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Studies in Properties of Microcrystalline and Paraffin Waxes with the Help of Gas Chromatography (GC), DSC, FT-IR and by Conventional Methods

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ABSTRACT

In this paper different properties of two paraffin waxes and two microcrystalline waxes have been studied using GC, DSC, FT-IR and conventional method of testing .Petroleum waxes are mixtures of hundreds and thousands of different hydrocarbons. Paraffin wax contains C18 to C40 straight chain saturated normal hydrocarbons whereas microcrystalline waxes are predominantly highly branched C27 to C68 hydrocarbons. Petroleum waxes were characterized by gas chromatography, Differential Scanning Calorimetry and FT-IR. The resulting GC, DSC and FT-IR data were correlated with various physical properties of the waxes, such as kinematic viscosity, needle penetration, melting point, refractive index, and flash point.

Keywords: GC, DSC, FT-IR, Petroleum Waxes, Properties.

I. INTRODUCTION

Petroleum waxes are complex mixtures of high molecular weight saturated hydrocarbons, predominantly alkanes in the range C18–C65. Paraffin waxes are produced from the vacuum distillates in lubrication oil refineries. The following de-waxing process of the vacuum distillates leads to by-products called slack waxes. Their oil residues have to be further reduced by different deoiling processes to oil contents < 0.5% . These raw paraffin waxes are then refined by hydro-finishing processes. During hydrogenation hetero- and aromatic substances are modified to harmless hydrocarbons. The obtained white and odour free fully-refined paraffin waxes are mainly used in food grade applications in a lot of different industries automotive, candle, cosmetics, polishing, rubber etc.

Micro-crystalline waxes are not obtained from vacuum distillation cuts, as the macro- and intermediate-paraffin waxes, but from the vacuum residue. The raw material for the production of microcrystalline wax is petrolatum or brightstock. Brightstock is derived from the heavy vacuum residue with the aid of propane de-asphalting, followed by de-aromatisation and solvent de-waxing.

The suitability of the wax for a particular industry depends upon the physical properties like melting point, melt viscosity, hardness, and crsytallinity among others. For example, in applications such as the paper industry, crystallinity of wax is an important parameter, whereas for hot-melt adhesives the viscosity is more important. For the application of coatings the hardness of the wax is an important parameter. For the paraffin wax hardness is one of the most important properties for its application in various industries. For the dental application the melting point is an important. Each application requires specific performance properties, and waxes are tailor-made for a particular application by the use of processes such as fractionation and blending.

In this paper the carbon number distribution have been studied using GC, the thermal transitions have been studied using DSC, the distribution of -CH- have been studied using the FT-IR. The properties like Penetration Index, melting point, kinematic viscosities, refractive index and flash point have been studied using ASTM methods of testing. These properties have been correlated with the data obtained from the GC, DSC and FT-IR analysis.

II. EXPERIMENTATION AND OBSERVATIONS:

The DSC was carried out using ASTM D 4419. The experiment has been done using aluminium container for taking sample and heated at a controlled rate of 5°C/Min in inert atmosphere. The GC was carried out using ASTM D 5442, Penetration Index of the wax was carried out using ASTM D 1321 and the Flash point of the samples was done by ASTM D 92. The melting point was done by ASTM D87. The kinematic viscosity was carried out using ASTM D 445. The observations have been tabulated in the following table.

2.1. Observation table

2.1.1. Conventional Analysis

Sr. No	Properties	FRPW	SRPW	SRMCW	FRMCW
1	R.I. @ 80˚C ASTM D 1218	1.426	1.429	1.444	1.443
2	Cong. Point, ˚C ASTM D 938	62	63	76	78
3	Melting Point, ˚C ASTM D 87	61	65	78	80
4	Drop Melting Point, ˚C ASTM D 127	66	66	81	82
5	Flash Point, ˚C ASTM D 92 (COC)	208	212	224	226
6	Pen. Index @ 25˚C ASTM D 1312	1.2	1.0	1.4	1.2
7	Viscosities @ 100˚C, cSt ASTM D 445	3.9	5.3	12.31	13.5

