier concentration from 1 to 1.5 wt.%. Also, the addition of 1 wt.% of a non-polar modifier concentrate; (C_{20}+C_{22}) *n*-alkanes prepared from the light slack wax saturate after adduction gave nearly the same filtration rate, yield and wax characteristics as the addition of 1 wt.% of (C_{20}+C_{22}) *n*-alkanes concentrate prepared from the light slack wax after adduction. Thus, from economic point of view, the non-polar modifier concentrate; (C_{20}+C_{22}) *n*-alkanes prepared from the light slack wax after adduction is selected as a preferable modifier used to improve the fractional crystallization of crude petrolatum at fractionating temperature of 20^{o}C and at the dilution solvent ratio of 8:1 by weight by using butyl acetate solvent for saving the step of saturate separation from light slack wax. On the other side, the addition of 1 wt.% of a non-polar modifier concentrate of the high carbon number; (C_{24}+C_{26}) *n*-alkanes prepared from the hard waxes isolated from light slack wax at 30^{o}C after adduction; gave higher filtration rate and lower needle penetration and oil content than both the addition of 1 wt.% of a non-polar modifier concentrate of the lower carbon number; (C_{20}+C_{22}) *n*-alkanes prepared from the light slack wax and its saturates after

adduction. This may be attributed to that, the modifier which posses high carbon number leads to high crystal grow and filtration rate and consequently good characteristics.

Comparing the effect of addition of 1 wt.% of the pure mixtures non-polar modifiers (Table 3) having the percentages of C_{20}, C_{22}, C_{24} and C_{26} as those in the prepared ones. It can be noticed that, addition of pure mixtures of (C_{20}+C_{22}) and (C_{24}+C_{26}) of non-polar modifiers during fractional crystallization process leads to the same trend as the prepared ones in raising the efficiency of the deoiling process.

The SEM photographs of the isolated hard waxes (microcrystalline waxes) are parallel to the above findings whereas, the crystals of the hard waxes isolated by using butyl acetate solvent with addition of 1 wt.% of non-polar modifiers; pure mixtures and prepared concentrates of (C_{20}+C_{22}) & (C_{24}+C_{26}), gave higher crystal growing than the isolated hard wax without using a modifier. Meanwhile, the crystals of the hard waxes isolated with addition of 1 wt.% of non-polar modifiers; pure mixtures and prepared concentrates of (C_{24}+C_{26}) gave somewhat crystal growing and posses more holes than the others (Compare Figs. 1a, b, c, d &e).

Fig. 1: SEM photographs of the hard waxes isolated without using a modifier (a) and with addition of 1 wt.% of pure mixtures C_{20}+C_{22} (b) & C_{24}+C_{26} (c) and prepared non-polar modifier concentrates C_{20}+C_{22} (d) & C_{24}+C_{26} (e) n-alkanes

X-ray diffraction patterns confirm the previous results whereas, the addition of 1 wt.% of non-polar modifiers; the pure mixtures and prepared concentrates of (C_{20}+C_{22}) *n*-alkanes gave nearly the same crystal sizes but higher than the crystal size of the hard wax isolated without using a modifier. Meanwhile, the addition of the pure mixtures and prepared concentrates of (C_{24}+C_{26}) *n*-alkanes gave well observed crystalline patterns with the highest crystal sizes (501.1 & 540.2 Å, respectively) than the formers, taking in consideration the prepared concentrates of (C_{24}+C_{26}) *n*-alkanes have higher crystal size than the pure mixture of (C_{24}+C_{26}) *n*-alkanes (Tables 2 & 3 and Fig. 2). This means that, the prepared concentrates of (C_{24}+C_{26}) contain carbon atoms having higher carbon

number than C_{26}, whereas, the modifier which posses high carbon number leads to high crystal grow and consequently high crystal size.

Fig. 2: X-ray diffraction patterns of the hard waxes isolated without using a modifier (a) and with addition of 1 wt.% of pure mixtures C_{20}+C_{22} (b) & C_{24}+C_{26} (c) and prepared non-polar modifier concentrates C_{20}+C_{22} (d) & C_{24}+C_{26} (e) n-alkanes

3.1.1. Isolated wax type

Examining the type of all the isolated waxes from Alexandria crude petrolatum by using butyl acetate solvent without and with the addition of non-polar modifiers; the prepared concentrates or mixtures of pure *n*-alkanes of (C_{20}+C_{22}) & (C_{24}+C_{26}) (Tables 2 & 3); on the basis of ***TAPPI-ASTM*** equation [17, 18] and petroleum wax specifications [23]; it can be noticed that all the hard waxes isolated lie in the category of microcrystalline waxes. Although, the addition of non-polar modifier concentrate of the high carbon number; (C_{24}+C_{26}) *n*-alkanes prepared from the hard waxes isolated from light slack wax at 30^{o}C after adduction is the most suitable modifier concentrate in respect to the filtration rate and quality of the hard waxes. Nevertheless from economic point of view, the non-polar modifier concentrate; (C_{20}+C_{22}) *n*-alkanes prepared from the light slack wax after adduction is selected as a preferable modifier for deoiling the crude petrolatum at fractionating temperature of 20^{o}C, at the dilution solvent ratio of 8:1 by weight and by using butyl acetate solvent for saving energy and eliminating multi-stages of fractional crystallization process to produce hard waxes with nearly similar characteristics. Consequently, the hard (microcrystalline) and soft (slop) waxes were separated from Alexandria crude petrolatum at these conditions.

