

CHAPTER III

EXPERIMENTAL

The objective of this research was to produce the microcrystalline waxes from bright stock. The production was established by sweating process and improved the properties of wax by oxidation process. These waxes were analyzed to determine the oil content, acid number, and some physical properties as follows:

1. Physical properties of microcrystalline waxes

Some physical properties of the microcrystalline waxes were determined such as drop melting point according to ASTM D 127-93 [15], kinematic viscosity at 100 °C according to the ASTM D 445-94 [21], penetration at 25 °C according to ASTM D 1321- [20], microscopic study and appearance.

2. Other components

3.1 The determination of oil content in microcrystalline wax followed ASTM D 721-93 [16].

3.2 The determination of acid number in oxidized microcrystalline wax followed ASTM D 1386-83 [17].

3.1 Materials and Chemicals

1. Bright Stock was obtained from BP Oil.
2. Stearic acid and sodium hydroxide were obtained from BDH.
3. Cobalt nitrate and xylene were obtained from Merck.

4. MEK (Methyl Ethyl Ketone) was obtained locally.

3.2 Apparatus and Instruments

1. Air pump	New Lion model NL12p
2. Analytical Balance	Mettler model PJ 3600, readability to 0.01 mg
3. Automatic Flash Point Tester	ISL model CFP 92
4. Automatic Viscometer and Viscosity Index	Cannon CAV-4
5. Filter Bottle	100 ml capacity, with fine sintered glass disk
6. Hotplate	Corning Stirrer/Hotplate
7. Microscope	Olympus
8. Oven	Memmert model UM 400
9. Penetrometer	Stanhope-Seta
10. Pycnometer	Kimax model 15113-25, 25 ml capacity
11. Reactor	PARR model 4842
12. Temp. Controlled Bath for oil content	Thomas Kagaku model TRL 115
13. Temp. Controlled Bath for specific gravity	Advantec model LCH 100
14. Thermometer	Temperature range from 0°C to 100 °C

3.3 Procedure

3.3.1 Wax Sweating Process

Bright Stock which was laid on the sieve had sweater pan supported under the waxes. Then, it was brought into the oven, which was set at sweating temperature. 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. The wax began to melt and the first liquid fraction drained from the bed through into the oven pan. The liquid drippings was collected in the bottom of the oven and drained into pan. The waxes were investigated for the optimum temperature and time for wax sweating. As each range of temperature, the wax on the sieve was tested for its drop melting point (ASTM D 127), oil content (ASTM D 721), and the percent yield.

3.3.2 Method of Wax Oxidation

3.3.2.1 Preparation of Cobalt stearate

Stearic acid (14 g) was melted and added to a solution of sodium hydroxide (4.4 g NaOH in 100 ml distilled water). The reaction mixture was heated and stirred with a mechanical stirring at over 100 °C. Then, the solution of cobalt nitrate (7.13 g $\text{Co}(\text{NO}_3)_2$ in 30 ml distilled water) was added into the mixture slowly and water was removed over 30 min to give pink solid (10 g, 65.3% yield).

3.3.2.2 Oxidation Procedure

The 300g of sweated wax were placed in a reactor with 1%, 2%, and 5% of cobalt stearate for each batch. The mixture was heated and stirred (speed 600 r.p.m.) at 110 °C and bubbled with air. When the reaction was finished, the mixture was then cooled to about 85-90 °C and the catalysts were filtered. This reaction was studied for the optimum percent catalyst and time for oxidation. The quality of oxidized wax was monitored by drop melting point (ASTM D127) and acid number (ASTM D1386).

3.4 Investigation of wax properties

Properties of wax were measured by the following test method as shown in Table 3.1.



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Table 3.1 The properties of wax

Testing Method	Standard
Drop Melting Point	ASTM D 127
Oil Content	ASTM D 721
Acid number	ASTM D 1386
Congealing Point	ASTM D 938
Specific gravity & Density @ 25 °C	ASTM D 70
Penetration @ 25 °C	ASTM D 1321
Kinematic Viscosity @ 100 °C	ASTM D 445
Flash Point	ASTM D 92
Estimate Molecular Weight	ASTM D 2502
Characteristic & Microscopy	-

3.4.1 Determination of Drop Melting Point (ASTM D127) [15]

Melting point of petroleum waxes in this research was studied by following ASTM D 127-3. The waxes were deposited on two thermometer bulbs by dipping chilled thermometers into melted waxes. The thermometers bearing the waxes were placed in test tubes and heated by means of water bath until the waxes melted and first drop fell from each thermometer bulb. Average of temperatures at which these drops fall was the drop melting point of the wax.

