

CHEMICAL EVALUATION OF PETROLEUM WAXES AVAILABLE IN PAKISTAN

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Locally available waxes Chinese wax, Attock wax, 100NHVI, 650NMVI and BSHVI were analysed/evaluated using physico-chemical methods, statistical methods and instrumental techniques. Nitrogen and sulphur compounds were present in 100 NHVI, 650 NMVI, and BSHVI which can be removed by acidic treatment. The combined olefinic and aromatic content of the waxes was found to be as follows: Chinese wax, 2.43%, Attock wax, 3.12%, 100NHVI, 12.50%, 650 NMVI, 37.23%, and BSHVI, 56.71% Chinese wax was found to be paraffinic, Attock wax contained naphthenic compounds, 100 NHVI contained both naphthenic and aromatic compounds, 650 NMVI was found to be high in naphthenic compounds, and BSHVI was found to be high in aromatic compounds. The content of n-alkanes and their carbon number distribution were Chinese wax, 93.63 and C₁₈ to C₃₆; Attock wax, 69.23 and C₂₀ to C₃₉; 100 NHVI, 48.14 and C₁₆ to C₃₅; 650 NMVI, 17.07 and C₁₆ to C₄₃; BSHVI, 5.39 and C₁₆ to C₄₄. The use of these waxes in candle making, emulsions and as a chemical raw material for fatty acids, alcohols, chlorinated hydrocarbons is discussed.

INTRODUCTION

Petroleum waxes are important raw material for the manufacture of candles, fatty acids, fatty alcohols, chlorinated hydrocarbons [1] and corrosion inhibitor additives [2]. The waxes are also used in coating paper, printing inks, textile, leather manufacture and pharmaceuticals [1]. The suitability of a wax for a specific application is determined by its physical properties like, hardness, plasticity, tensile strength and chemical nature i.e. paraffinic, naphthenic, aromatic, carbon chain length etc.

The waxes are isolated from the waxy crudes which may contain up to 20% wax [3] by deparaffination with urea prior to distillation [4]. The non-waxy crudes which may contain as low as 0.3 per cent wax [5], on the other hand, are fractionated and the waxes are recovered from the lube oil fractions by urea adduction or solvent extraction [6]. The solvent extraction procedure is practiced in Pakistan.

A refined wax is marketed by the Attock Oil Refinery Limited, Rawalpindi. The slack waxes produced by the National Refinery Limited; Karachi are used primarily as boiler fuel. Thus about 25000 tons of refined and slack wax are available in Pakistan annually [7]. In order to meet

countries demand, about 10,000 tons of paraffin wax were imported in 1981-82 [8]. The imports for the proceeding years are shown in Table 1.

The nature of wax depends upon the origin of the crude oil and the technique of wax production. The present

Table 1. Import of paraffin wax in Pakistan.

Year	Quantity in metric tons	Value in Rupees
1977-78		14931000 ¹
1978-79		31461000 ¹
1979-80	4,987	28192335 ²
1980-81	7,609	57193954 ³
1981-82	9,542	65096193 ⁴
1981-Oct.'82	1,939	12415830 ⁵

1. Foreign Trade, Statistics Division, Govt. of Pakistan Vol. 6, No. 12, June 1979 page 79-80. 2. Statistical Bulletin, Federal Bureau of Statistics, Statistics Division Govt. of Pakistan 28, No. 7 July 1980 p.130. 3. *ibid.*, 29, No.8 Aug. 1981 p.140. 4. *ibid.*, 30, No.8 Aug. 1982 p. 169. 5. *ibid.*, 30, No. 12 Dec. 1982 p. 186.

work was undertaken to characterise and evaluate the available refined and slack waxes, to determine the methodology for the refining of slack waxes to suit specific applications, to find better usage of the slack waxes other than as fuel and to evaluate the refined waxes as a raw material for physical and chemical applications.

MATERIALS AND METHODS

A. Materials. Wax varieties available in Pakistan were collected for evaluation in June 1978. A white refined wax which was procured from the local market in Lahore, had been imported from the Peoples Republic of China. This wax originates from Chinese petroleum crude and will be designated as Chinese wax. The refined wax from Attock Oil Refinery Limited originates from Pakistani Petroleum crude and will be referred to as Attock wax. The three slack waxes from National Refinery Limited Karachi bear the identification marks 100 NHVI, 650 NMVI and BSHVI and originate from Arabian light crude ex-Kuwait with a wax content of about 3% [7]. Molecular Sieves (5A, 1/16 in pellets from Alltech Associates) were activated in a vacuum oven at 250° for 6 hours and then stored in desiccator.