3.2. Production of petroleum products

Production of different types of petroleum products was achieved by using both the products of the solvent fractional crystallization of crude petrolatum; the hard wax (microcrystalline wax), the soft wax (slop wax) and it's saturate. The physical characteristics and molecular type composition of the isolated petroleum products are

represented in Table 4. It can be produced; beside the microcrystalline wax; the hardened ceresin wax and technical petrolatums from microcrystalline wax. Meanwhile, it can be produced the medicinal and ultrapure liquid petrolatums from the soft wax (slop wax) saturate.

Table 4: The physical characteristics and molecular type composition of the produced hard and soft waxes

3.2.1. Formulation of ceresins

There is a considerable interest to produce high melting microcrystalline waxes (ceresins) due to their many diverse applications all over the world. Thus, formulation of hardened ceresin wax was achieved through blending the microcrystalline wax with low density polyethylene polymer (LDPE). The effect of polyethylene polymer addition on the physical characteristics of the blends is represented in Table 5. It can be noticed that all the blends lie in the category of hardened ceresin wax grades, whereas, their congealing points are higher than 85^{o}C, viscosities at 98.9^{o}C >10 mm^{2}/s, oil contents < 2 wt.% and needle penetrations are between 5 to 15. The ceresin grades can be used in various applications such as paper industry, crayons, inks, coatings, electronic insulation and hot melt adhesives [4, 24].

Table 5: Effect of the addition of low density poly ethylene polymer (LDPE) on the physical characteristics and type of microcrystalline wax

3.2.2. Microcrystalline wax and heavy paraffin oil blends

Eight formulated blends were made by blending of microcrystalline wax with heavy paraffin oil (1-8 blends). The effect of the addition of heavy paraffin oil on the physical characteristics of microcrystalline wax is shown in Figure 3. From the data observed in Figure 3, it can be concluded that, the formulated blends (3–8) are lied within the limits of the standard specifications of *US Pharmacopoeia and National Formulary* of petrolatum [25] and can be used for industrial fields as lubrication of pharmaceutical

machines. Meanwhile, two of them (7 & 8); which have low melting points (38-46^{o}C) and high needle penetrations(200-300); are classified as liquid petrolatum according to the standard specifications of *Ultra Chemical Inc.* of liquid petrolatum [26].

Fig. 3: Physical characteristics for the formulated blends (1–8) containing microcrystalline wax and heavy paraffin oil according to the standard specifications of US Pharmacopoeia and National Formulary, 2011

3.2.3. Slop wax saturate and light paraffin oil blends

An attempt to produce other grades of petrolatums from slop wax saturates; which are mainly low melting iso- and cyclo-paraffins; by blending with the light paraffin oil. Thus, the soft wax produced during petrolatum deoiling process was subjected to liquid–solid column chromatography to separate aromatics free saturate components. Data are represented in Table 4.

It is obvious from the data that, the total aromatics are completely removed from the slop wax and consequently the total saturates reached 100 wt.% upon purification treatment, i.e. aromatics free wax is produced with lower congealing point than that of microcrystalline wax. Thus, the purified soft wax saturate can be blended with different percentages of light paraffin oil to produce different grades of medicinal petrolatum.

Six blends were made by blending of soft wax saturate with the light medicinal paraffin oil (9-14 blends). The effect of the addition of light paraffin oil on the physical characteristics of soft wax saturate is observed in Figure 4. According to the standard specifications of *US Pharmacopoeia and National Formulary***,** all the formulated blends (9–14) are classified as medicinal petrolatum and can be used in the pharmaceutical, cosmetic and food fields. Meanwhile, three of them (12–14) are also within the limits of standard specifications of *Ultra Chemical Inc.* of ultrapure liquid petrolatum as they have extra low congealing points (38-46^{o}C) and high penetration values (200-300 dmm at 25^{o}C) and can be used in formulating bar soaps, creams, lotions and hair preparations [26].

Fig. 4: Physical characteristics for the formulated blends (9–14) containing slop wax saturate and light paraffin oil according to the standard specifications of US Pharmacopoeia & National formulary 2011 and Ultra Chemical Inc.