3.4.2 Determination of Oil Content in Wax (ASTM D127) [16]

The oil content of a wax may have significant effects on several of its properties, such as strength, hardness, flexibility, scuff resistance, coefficient of friction, coefficient of expansion, melting point and oil straining.

The oil content of petroleum waxes was determined by following ASTM D 721-93. A portion of 1 g of wax was dissolved in 15 ml of MEK into a test tube; and this solution was homogenized by stirring in a heating bath. The solution was cooled by a cooling bath, wiped dry on outside test tube with a cloth and weigh to the nearest 0.1 g. The solution was cooled to $-32\text{ }^{\circ}\text{C}$ to precipitate the wax, immersed in the mixture with filter stick which had previously been cooled by placing it in the test tube and holding at $-32\text{ }^{\circ}\text{C}$ in the cooling bath for 10 min, and filtered by applying air pressure with flow rate approximately 500 ml/min to the filtration assembly. A 4 ml of filtrate was collected in a weighing bottle, and weighed it to the nearest 10 mg. The oil content of the filtrate was determined by evaporating the MEK at $35\text{ }^{\circ}\text{C}$ with the air for 30 min, and weighing the residue at nearest 0.1 mg.

Calculate the amount of oil in the wax as follow

$$\text{Oil in wax, weight \%} = (100.A.B / C.D) - 0.15 \dots\dots \text{Equation 3.1}$$

Where: A is weight of oil residue, g,

B is weight of wax, g,

C is weight of solvent, g, obtained by subtracting weight of test tube plus wax from weight of test tube and contents,

D is weight of solvent evaporated, g, obtained by subtracting weight of weighing bottle plus oil residue from weight of weighing bottle plus filtrate, and
 0.15 is average factor correcting for the solubility of wax in the solvent at $-32\text{ }^{\circ}\text{C}$

3.4.3 Determination of Acid Number of oxidized microcrystalline waxes (ASTM D 1386-98) [17]

This test method was used to determine the property of acid functionality. The acid number was the number of milligrams of KOH required to neutralize 1 g of the wax or waxy material.

The standard practice was determined the acid number by warming 1 to 2 g of the wax with 40 ml of xylene in a 250 ml erlenmeyer flask. The 3 to 5 drops of phenolphthalein were added and the titration was made with vigorous shaking against a solution of approximately 0.1 N ethanolic KOH until a semi-pink color appears. Record the number of ml of standard alkali solution used.

Calculate the acid number of oxidized microcrystalline was as follows:

$$\text{Acid number} = \frac{(AN \times 56.1)}{B} \dots\dots\dots \text{Equation (3.2)}$$

Where: A is milliliters of alkali solution required for titration of the sample,

N is normality of the alkali solution,

B is weight of wax, g, and

56.1 is molecular weight of KOH

3.4.4 Determination of Congealing Point of Petroleum Waxes, Including Petrolatum (ASTM D 938) [18]

Congealing point was a wax property that was of interest to many petroleum wax consumers. This procedure described here measures the temperature at which a sample being cooled develops a “set” or resistance to flow. At that temperature, the wax may be at or close to the solid state, or it may semisolid and quite unctuous, depending on the composition of the wax or petrolatum begins tested. In the case of petrolatum, congealing property was associated with the formation of gel structure as the sample cools. The procedure in this research was determined by following ASTM D 938-92.

A sample of wax was melted and a droplet was made to adhere to the bulb of a thermometer. Using a prewarmed flask as an air jacket, the droplet on the bulb was allowed to cool at a fixed rate until it congeals. The congealing point was observed as the temperature at which the droplet ceases to flow as the thermometer was turned.

3.4.5 Determination of Specific Gravity (ASTM D 70) [19]

Specific gravity of petroleum waxes in this research was determined by following ASTM D 70. This value was measure by using a Pycnometer Specific-Gravity bottle, capacity 10 ml, having a ground glass stopper with small hole in center.

Wax was melted at 90 °C and poured into the Pycnometer Specific-Gravity bottle. The bottle was filled with water stopper and wiped dry, weight at 25 °C, submerged the bottle in the water slowly so that no air bubbles binding to surface of wax and weight the whole. The wax in the bottle was weighted accurately to 0.0001 g at 25 °C.

The specific gravity, at 25/25 °C, of the wax was calculated as follows:

$$\text{Sp Gr} = [C - A] / [(B-A) - (D-C)] \dots \dots \dots \text{equation 3.4}$$

Where A is weight of bottle plus stopper, g,

B is weight of bottle plus stopper filled with water, g,

C is weight of bottle plus stopper filled with wax, g, and

D is weight of bottle plus stopper filled with wax and water, g.