B. General Analytical Methods. Carbon/hydrogen, sulphur and average molecular weights were determined by Galbraith Laboratories, Inc. Knoxville, Tenn. Nitrogen was determined by chemiluminescence using an Antek Model 771 pyroreactor and Antek Model 720 digital nitrogen detector. The nitrogen content was determined from the standard curve. Refractive indices were measured at 70° using a refractometer made by Bausch and Lomb Optical Company, Rochester N.Y. The densities were determined at 70° using specific gravity bottle. The weight of water was determined at 20°. The d_4^{70} was calculated from the tables. UV spectra were recorded in cyclohexane solution using a Cary 17 spectrophotometer. Infrared spectra were obtained on 5% (weight to volume) solution of samples in carbon tetrachloride, using 0.5 mm sodium chloride sealed cells and a Perkin Elmer Model 621 double-beam IR spectrophotometer using solvent compensation.

C. Isolation of Saturates by ASTM D-1019-68 (78) [9]. Half a gram of the wax was dissolved in cyclohexane (15 ml), stirred, and cooled in an ice bath. More solvent was added if the solution gelled on cooling. A solution of P₂O₅ in sulphuric acid (1 ml) was added drop-wise, and the mixture was stirred at 0° for 2 hours, allowed to warm to room temperature, and then stirred for 1 hour. After allowing to stand for a while the reaction product separated into two layers except for BSHVI which remained homogene-

ous. The organic layer was coloured slightly in Chinese and Attock waxes but much deeper in BSHVI. The product was centrifuged for 10 to 30 min., depending upon the colour of the cyclohexane layer. The product from BSHVI had to be diluted with water and extracted with more cyclohexane. This cyclohexane solution was filtered over silica gel (10 to 40 times by weight of the wax sample) to get a clear solution. The yields are Chinese wax, 97.57, Attock wax, 96.88; 100 NHVI, 87.50; 650 NMVI, 62.77; BSHVI, 43.28. The samples are designated as saturates or with a suffix "S".

D. Separation of n-Alkanes and Branched Plus Cyclic Alkanes. The wax (0.5 g) was dissolved in cyclohexane (100 ml) and was refluxed with molecular sieves (10 g). The progress of absorption was followed by running GLC's of aliquots from the solution at time intervals. Absorption was complete in 72 hours. The sieves were filtered, washed with hot cyclohexane thrice, and soxhlet extracted with 2-propanol: benzene (2:1) for 6 hours to remove the components adhering to the surface of sieves. The filtrate washings and extract were combined and the solvent was removed to give the unabsorbed material. The air dried sieves were ground, placed in a teflon beaker with a stirring bar, covered with cyclohexane, cooled in an ice bath and digested by dropwise addition of 24% HF (40 ml). When the sieves dissolved to give a silver gray solution, more cyclohexane was added and the layers separated. The organic layer was washed with water to neutral and passed through neutral alumina (5g, AG-7 Bio-Red Laboratories, 100-200 mesh). Removal of the solvent from this filtrate gave n-alkanes. The recoveries were higher than 96%, but they were normalised to 100%.

E. Gas-liquid Chromatography. GLC was performed using Hewlett Packard Model 5700 A Gas Chromatograph having a flame ionisation detector. A stainless steel column (305 cm x 0.32 cm) packed with 3% Dexsil 300, coated on 80-100 chromsorb WAW (supelco) was used for the separations. Helium 30 ml/min was employed as the carrier gas; whereas hydrogen (30 ml/min) and air (240 ml/min) were used for the flame. The signals were registered with a Rikadenki Recorder Model B-281. The attenuator was set at 10x8 and the chart speed was 15 cm/h peak areas were recorded using a Hewlett Packard 3373 B integrator. Area under each peak was calculated as the per cent of the total area. For the determination of minimum number of components present in each wax and the carbon number distribution the oven temperature of the gas chromatograph was programmed from 190 to 300° at 2°/min and was held at 300° until the baseline was stable. 0.15 μ l of a 20% solution of sample in cyclohexane was injected on to

the column. For the quantitative estimation of n-alkanes, the oven temperature was programmed from 150 to 300° with a hold at 300° until the baseline was stable 0.1 µl of a 20% solution in cyclohexane was injected on the column. The identification of peaks was done by comparing the retention times and coinjecting the standard samples.