Moreover, by testing the formulated blends (3-8) and (9-14), it can be concluded that all the formulated blends confirm the other specifications of petrolatum according to the definition of *US Pharmacopoeia & National Formulary* (Table 6). On the other hand, the remainder oil; after the separation of the saturates from the slop wax by liquid-solid chromatographic technique; contains an appreciable amounts of mono- and di-aromatic constituents (39.91 & 60.09 wt.%, respectively) (Table 4) which can be used as extender oil in ink and rubber manufactures [27].

Table 6: The standard specifications of US Pharmacopoeia & National Formulary 2011 for the formulated blends

4. Conclusions

The study shows that, from economic point of view, the non-polar modifier concentrate; (C_{20}+C_{22}) *n*-alkanes prepared from the light slack wax after adduction is selected as a preferable modifier to raise and improve the efficiency of crude petrolatum deoiling at fractionating temperature of 20^{o}C, at the dilution and washing solvent ratios of 8:1 and 2:1 by weight, respectively and by using butyl acetate solvent for saving energy and eliminating multi-stages fractional crystallization process to produce hard waxes lie in the category of microcrystalline waxes with nearly similar characteristics.

Production of different types of petroleum products was achieved by using both the products of solvent fractional crystallization of crude petrolatum; the hard wax (microcrystalline wax) and the soft wax (slop wax). Different grades of hardened ceresin; having high congealing points; were formulated by addition of 2 to 10 wt.% of low density poly ethylene (LDPE) with the separated microcrystalline wax. The ceresin grades can be used in various applications such as paper industry, crayons, inks, coatings, electronic insulation and hot melt adhesives.

Fourteen formulated blends of petrolatum were prepared based on the produced microcrystalline wax and soft wax saturate with heavy and light paraffin oils, respectively. It can be concluded that, twelve formulated blends (3-8) and (9-14) are lied within the limits of the standard specifications of *US Pharmacopoeia and National Formulary 2011* of petrolatum and medicinal petrolatum, respectively. They can be used for industrial fields as lubrication of pharmaceutical machines and in most of the pharmaceutical, cosmetic and food fields, respectively. Meanwhile, the two formulated blends (7 & 8) and the three others (12–14) are classified as liquid and ultrapure liquid petrolatums, respectively according to the standard specifications of *Ultra Chemical Inc.* besides the limits of *US Pharmacopoeia and National Formulary 2011*. On the other hand, the remainder oil produced which contains appreciable amounts of mono- and di-aromatic constituents; can be used as extender oil in ink and rubber manufactures.

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Table 1

Characteristics	Test method	Alexandria crude petrolatum
Congealing point, ^{o}C	ASTM D-938	66
Kinematic viscosity, 98.9^{o}C	ASTM D-445	14.25
Refractive index, 98.9^{o}C	ASTM D-1747	1.4478
Density, 70^{o}C	ASTM D-1418	0.8262
Mean molecular weight	ASTM D-2502	680
Oil content, wt. %	ASTM D-721	11.01
Needle penetration, 25^{o}C	ASTM D-1321	93
Sulfur content, wt. %	ASTM D-4294	0.65
Color	ASTM D-1500	4.0
Molecular Type Composition		
Total saturates, wt.		73.83
Total aromatics, wt. %		26.17
Mono-aromatics, wt. %		12.14
Di- aromatics, wt. %		14.03

Table 2

Characteristics	Hard waxes isolated					
	Without modifier	By using prepared non-polar modifier concentrates				
		$(C_{20}+C_{22})$*			$(C_{20}+C_{22})$**	$(C_{24}+C_{26})$***
		0.5 %	1 %	1.5 %	1 %	1 %
Yield on crude petrolatum, wt.%	54.67	47.89	47.33	47.38	47.74	47.10
Congealing point, ^{0}C	74	76.5	77	77	77	77
Kinematic viscosity at 98.9 ^{0}C, mm^2/s	13.00	11.56	11.51	11.50	11.52	11.48
Refractive index at 98.9 ^{0}C	1.4396	1.4364	1.4364	1.4361	1.4368	1.4365
Refractive index by TPPI-ASTM eq^n	1.4315	1.4324	1.4325	1.4325	1.4325	1.4325
Mean molecular weight	751	774	782	784	780	786
Oil content, wt.%	1.16	0.19	0.16	0.16	0.16	0.14
Needle penetration at 25 ^{0}C	25	19	17	17	17	15
Color	2.0	2.0	2.0	2.0	2.0	2.0
Filtration rate, kg/m^2.h	415	529	562	562	561	569
Crystal size (X-ray diffraction)	316.3	385.1	412.2	412.5	412.0	540.2
Type of wax		Microcrystalline wax				

$(C_{20}+C_{22})$*: Non-polar modifier concentrate prepared by adduction of light slack wax
$(C_{20}+C_{22})$:** Non-polar modifier concentrate prepared by adduction of light slack saturates
$(C_{24}+C_{26})$*:** Non-polar modifier concentrate prepared by adduction of the hard waxes isolated from light slack wax at 30^{0}C
eq^n: Equation