2.1.2. DSC Analysis

Sr. NO.	Properties	FRPW	SRPW	SRMCW	FRMCW
1	Peak Temperature, ˚C	66.10	69.10	56.70	67.80
2	Energy, j/g	171	156	178	157

2.1.3. Gas Chromatography analysis (GC)

Sr. NO.	Properties	FRPW	SRPW	SRMCW	FRMCW
1	n - Paraffin's (%)	74.713	76.418	68.754	42.061
2	iso - Paraffin's (%)	25.223	23.582	31.246	57.895

2.1.4. FTIR Analysi

2.1.4.1. FTIR Analysis of Fully Refined Microcrystalline wax

S.NO	Wave number	Compound or Functional Groups
1	2924	-CH3 –asymmetric stretching of CH3
2	2854	(med) C-H (Aldehyde C-H)
3	2359	CO2(Atmospheric absorption)
4	1718	C = C, V(C=C)
5	1466	CH2 bend
6	1375	CH3 symmetric deformation
7	896	Strong =C-H and =CH2
8	722	CH2 rocking

2.1.4.2. FTIR Analysis of Fully Refined Paraffin Wax

S.NO	Wave number(cm-1)	Compound or functional group
1	2921	-CH3 –asymmetric stretching of CH3
2	2341	CO2 (Atmospheric absorption)
3	1718	C = C, V(C=C)
4	1461	CH2 bend
5	1379	CH3 symmetric deformation
6	1125	Impurities on KBr disks
7	889	Strong =C-H and =CH2
8	730	CH2 rocking

2.1.4.3. FTIR Analysis of Semi refined Paraffin Wax

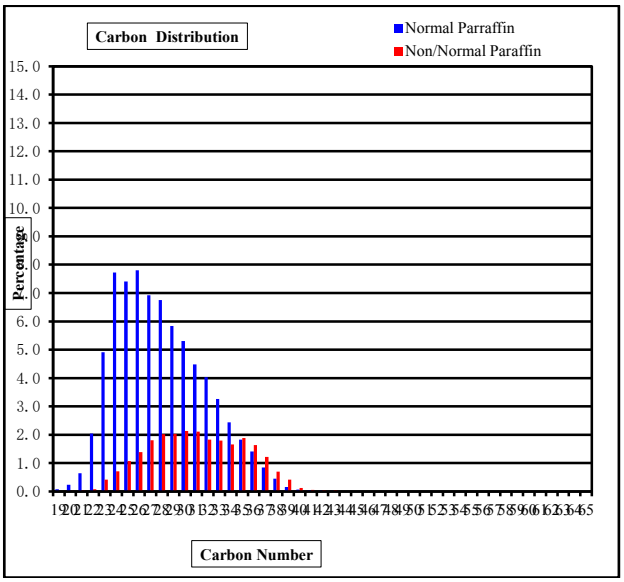
S.NO	Wave number(cm-1)	Compound or functional group
1	2921	-CH3 –asymmetric stretching of CH3
2	2341	CO2 (Atmospheric absorption)
3	1718	C = C, V(C=C)
4	1461	CH2 bend
5	1125	Impurities on KBr disks
6	889	Strong =C-H and =CH2
7	730	CH2 rocking

2.1.4.4. FTIR Analysis of Semi refined Microcrystalline Wax

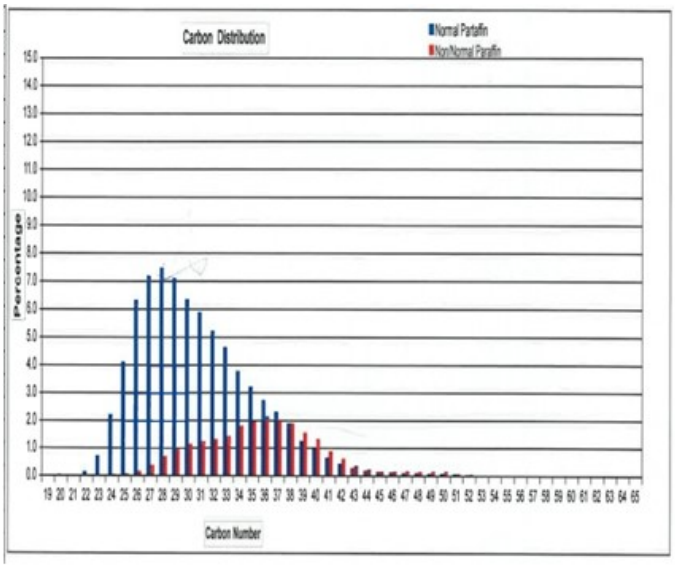
S.NO	Wave number	Compound or Functional Groups
1	2924	-CH3 –asymmetric stretching of CH3
2	2854	(med) C-H (Aldehyde C-H)
3	2359	CO2(Atmospheric absorption)
4	1718	C = C, V(C=C)
5	1466	CH2 bend
6	1375	CH3 symmetric deformation
7	896	Strong =C-H and =CH2
8	722	CH2 rocking