F. Combined Gas Chromatography-Mass Spectrometry. Combined GLC/MS investigations were performed with a Hewlett Packard 5700A Gas Chromatograph coupled directly to a KRATOES (AEI) MS-12 mass spectrometer. A stainless steel support coated open tubular column (15.2 m x 0.05 cm) with Dexsil 300 as a stationary phase was used for the separation. Helium at a flow rate of approximately 5 ml/min was used as the carrier gas. GLC/MS data acquisition and processing was performed using a Finigan INCOS Model 2300 mass spectrometer. The oven temperature was programmed from 160 to 300° at 2°/min. The temperature was held at 300° until the baseline was established. A sample size of 0.02 µl was injected directly on to the column without a splitter. The mass spectra were recorded at 70 eV ionizing potential and 8 KV ion accelerating potential at a magnetic scan rate of 4 seconds per decade. Components were identified by library matching, when possible, and by interpretation of the fragmentation pattern of the mass spectra. The results are shown in Table 5.

RESULTS AND DISCUSSION

The refined waxes- Chinese wax and Attock wax are white solids whereas the slack waxes-100 NHVI, 650 NMVI and BSHVI are tacky semi solids. The saturates obtained from slack waxes were also tacky semi-solids.

The melting points of wax samples were determined in a capillary tube and are reported in Table 2. The higher melting range of Attock Wax than Chinese wax, indicates the presence of higher homologues in the former than in the latter. The observed melting ranges for the slack waxes are much broader than refined waxes. The standard procedure for determining the melting points of waxes[10] could not be followed due to the semi-solid and tacky nature of the slack waxes.

The elemental composition of wax samples and their saturates are shown in Table 2. It is seen that the Chinese wax and Attock wax are totally composed of carbon and hydrogen whereas the slack waxes, 100 NHVI, 650, NMVI and BSHVI contain non-hydrocarbon compounds containing sulphur and nitrogen. The nitrogen compounds were totally removed during acid treatment.

The average molecular weights of wax samples, satu-

rates, and the n-alkanes corresponding to the average molecular weights calculated by the usual formula ($C_n H_{2n+2}$), are shown in this Table 2. If the waxes were mainly composed of gradually distributed n-alkanes, as they should be, then the physico-chemical constants of this calculated n-alkane for a particular wax sample should be the same as those determined experimentally for that wax sample. The presence of molecules other than n-alkanes will cause a deviation in these constants which will be discussed below:

The hydrogen/carbon ratio which is inversely proportional to unsaturation, cyclic and aromatic nature, is the highest in Chinese wax and the lowest in BSHVI (Table-2). Comparing these ratios with those for the calculated n-alkane, one observes deviations which are least in Chinese wax and highest in BSHVI. The H/C ratio of the saturates from 100 NHVI and BSHVI is higher than parent waxes but is still lower than the calculated n-alkane. This shows the presence of cyclic/naphthenic compounds in addition to the aromatic/olefinic compounds.

The refractive indexes of the wax samples were determined at 70° and are reported in Table 2. The refractive index of the calculated n-alkane for each wax at 70° was taken from the literature[11], and are shown in Table 2. Some of the values were calculated from the refractive indexes available at other temperatures[11-12], using the following equation[13].

$$n_D^{70} = n_D^t + (t - 70) \times \frac{dn}{dt}$$

The increment for refractive index ($\frac{dn}{dt}$) calculated from the given values was found to be 0.0004.

The observed refractive indices of the wax samples are compared with the expected ones. The observed values were found to be higher than the expected ones except in Attock wax. The difference was the least in Chinese wax and the highest in BSHVI. These differences may be due to the presence of sulphur containing, naphthenic, or aromatic compounds which usually have higher refractive indices than the n-alkanes of the same molecular formula.

Further evidence to the presence of aromatics and naphthenic compounds was obtained from the density determinations. The density of a material depends not only on the atomic values of elements present in it but also on the voids between various molecules. As a result the densities of cyclic/aromatic compounds are higher than those of the aliphatic of the same carbon number. In n-alkanes the density is a function of chain length e.g. d_4^{20} for n-tetracosane and n-pentacosane are 0.7991 and 0.8012 respectively[12]. Table 2 shows the d_4^{70} of these waxes ranging

Table 2. Elemental analysis and physical constants of waxes and their saturate fractions.