Table 3

Characteristics	Hard waxes isolated		
	Without modifiers	By using 1 wt.% of pure *n*-alkane mixtures	
		n-C_{20}+n-C_{22}	*n*-C_{24}+n-C_{26}
Yield on crude petrolatum, wt.%	54.67	48.33	47.93
Congealing point, ^{0}C	74	76.5	77
Kinematic viscosity at 98.9 ^{0}C, mm^2/s	13.00	11.53	11.51
Refractive index at 98.9 ^{0}C	1.4396	1.4373	1.4372
Refractive index by TPPI-ASTM equation	1.4315	1.4324	1.4325
Mean molecular weight	751	775	782
Oil content, wt.%	1.16	0.17	0.14
Needle penetration at 25 ^{0}C	25	17	16
Filtration rate, kg/m^2.h	415	560	565
Crystal size (X-ray diffraction)	316.3	411.0	501.1
Type of wax	Microcrystalline wax**es**		

Table 4

Characteristics	Isolated petroleum products			
	Micro-crystalline Wax	Slop wax	Slop wax saturate	Remainder oil
Yield on crude petrolatum, wt.%	47.33	52.67	29.92	22.75
Congealing point, ^{0}C	77	55	63	-----
Kinematic viscosity at 98.9 ^{0}C, mm^2/s	11.51	16.00	11.00	-----
Refractive index at 98.9 ^{0}C	1.4364	1.4579	1.4319	-----
Specific gravity, 60 ^{0}C	0.8221	0.8435	08308	-----
Mean molecular weight	782	557	682	-----
Oil content, wt. %	0.16	13.00	0.10	-----
Needle penetration at 25 ^{0}C	17	-----	-----	-----
Cone penetration at 25 ^{0}C	-----	80	45	-----
Sulfur content, wt.%	0.23	1.12	-----	-----
Color	2.0	8.0	0.0	-----
Molecular Type Composition				
Total saturates content, wt.%	84.20	56.80	100	0.00
Total aromatics content, wt.%	15.80	43.20	0.0	100
Mono-aromatic content, wt.%	15.80	17.24	0.0	39.91
Di-aromatic content, wt.%	-----	25.96	0.0	60.09

Table 5

Characteristics	Micro-crystalline wax	Micro-crystalline wax with LDPE				
		2%	4%	6%	8%	10%
Congealing point, ^{0}C	77	86	90	93.5	97	99
Oil content, wt.%	0.16	0.07	0.06	0.03	0.01	0.01
Needle penetration at 25 ^{0}C	17	11	9.5	8	7.5	7
Kinematic viscosity, 98.9 ^{0}C, mm^2/s	11.51	11.88	12.34	12.68	13.00	13.22
Mean molecular weight	782	795	804	818	830	843
Color	2.0	2.0	2.0	1.5	1.5	1.0
Type of wax	-----	Hardened ceresin				

Table 6

US Pharmacopoeia & National Formulary 2011 specifications	Group 1						Group 2					
	3	4	5	6	7	8	9	10	11	12	13	14
Solubility: Insoluble in water and ethanol: Soluble in chloroform, in ether & in petroleum spirit 40-60^{0}C	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
Acidity: No red or pink color to 0.1 ml of methyl orange	N	N	N	N	N	N	N	N	N	N	N	N
Alkalinity: The solution doesn't acquire a pink color to one drop of phenolphthalein	N	N	N	N	N	N	N	N	N	N	N	N
Organic acids: For production of a sharp pink and end point not more than 400 µL of 0.1 N sodium hydroxide is required	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
Color: There is no fluorescence when the sample being held directly against a white background.	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
Residue on ignition: It volatilizes without emitting an acrid odor and on ignition yields not more than 0.1% of residue and 0.05% for white petrolatum	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
Fixed oils, fats and rosin: No oily or solid matter separates	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass	pass
UV absorbance, 290 nm	-----	-----	-----	-----	-----	-----	0.096	0.088	0.079	0.070	0.061	0.051