The density, at 25/25 °C, of the wax was calculated as follows:

$$\text{Density} = (\text{Sp Gr}) \times (0.9971) \dots \dots \dots \text{equation 3.5}$$

Where Sp Gr is specific gravity at 25/25 °C

0.9971 is a constant.

3.4.6 Determination of Needle Penetration of Petroleum Waxes (ASTM D 1321) [20]

Petroleum waxes differ in hardness. This test method was used to measure hardness of waxes and this method was determined by following ASTM D 1321-97.

The sample was melted, heated to 17 °C above its congealing point, purred into a container, and then air cooled under controlled conditions. The sample was conditioned at test temperature in a water bath. Penetration is measured with a

penetrometer, which applies a standard needle to the sample for 5 s under a load of 100 g. The apparatus is shown in figure 3.1.

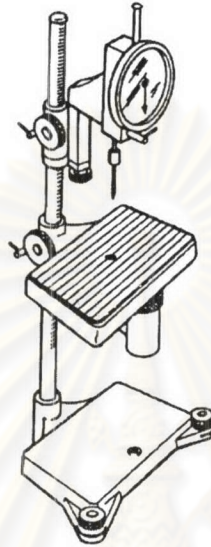


Figure 3.1 Penetrometer

3.4.7 Determination of Kinematic Viscosity (ASTM D 445) [21]

Kinematic viscosity (ν) of petroleum waxes was determined by following ASTM D 445-94.

The wax was heated at 70 °C to flow freely and fill the fixed volume of calibrated glass capillary viscometer (in range 7 to 35 cSt). The viscometer with liquided-wax was immersed in temperature-controlled bath at 80 °C. The volume of liquided-wax was adjusted to coincide with the filling mark of viscometer. Time was measured in seconds from the first timing mark to the second mark. The kinematic viscosity was product of the measured flow time and calibration constant of the viscometer.

Calculate the kinematic viscosity, ν , from the measured flow time, t , and the viscosity constant, C , by means of the following equation:

$$\nu = C.t \dots \dots \dots \text{equation 3.3}$$

Where ν is kinematic viscosity, mm^2/s or cSt ,
 C is calibration constant of the viscometer, $(\text{mm}^2/\text{s})/\text{s}$ and
 t is mean flow time, s .

3.4.8 Determination of Flash Point Cleveland Open Cup (ASTM D 92) [22]

The flash point was a measurement of tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It was only one of a number of properties that should be considered in assessing the overall flammability hazard of a material. This method was determined by following ASTM D 92-98a.

Approximately 70 ml of test specimen was filled into a test cup. The temperature of the test specimen was increased rapidly at first and then at a slower constant rate as the flash point was approached. At specified intervals a test flame was passed across the cup. The flash point was the lowest liquid temperature at which application of the test flame causes the vapors of the test specimen of the sample to ignite.

3.4.9 Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum waxes From Viscosity Measurements (ASTM D 2502)

[23]

This test method provides a means of calculating the mean molecular weight (Relative molecular mass) of petroleum waxes from another physical measurement. Molecular weight (relative molecular mass) was a fundamental physical constant that can be used in conjunction with other physical properties to characterize hydrocarbon mixtures. The method was applied from ASTM D 2502-92.

The kinematic viscosity of the waxes was determined at 100 and 210°F (37.78 and 98.89°C). A function “*H*” of the 100°F viscosity was established by reference to a tabulation of *H* function versus 100°F viscosity as show in Table 3.2. The *H* value and the 210°F viscosity are then used to estimate the molecular weight from a correlation chart, shown in Figure 3.2.

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Table 3.2 Tabulation of H function

TABLE 1 Tabulation of H Function

Kinematic Viscosity, cSt, at 100°F (37.78°C)	H				
	0	0.2	0.4	0.6	0.8
2	-178	-151	-126	-104	-85
3	-67	-52	-38	-25	-13
4	-1	9	19	28	36
5	44	52	59	66	73
6	79	85	90	96	101
7	106	111	116	120	124
8	128	132	136	140	144
9	147	151	154	157	160
10	163	166	169	172	175
11	178	180	183	185	188
12	190	192	195	197	199
13	201	203	206	208	210
14	211	213	215	217	219
15	221	222	224	226	227
16	229	231	232	234	235
17	237	238	240	241	243
18	244	245	247	248	249
19	251	252	253	255	256
20	257	258	259	261	262
21	263	264	265	266	267
22	269	270	271	272	273
23	274	275	276	277	278
24	279	280	281	281	282
25	283	284	285	286	287
26	288	289	289	290	291
27	292	293	294	294	295
28	296	297	298	298	299
29	300	301	301	302	303
30	304	304	305	306	306
31	307	308	308	309	310
32	310	311	312	312	313
33	314	314	315	316	316
34	317	317	318	319	319
35	320	320	321	322	322
36	323	323	324	325	325
37	326	326	327	327	328
38	328	329	329	330	331
39	331	332	332	333	333