Description of wax	Carbon %	Hydrogen %	Sulfur %	Nitro gen ppm	Atomic ratio H/C	Av. mol. wt. ¹	Alkane corresponding		Melting point in °C	Refractive index		Density	
							to av. mol. wt.			observ- ed	Lit/calcu- lated	observ- ed	calcu- lated
Chinese wax	85.41	14.57	—	—	2.03	344	C _{24.4} H _{50.8}		50-57	1.4295	1.4283	.7662	.7752
Attock wax	85.60	14.43	—	—	2.01	492	C ₃₅ H ₇₂		48-62	1.4392	1.4462	.7868	.7930
100 NHVI	85.26	14.26	0.40	2	1.99	345	C _{24.5} H ₅₁		24-49	1.4444	1.4293	.7900	.7759
100 NHVI-S ³	85.37	14.50	171 ⁴	—	2.02	284	C _{20.11} H _{42.22}		26-53	1.4364	1.4229	.7770	.7636
650 NMVI	85.33	13.88	0.64	12	1.94	443	C _{31.5} H ₆₅		20-50	1.4573	1.4359	.8308	.7885
650 NMVI-S	86.37	13.55	347 ⁴	—	1.87	330	C _{23.43} H _{48.86}		20-50	1.4480	1.4270	.8021	.7732
BSHVI	85.66	13.30	1.16	303	1.85	508	C _{36.11} H _{74.22}		36-65	1.4671	1.4470	.8428	.7942
BSHVI-S	85.90	13.96	112 ⁴	—	1.93	384	C _{27.5} H ₅₇		36-65	1.4490	1.4324	.7986	.7742

¹ Average molecular weight determined by VPO in benzene. ² Refractive index of the n-alkane calculated on Av.mol.wt.basis.

³The suffix S means the saturate fraction obtained from that particular wax. ⁴Concentrations in parts for million (ppm).

between 0.7662 and 0.8428. Keeping in view the melting point of these waxes, all other values except paraffin wax are higher than standard ones (d_4^{63} for paraffin wax m.p. 49.5 and 60.5° is 0.776 and 0.783 respectively [14]). The densities of the calculated hydrocarbon corresponding to average molecular weight were calculated from Traubes equation[14]:

$$d = \frac{M}{\Sigma AV + 25.9}$$

Where d is the density at 15°, M is molecular weight of the hydrocarbon, AV is the molecular volume (atomic volume of C, 9.9, H, 3.1) and 25.9 is a constant termed CO volume. These values were corrected to 70° by the following equation[13].

$$d_4^{70} = d_4^{15} + (15-70) \frac{dd}{dt}$$

$\frac{dd}{dt}$ for most of n-alkanes was found to be between 5.90×10^{-4} to 6.0×10^{-4} . Application of this procedure to n-tetracosane gave d_4^{70} , 0.7746 (observed 0.7682). The higher observed values in slack waxes and their saturates show the presence of naphthenic and or aromatic compounds.

A qualitative indication for the presence of aromatic compounds was derived from a small band at 1600 cm^{-1} in the IR spectra of these waxes, specially in 100 NHVI, 650 NMVI, and BSHVI. The quantitative comparison was

more readily obtained from the ultraviolet absorption. All the waxes exhibited similar absorption patterns with slight changes in the position of maxima. The absorption increased as the spectrum was scanned from 400 to 200 nm. The extinction co-efficients were calculated on the basis of 1 g wax per liter. Chinese and Attock waxes showed λ_{max} at 258 nm and ϵ as 10.2 and 10.3. The values for other varieties were 100 NHVI λ_{max} 261, ϵ 149; 650 NMVI, λ_{max} 262 nm ϵ 238.3 and BSHVI, λ_{max} 262, ϵ 643.

The chemical evidence for the presence of olefins/aromatic compounds was obtained by the reaction of sulphonating reagent with these waxes. The loss of weight could be correlated with the ϵ values, if not quantitatively.