N: Neutral

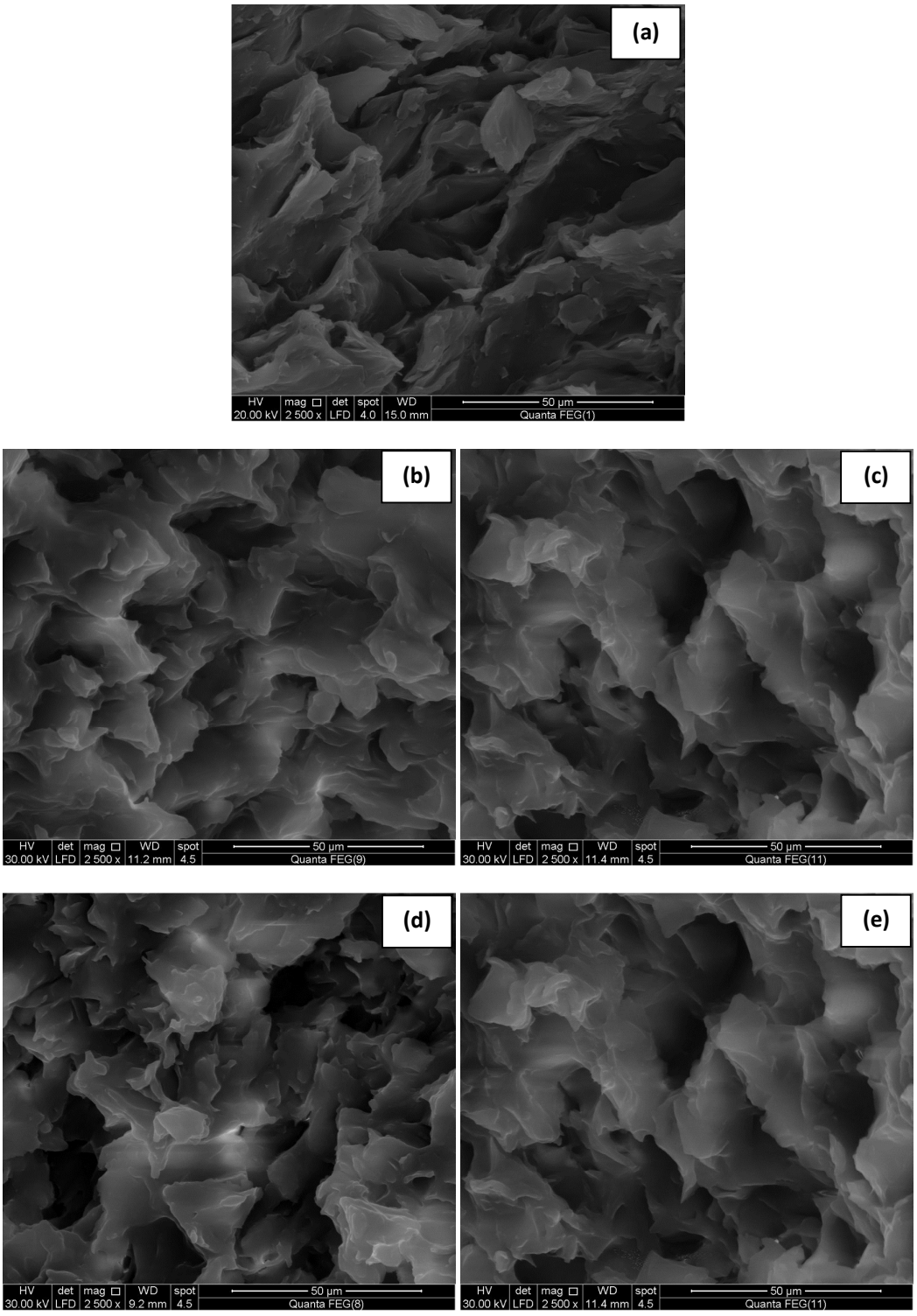


Fig. 1