2.2 Graphs

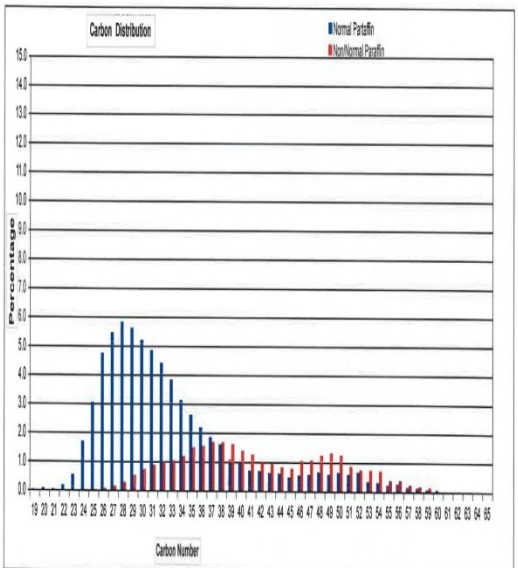
2.2.1. GC Graphs



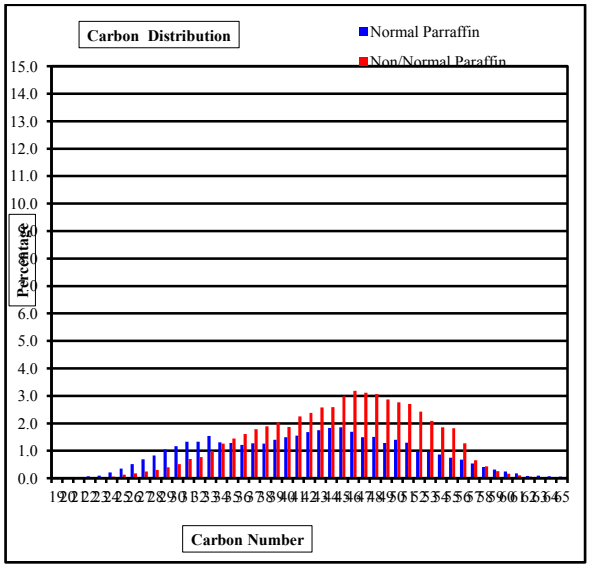
1. GC of FRPW



2. GC of SRPW

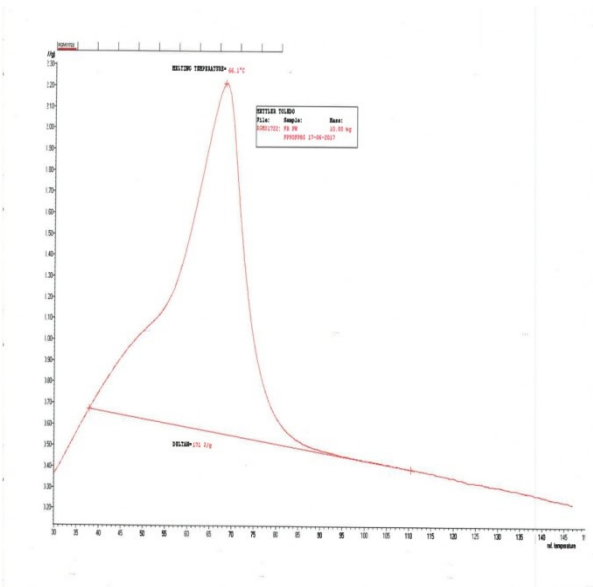


3. GC of SRMCW

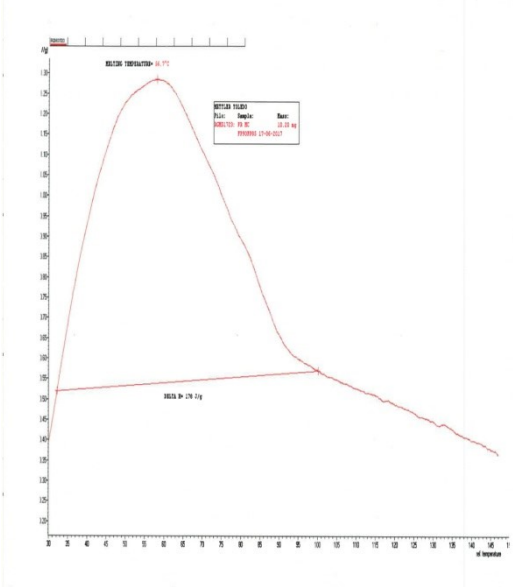


4. GC of FRMCW

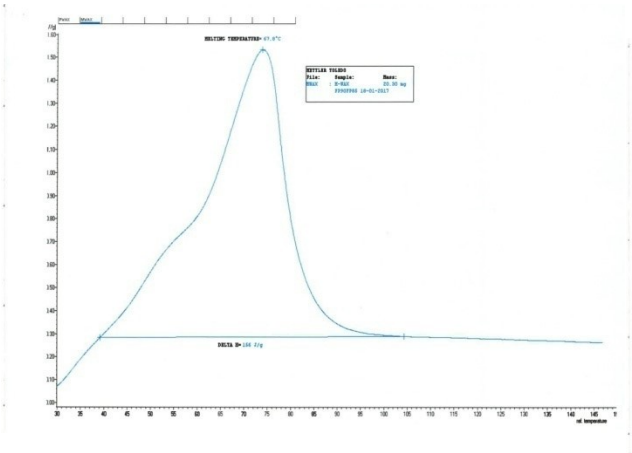
2.2.2 DSC Graphs:



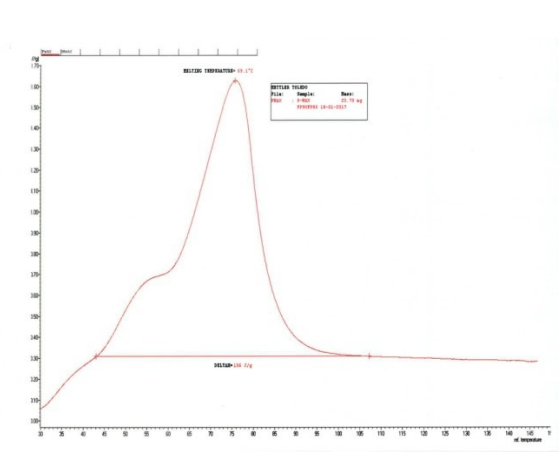
1. Graph of FRPW



2. Grapht of FRMCW

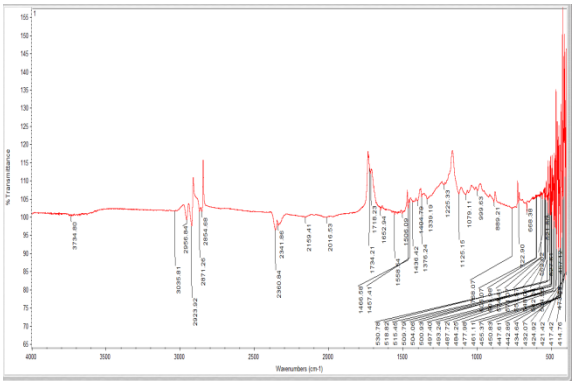


3. Graph of SRPW

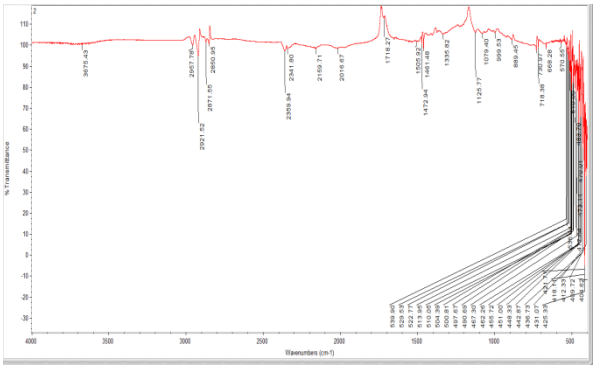


4. Graph of SRMCW

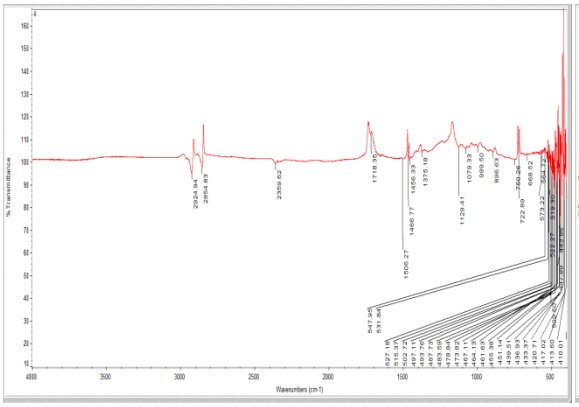
2.2.3. FTIR Graphs:



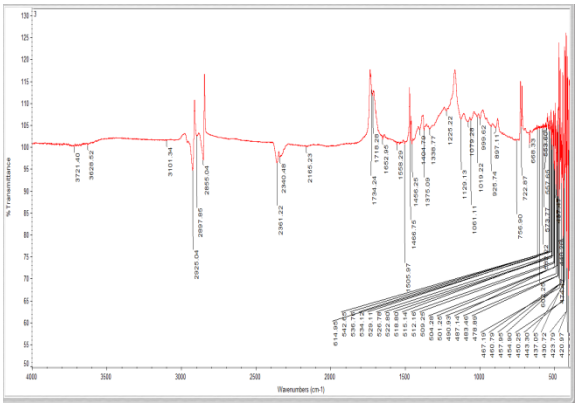
1. FTIR of FRPW



2. FTIR of SRPW



3. FTIR of SRMCW



4. FTIR of FRMCW

III. Results and Discussion

3.1. Gas Chromatography

From GC of Fully Refined Paraffin Wax we can say:

1. Fully Refined Paraffin Wax contains n-paraffin in range C_{19} to C_{49} and Iso- Paraffin in range C_{20} to C_{44}.
2. After minutely observing it can be seen that C_{21} to C_{38} n-Paraffins are more dominant and accounts for 72%.
3. C_{23} to C_{39} iso-paraffin are more dominant and accounts for 25%.
4. C_{26} n-paraffin present maximum and accounts for 7.798% and C_{30} iso –paraffin present maximum and accounts for 2.134%.
5. Actual content of n-paraffin is 74.713% and iso-paraffin is 25.223%.
6. Fully Refined Paraffin Wax obtained from top spindle cut in LOBS manufacture and its kinematic viscosity is approximately 3 cSt.
7. By adding n-paraffins and iso-paraffins total paraffins hydrocarbon are 99.936 and by deducting from 100 we get 0.064% are other than paraffins.

From GC of Semi Refined Paraffin Wax we can say:

1. Semi Refined Paraffin Wax contains n-paraffin in range C_{19} to C_{55} and Iso- Paraffin in range C_{20} to C_{55}.
2. After minutely observing it can be seen that C_{23} to C_{41} n-Paraffins are more dominant and accounts for 75%.
3. C_{28} to C_{42} iso-paraffin are more dominant and accounts for 21%.
4. C_{28} n-paraffin present maximum and accounts for 7.498% and C_{36} iso –paraffin present maximum and accounts for 2.145%.

5. Actual content of n-paraffin is 76.418% and iso-paraffin is 24.582%.
6. Semi Refined Paraffin Wax obtained from light neutral cut in LOBS manufacture and its kinematic viscosity is approximately 5 cSt.