The information gathered from the experimental data shows that all the waxes and the saturated fractions obtained from slack waxes contain paraffinic, olefinic, naphthenic and aromatic compounds. The slack waxes contain heterogeneous molecules containing sulphur and nitrogen in addition to the hydrocarbon molecules. Therefore the distribution of carbon in various class compounds was calculated by statistical methods described in the following paragraphs.

A number of statistical methods, based on melting point (m.p.) average molecular weight (M.W.) refractive index (n) density (d) and viscosity (η) have been developed [15-19]. These methods determine the paraffinic carbon C_P naphthenic carbon C_N ; aromatic carbon, C_A ; carbon in rings, C_R ; the total number of rings/molecule, R_T ; aromatic rings/molecule, R_A and naphthenic rings/molecule R_N .

The method developed by the Melpolder *et al.* [16] and Gross and Grodde [17] require the ASTM melting points and viscosity measurements. Due to the presence of aromatics and broad range of melting points, these methods could not be applied in the present study.

The results obtained from n-d-M method through a series of equations [18] are shown in Table 3. In case of Chinese and Attock waxes the R_T and C_R values are negative. Calculating R_T and C_R using literature values for n-alkanes also produces negative values. The R_T values for 100 NHVI wax (0.02) is lower than the R_T value of the saturates (2.8) obtained from 100 NHVI. This value does not agree with the lack of UV absorption of latter sample. The results obtained from 650 NMVI and BSHVI and corresponding saturates seem reasonable. Both R_T and C_R values are higher in original samples than in their corresponding saturates. The R_A value in BSHVI (0.68) is higher than in 650 NMVI (0.21) showing that BSHVI wax is much more aromatic than 650 NMVI. This is also substantiated by UV absorption. The R_N in 650 NMVI is higher (1.39) than in BSHVI (0.85). The R_N values decrease greatly for corresponding saturates, which certainly should contain all the naphthenic materials. This result is not readily explained. The observed discrepancies are perhaps related to the fact that Waterman ring analysis is applicable to petroleum fractions, distillates, and extracts containing all classes of compounds but fail in cases where concentrations of specific hydrocarbon types are studied.

The Hersch-Fenske method [19], which is a modification of n-d-M method, is applicable to waxes that contain no aromatics. This method was applied to Chinese wax, Attock wax, and saturates from 100 NHVI, 650 NMVI, and BSHVI. The refractive indices at 20° required in these equations were calculated from refractive indexes at 70° (because these waxes are not liquid at 20°) by the equation described above. The R_N , C_N , and per cent C_N values obtained are shown in Table 3. Chinese wax with an n-alkane content of 93.63% (Table 4) shows a C_N and R_N of -2 and -0.27 respectively. The Attock wax with an n-alkane content of 69.23% has an R_N of 0.39 and a C_N of 2.74. These values are in accordance with the equal UV absorption of Chinese and Attock wax but higher density of the later (Table 2). Comparing the results obtained for saturates from 100 NHVI, 650 NMVI, and BSHVI, the lowest value R_N is for 100 NHVI (0.18), then BSHVI (1.34), and finally 650 NMVI (1.35). These values are in the same order as concluded from their densities. Taking into account the material recovered during acid treatment, the 650 NMVI has a higher R_N than BSHVI. This result was also shown by the n-d-M method [18].

A knowledge of the individual constituents in wax samples is important to determine their possible applications and to modify them to suit specific requirements. For the preliminary investigation the waxes were subjected to GLC. The minimum number of components resolved in this

Table 3. Distribution of carbon atoms in wax samples as determined by n-d-M and Hersch-Fenske methods.

Description of wax	Rings total R_T	Rings aromatics R_A	Rings naphthenic R_N	Carbon in rings C_R	Carbon aromatic C_A	Carbon naphthenic C_N	Carbon paraffinic C_P
Chinese wax	-0.01	-0.09	-0.08 (-0.27) ¹	-1.1	-2.39	-2.50 (-2.00)	100.11
Attock wax	-0.22	0.21	-0.43 (0.39)	-3.41	3.84	-7.25 (2.74)	103.41
100 NHVI	0.02	0.49	-0.47	3.23	12.41	-9.18	96.77
100 NHVI-S	0.28	0.27	0.01 (0.81)	7.89	8.50	-0.61 (5.05)	92.11
650 NMVI	1.60	0.21	1.39	27.14	4.16	22.98	72.86
650 NMVI-S	0.80	0.33	0.47 (1.35)	18.88	8.94	9.94 (7.84)	81.12
BSHVI	1.53	0.68	0.85	21.87	11.26	10.61	78.63
BSHVI-S	0.36	0.47	-0.11 (1.34)	7.43	10.68	-3.25 (7.78)	92.57

¹ Values according to Hersch-Fenske method

Table 4. Percentages of normal branched-cycles alkanes using molecular sieves as absorbent.