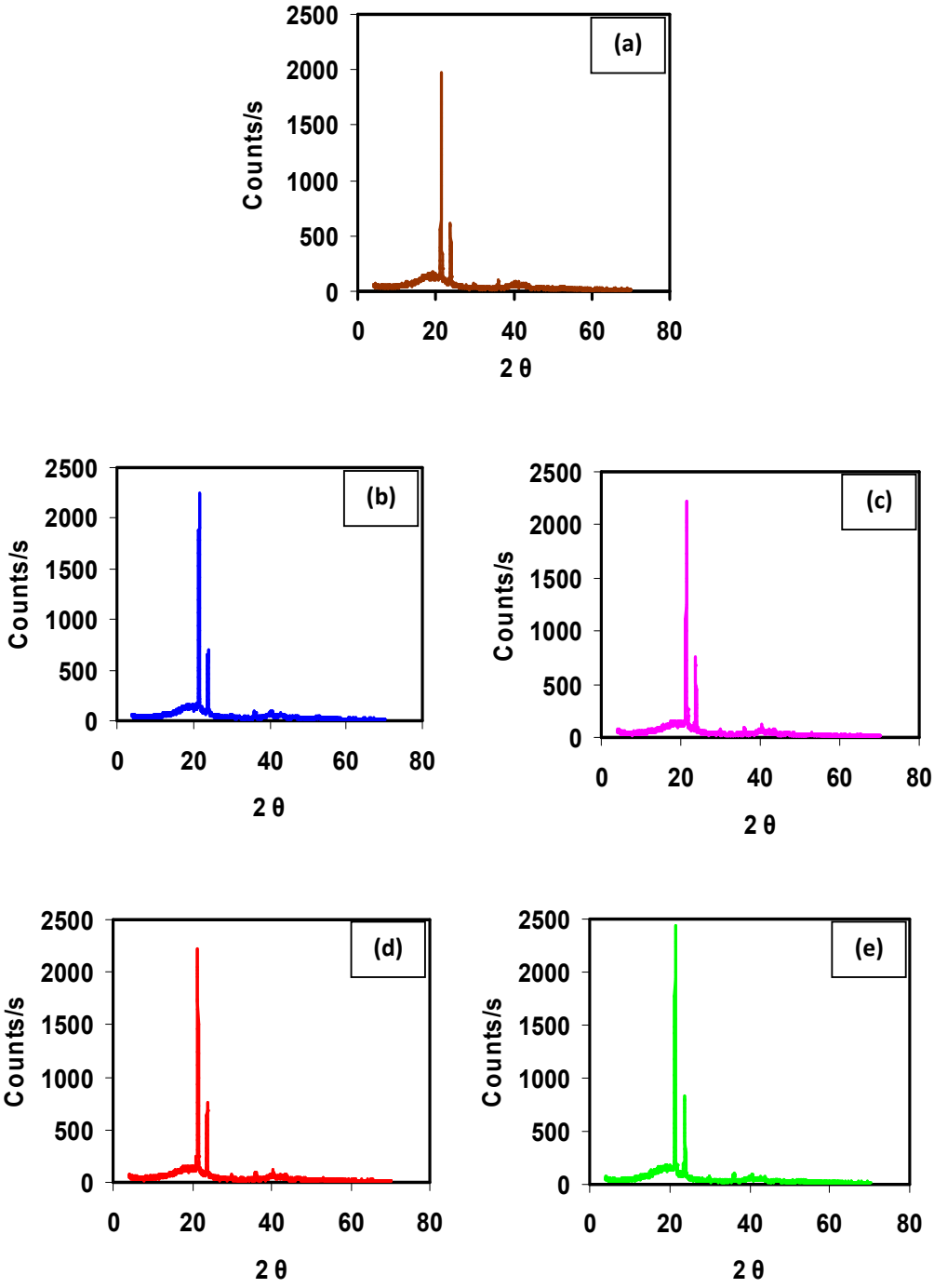


Fig. 2