From GC of Semi Refined Microcrystalline Wax we can say:

1. Semi Refined Microcrystalline Wax contains n-paraffin in range C_{19} to C_{60} and Iso- Paraffin in range C_{20} to C_{59}.
2. After minutely observing it can be seen that C_{23} to C_{52} n-Paraffins are more dominant and accounts for 65%.
3. C_{29} to C_{55} iso-paraffin are more dominant and accounts for 30%.
4. C_{28} n-paraffin present maximum and accounts for 5.849% and C_{37} iso –paraffin present maximum and accounts for 1.711%.
5. Actual content of n-paraffin is 68.754% and iso-paraffin is 31.246%.
6. Semi Refined Microcrystalline Wax obtained from heavy neutral cut in LOBS manufacture and its kinematic viscosity is approximately 8 cSt.

From GC of Fully Refined Microcrystalline Wax we can say:

1. Fully Refined Microcrystalline Wax contains n-paraffin in range C_{19} to C_{65} and Iso- Paraffin in range C_{22} to C_{63}.
2. After minutely observing it can be seen that C_{26} to C_{58} n-Paraffins are more dominant and accounts for 40%.
3. C_{30} to C_{58} iso-paraffin are more dominant and accounts for 56%.
4. C_{45} n-paraffin present maximum and accounts for 1.858% and C_{48} iso –paraffin present maximum and accounts for 3.185%.
5. Actual content of n-paraffin is 42.061% and iso-paraffin is 57.895%.
6. Fully Refined Microcrystalline Wax obtained from heavy neutral cut in LOBS manufacture and its kinematic viscosity is approximately 11 cSt.
7. By adding n-paraffins and iso-paraffins total paraffins hydrocarbon are 99.956% and by deducting from 100 we get 0.044% are other than paraffins.

3.2. DSC:

DSC measures the transition temperature of waxes. The operating temperature range extends from 15 to 150^{o}C. The melting point of FRPW is usually in between 58 to 62˚C and SRPW is usually in between 65 to 68˚C by cooling curve method of melting point and by DSC peak temperature (when wax melts completely) is 66.1˚C and 69.1˚C in our samples of FRPW and SRPW, for FRPW and SRPW values are more or less in same range by both DSC and Cooling curve method, but for other waxes we studied the melting point by DSC peak temperature are less than by the cooling curve method except for the carnauba and oxidized polyethylene wax where they are otherwise. The difference in melting point by cooling curve method and DSC method is due to difference in amount and distribution of normal paraffin, iso-paraffin and cyclo-paraffins. The difference in the distribution of carbon number is different in all the four waxes as justified by the GC results. The difference in the DSC peak temperature and the melting point by cooling curve method is because of above reason.

3.3. FT-IR:

The FTIR spectra of petroleum waxes which reveals the presence of carbon-hydrogen stretching and bending absorption bands in the range of 1,000 to 3,000 cm−1.The symmetric carbon-hydrogen bending absorption of the CH3 group at 1,379 cm−1, the CH deformation around 1,462 cm−1,and the CH2 rocking absorption band at 727 cm−1 confirm the linear saturated aliphatic structure of the wax. The FT-IR spectra also help in determines the composition of the waxes by giving idea about the hydrocarbons present in it.

3.4. Conventional Analysis:

The R.I. of the microcrystalline wax, are higher than the Paraffin wax because of the presence of more iso-paraffins and aromatic content in it as justified by the GC analysis. The flash point by COC of FRPW, SRPW, SRMCW and FRMCW are in the agreement with the literature data. The MCW have been obtained from the bottom cut having higher flash point were as paraffin waxes have been obtained from uppermost cut having lower flash point as can be observed by looking into the viscosities of these waxes. The penetration index of all

the four waxes are different, their values depends on their melting point but waxes having same melting point have different penetration index depending upon the oil content and the distribution of hydrocarbon in the respective wax.

IV. CONCLUSION

The melting point of all the four waxes by cooling curve method are more or less in same range as by DSC method. The other properties like R.I., flash point, penetration index results are in agreement with the GC results which gives the information about the carbon number distribution and carbon number range. Also with the FT-IR results which gives the details about functional group.

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