Description of wax	Recovery	Absorbed	Unabsorbed
Chinese wax	96.03	93.63	6.37
Attock wax	98.30	69.23	30.77
100 NHVI	96.01	48.14	51.86
100 NHVI-S	97.85	55.20	44.8
650 NMVI	98.50	17.07	82.93
650 NMVI-S	100	27.25	72.75
BSHVI	99.58	5.39	94.61
BSHVI-S	96.77	12.25	87.75

chromatography were: Chinese wax, 60; Attock wax, 64; 100 NHVI 80; 650 NMVI, 84; BSHVI, 74. In addition to these peaks all the waxes showed envelopes due to unresolved components in their chromatograms. The envelopes was the smallest in Chinese wax and the largest in BSHVI among all the samples investigated. This data indicates that the refined as well as slack waxes are contaminated with other unresolved components which may be isoparaffins, olefins, naphthenes and aromatics as has been reported in literature but to a small extent[5]. Therefore, the n-alkanes were isolated by molecular sieve absorption.

Several procedures are described in literature [20-23]. However, the one described by Washall *et al.* [20] was preferred because it has been claimed to be the most suitable for paraffin and micro-crystalline waxes without prior removal of aromatics and other components. We experienced that the unabsorbed material was contaminated with additional components due to the interaction of decalin molecules on molecular sieves. Replacement of decalin by cyclohexane although required longer time but gave better results. The n-alkane contents are given in Table 4. Chinese wax has the highest n-alkane content and BSHVI the lowest n-alkane content among all the wax samples.

The percentage of individual n-alkanes obtained from all the wax samples was estimated by GLC and are shown in Fig.1. The odd and even numbered hydrocarbons are distributed in natural fashion. The n-alkane range for the wax samples is: Chinese wax, C₁₈ to C₃₆; Attock wax C₂₀ to C₃₉; 100 NHVI, C₁₆ to C₃₅; 650 NMVI, C₁₆ to C₄₃ and BSHVI C₁₆ to C₄₄. The distribution curves of the Chinese wax and 100 NHVI wax are very identical. The maxima in both these curves differs only by one carbon atom. With successful refining the 100 NHVI could yield a wax very similar to Chinese wax in so many applications. The dis-

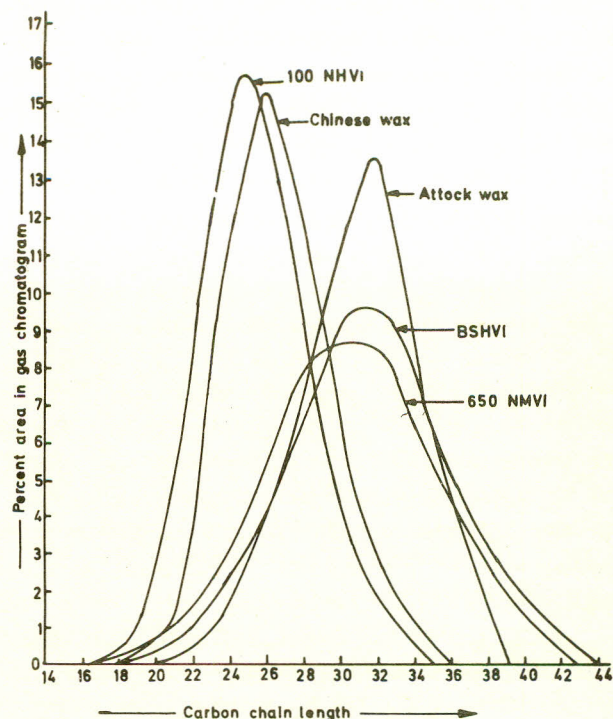


Fig. 1.n - Alkane distribution of wax sample.

tribution curve for Attock wax is also similar to Chinese wax but has a wider range of hydrocarbons. The most predominant component is C₃₁. This is one carbon atom higher than observed for the 650 NMVI and BSHVI samples. The distribution curves for 650 NMVI and BSHVI are flat and show a much wider range of hydrocarbons than the other samples studied. Refining of these two varieties may yield a product lower in melting point than Attock wax but the products may be good oxidation substrates.