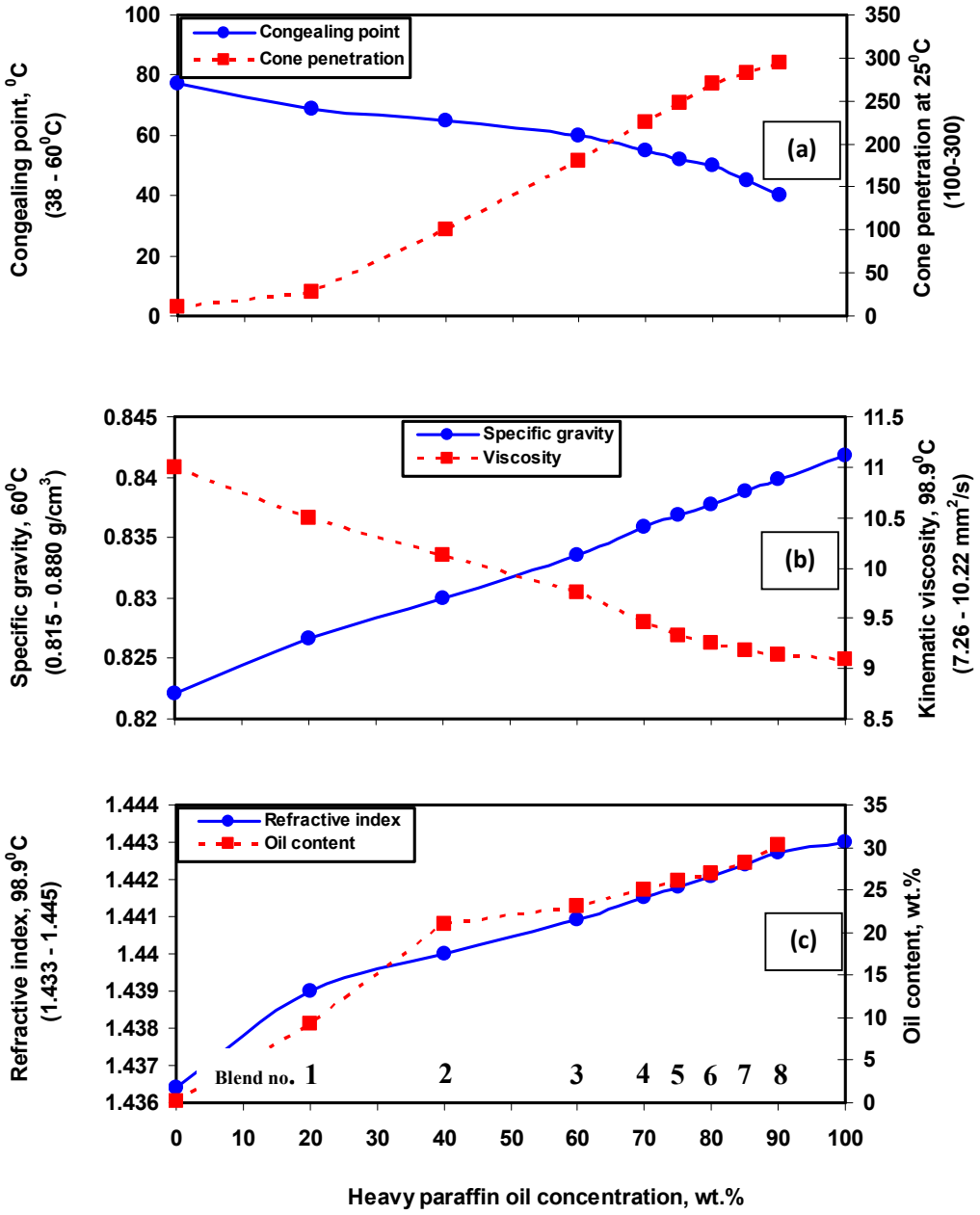
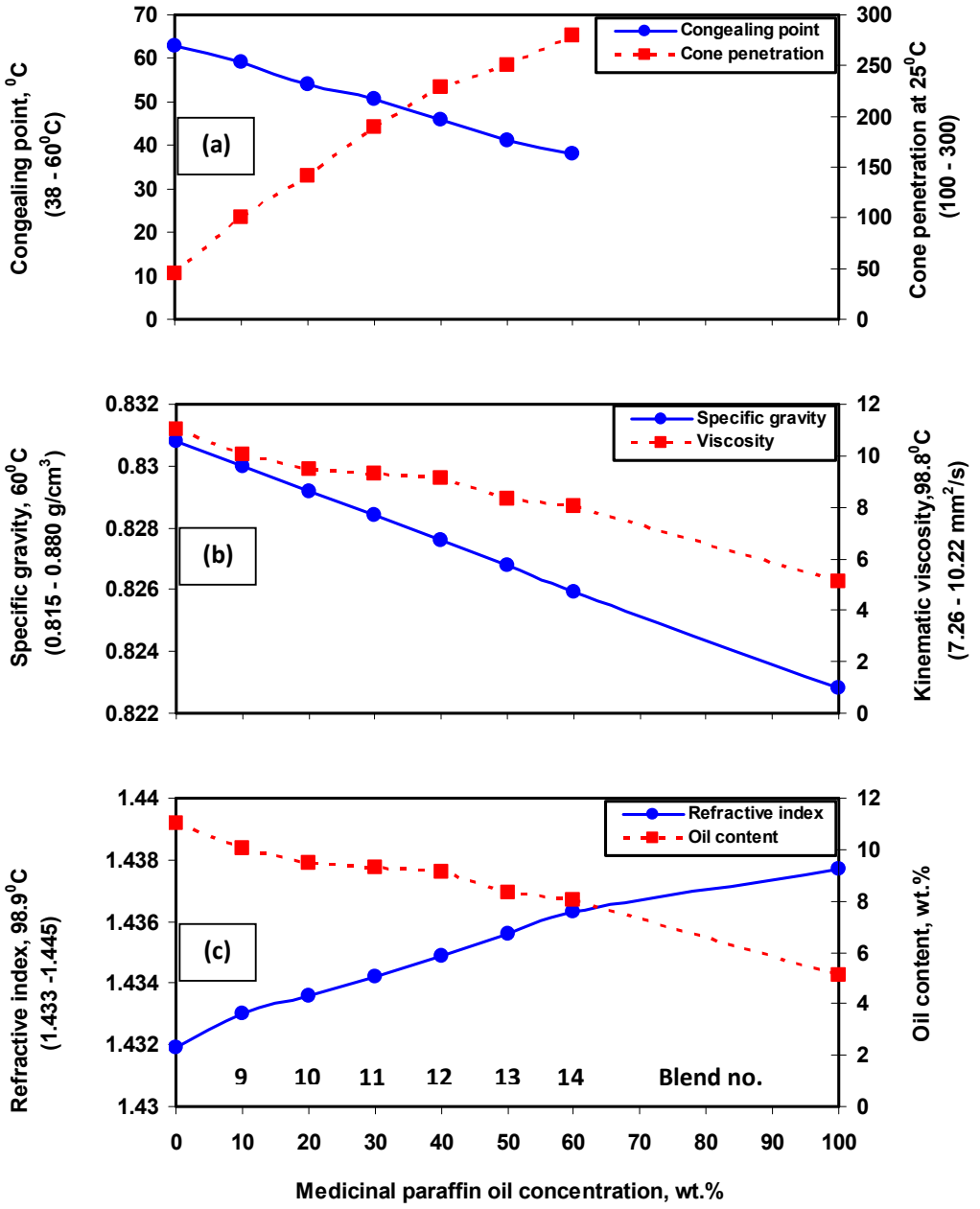