	H									
	0	1	2	3	4	5	6	7	8	9
40	334	336	339	341	343	345	347	349	352	354
50	355	357	359	361	363	364	366	368	369	371
60	372	374	375	377	378	380	381	382	384	385
70	386	387	388	390	391	392	393	394	395	397
80	398	399	400	401	402	403	404	405	406	407
90	408	409	410	410	411	412	413	414	415	415
100	416	417	418	419	420	420	421	422	423	423
110	424	425	425	426	427	428	428	429	430	430
120	431	432	432	433	433	434	435	435	436	437
130	437	438	438	439	439	440	441	441	442	442
140	443	443	444	444	445	446	446	447	447	448
150	448	449	449	450	450	450	451	451	452	452
160	453	453	454	454	455	455	456	456	456	457
170	457	458	458	459	459	460	460	460	461	461
180	461	462	462	463	463	463	464	464	465	465
190	465	466	466	466	467	467	468	468	468	469

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Table 3.2 Tabulation of H function (continued)

TABLE 1 Continued

Kinematic Viscosity, cSt at 100°F (37.78°C)	H									
	0	10	20	30	40	50	60	70	80	90
200	469	473	476	479	482	485	487	490	492	495
300	497	499	501	503	505	507	509	511	512	514
400	515	517	518	520	521	523	524	525	527	528
500	529	530	531	533	534	535	536	537	538	539
600	540	541	542	543	544	545	546	547	547	548
700	549	550	551	551	552	553	554	554	555	556
800	557	557	558	559	559	560	561	562	562	563
900	563	564	565	565	566	566	567	567	568	569
<hr/>										
	0	100	200	300	400	500	600	700	800	900
1 000	569	574	578	583	587	591	594	597	600	603
2 000	605	608	610	612	614	616	618	620	621	623
3 000	625	626	628	629	631	632	633	634	636	637
4 000	638	639	640	641	642	643	644	645	646	647
5 000	648	649	650	651	652	652	653	654	655	656
6 000	656	657	658	658	659	660	660	661	662	662
7 000	663	664	664	665	665	666	666	667	667	668
8 000	668	669	670	670	671	671	671	672	672	673
9 000	673	674	674	675	675	676	676	677	677	677
<hr/>										
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000
10 000	678	681	684	688	691	694	696	699	701	703
20 000	705	707	709	711	712	714	715	717	718	719
30 000	720	722	723	724	725	726	727	728	729	730
40 000	731	732	732	733	734	735	736	736	737	738
50 000	739	739	740	741	741	742	743	743	744	744
60 000	745	746	746	747	747	748	748	749	749	750
70 000	750	751	751	752	752	753	753	753	754	754
80 000	755	755	756	756	756	757	757	758	758	758
90 000	759	759	759	760	760	760	761	761	761	762
100 000	762	762	763	763	763	764	764	764	764	765

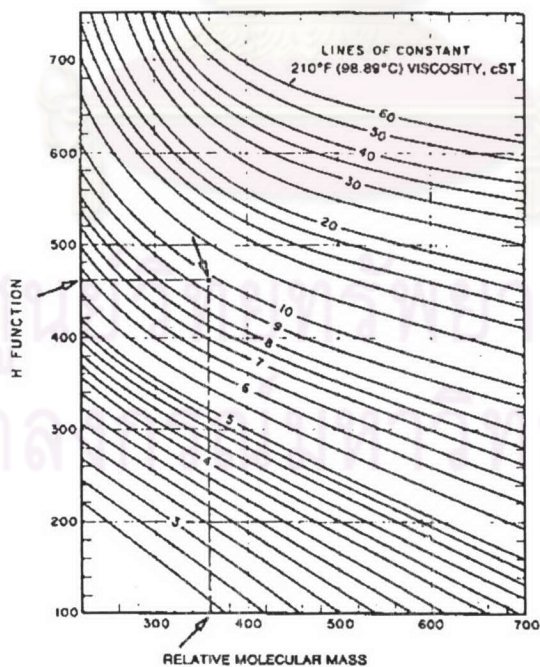


Figure 3.2 Viscosity molecular weight chart

3.4.10 Determination of microscopy of waxes

The appearance of the wax crystals in this research was performed by using microscopic study. The waxes were heated by electrical controller and cooled down from high temperature at a set rate. Photomicrographs were made of the crystal during the process of development by using magnification of 250x.



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