The unabsorbed portions from these waxes was subjected to combined gas chromatography/mass spectrometry. The unabsorbed fractions were expected to contain branched/cyclic hydrocarbons, olefins, aromatics, and other components containing nitrogen, oxygen and sulphur. Interpretation of the spectra obtained for these samples was difficult due to un-resolved envelopes GLC/MS of the un-absorbed material from the saturates obtained from these waxes were also not resolved. The lack of resolution in these samples may be explained on the basis of:

a. Complex nature of the samples. (b) Necessity of using the column at the maximum recommended temperature for the support. At this temperature resolution is decreased. (c) Loss of resolution in the transfer line between the gas chromatography and the mass spectrometer.

Study of the results indicated that the envelopes are comprised of closely boiling un-resolved components which

Table 5. Branched alkane isomers of the wax samples determined by GC/MS.

Molecular formula	Chinese wax	Attock wax
C ₂₅ H ₅₂	++	-*
C ₂₆ H ₅₄	+	-
C ₂₇ H ₅₆	+	-
C ₂₈ H ₅₈	+	+
C ₂₉ H ₆₀	+	+
C ₃₀ H ₆₂	+	+
C ₃₁ H ₆₄	+	+
C ₃₂ H ₆₆	+	+
C ₃₃ H ₆₈	+	+
C ₃₄ H ₇₀	-	+
C ₃₅ H ₇₂	-	+

*+ means detected; *- means not detected.

are primarily olefins and branched alkanes. Some of the components in Chinese and Attock waxes which were resolved sufficiently for identification are listed in Table 5. Branching occurs with a methyl group at 2,3 or 4 position which is in accordance with the findings of Rossini, Mair, and Glasgow[24] that the slightly branched paraffins predominate over highly branched ones and the 2-and 3-methyl derivatives are the most abundant. The olefines C₂₉H₅₈, C₃₀H₆₀ and C₃₂H₆₄; an aromatic compound C₃₁H₄₃, and a tricyclic C₂₅H₄₈; were also detected in Attock wax. The presence of this naphthenic compound in this sample is in accordance with its higher density (Table 2).

CONCLUSION

All the waxes characterized during the current study may be suitable as corrosion inhibitor additives after proper oxidation, provided they do not contain other corrosive or abrasive materials.

Chinese and Attock waxes are suitable for candle-making, packing, coating, and emulsion. The 100 NHVI, 650 NMVI, and BSHVI waxes have either low melting points or sticky due to the presence of branched and cyclic hydrocarbons. These waxes may be added to other raw materials such as polyethylene and then processed for candle-making as claimed in German patent[25].

As a chemical raw material for manufacture of chlorinated hydrocarbons, fatty acids, fatty alcohols, and surfactants, the waxes must comprise of n-alkanes only. The

presence of branched/cyclic alkanes is undesirable because they yield unstable chlorinated compounds which impair the quality of the product. The fatty acids, alcohols, detergent produced from these branched/cyclic alkanes are not bio-degradable and cause pollution problems. Moreover, the detergent properties of a soap or surfactant are related to chain length, with the most desirable being 12 to 18 carbons in length. Chinese wax may be most suitable for chlorinated hydrocarbons. Chinese and Attock waxes may serve the purpose for fatty acids and fatty alcohols although the presence of some branching in Attock wax may preclude these uses. The 100 NHVI material may also be suitable if it is refined by some physical process such as sweating, urea extraction, or aluminosilicate absorption; a chemical process like acid treatment; or a combination of processes. After proper refining this may yield a wax of the same quality as Chinese wax and thus help substituting the import.

The other two varieties, 650 NMVI and BSHVI, contain much lower percentage of n-alkanes (17.7 and 5.39 per cent respectively). These low amounts may not be economical to process for usage as waxes. After the removal of unsaturates from these varieties (which amount to 37.22 and 55.04 per cent respectively) they may be good raw materials for impregnating corrugated board containers, antirust compositions, or as a source of iso acids used for lubricating purposes. They might also be used for the production of C₅ to C₁₀ acids, which have an increasing demand for the esterification of polyols[26].

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