Fig. 3



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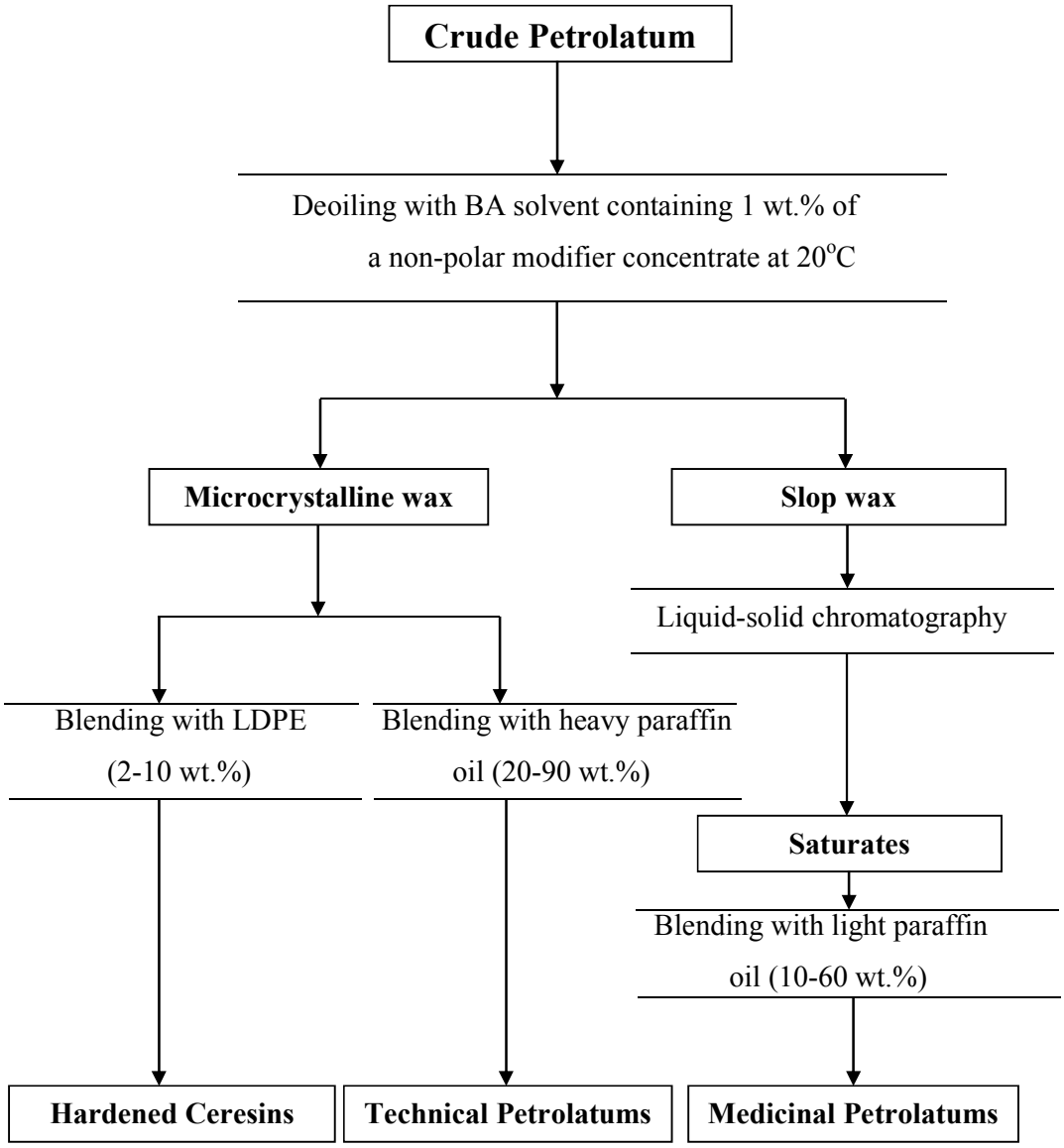

Scheme 1

Graphical Abstract

Deoiling of crude petrolatum was intensified by addition of 1 wt.% of non-polar modifier concentrates separated from slack wax waste; (C_{20}+C_{22}) *n*-alkane mixture. X-ray diffraction patterns observed that, the addition of 1 wt.% of non-polar modifier concentrates gave hard waxes having higher crystal sizes than the hard waxes separated without using a modifier.