Refining of Tall Oil Pitch

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ABSTRACT

Six grades of tall oil pitch (TOP) were subjected to extraction by n-hexane and subsequent adsorption by SiO_2-activated carbon blend. Treated pitch samples contained 32.9-48.4% free acids, 24.2-35.0% esterified acids, and 25.0-36% unsaponifiable neutral compounds. Each of the above fractions was analyzed by high resolution gas chromatography. The portion insoluble in n-hexane contained 83.9% free acids, 10.6% esterified acids, and 5.5% unsaponifiable neutral compounds, indicating enrichment of the acidic compounds in this fraction. The decolorizing effect was observed in all treated TOP grades.

INTRODUCTION

Tall oil pitch (TOP) is obtained as a nonvolatile residue in the fractional distillation process of tall oil. The yield of TOP in the refining process amounts to 15-40% depending primarily on the quality of the crude tall oil. The total world production of tall oil pitch is over 200,000 tons/year. The utilization of this waste product is still an unsolved problem, even if a part of it may be used in such products as asphalt emulsions and printing inks. The recovery of sitosterols from TOP has been suggested (1). Recently it has been discovered that TOP possesses film-forming properties in combination with polyisocyanates and, therefore, it may be used as a starting material for polyurethane lacquers (2,3).

The variations in the chemical composition, the dark color, as well as the impurities present in different TOP grades are defects which limit the use of this product for coating and other purposes.

In the literature a method has been described where Fuller's earth has been used to remove color and odor from crude tall oil (4).

The object of this work was to investigate refining techniques suitable for removing colored and other disturbing components from TOP. The solvent extraction and subsequent adsorption technique was tried on six different TOP grades, whose chemical composition was determined previously (5). The fractions of treated samples were analyzed by high resolution gas chromatography-mass spectrometry.

EXPERIMENTAL PROCEDURES

Samples were of ordinary grades of tall oil pitch received from three distillation plants in Finland and one in the United States. Four Finnish and two United States grades were investigated.

Ten grams TOP was dissolved in 200 ml n-hexane and the insoluble part was removed by centrifuging, dried and weighed. N-hexane solution was treated with 10 g Aerosil 380-Norit ZN 2 blend (1:1) by shaking vigorously for 2 hr and settling for 4 hr. Thereafter, the solids were removed by centrifuging, dried and weighed. N-hexane was distilled off in a rotavapor, and the residue, the treated TOP, was subjected to fractionation and subsequent gas chromatographic analyses as described earlier (5).

Aerosil 380 and Norit ZN 2 are technical SiO_2 and activated carbon grades manufactured by Degussa and Activated Carbon Co., respectively. They are commonly used for refining of vegetable oils and fats.

RESULTS AND DISCUSSION

The properties of the original and treated TOP samples are given in Table I. It is seen from Table I that the ester number, which is the difference between acid and saponification values, varies between 63 and 66 in the original Finnish TOP grades. Values in the United States grades are 76 and 74, which point to the higher degree of esterification than in the Finnish grades. The high ash content of 1.4% in sample F_1 indicates the presence of impurities derived from soap left in the crude tall oil. In an earlier investigation, fatty acid soaps were found in a similar type of TOP as sample F_1 (Erä, V., unpublished results). In the treated samples B_2, C_2, D_2 and E_2, the drop of acid number was 5-10 points indicating the removal of the acidic components during the refining process. The lowering of the softening point in all TOP samples shows that a part of the removed material may consist of solid components. The portion insoluble in n-hexane varies between 11-22% depending on the quality of TOP. The fraction of TOP adsorbed in SiO_2-activated carbon blend amounts to 11-12%, indicating the selective removal of some compounds from all TOP grades.

Table II gives an example of the component group composition of three original (B_1 - D_1) and treated (B_2 -

TABLE I

Properties of the Original (A_1 - F_1) and Treated (A_2 - F_2) Tall Oil Pitch Grades

	Finnish								American			
Origin	A_1	A_2	B_1	B_2	C_1	C_2	D_1	D_2	E_1	E_2	F_1	F_2
Acid value	31	30	51	45	45	36	39	29	30	25	27	27
Saponification value	94	92	115	111	110	104	105	100	106	96	101	99
Softening point, °C^a	38-40	33-35	33-35	25-26	36-38	~25	34-36	24-25	32-34	~25	30-33	25-26
Ash content, %	0.1		0.1		0.6		0.2		0.4		1.4	
Insoluble in n-hexane, %	11.1		12.0		22.0		17.0		17.0		15.0	
Absorbed in SiO_2-activated carbon blend, %^{2}	12.0		11.0		12.0		12.0		11.0		11.0	
Yield of treated TOP, %	77.0		75.0		66.0		71.0		72.0		75.0	

^{a}Determined by thermo-microscope.

TABLE II

Component Group Composition of Three Original (B_1 - D_1) and Treated (B_2 - D_2) Tall Oil Pitch Grades

Constituents	B_1	B_2	C_1	C_2	D_1	D_2
Free acids total	51.6	45.0	48.6	37.7	44.6	32.9
Fatty acids	1.8	3.6	1.3	1.9	0.8	1.6
Resin acids	12.5	8.9	9.7	7.3	6.1	5.2
Other acids	37.3	32.5	37.6	28.5	37.7	26.1
Esterified acids, total	23.2	24.2	23.3	30.5	26.8	31.1
Fatty acids	12.9	14.7	13.3	17.1	15.2	15.1
Resin acids	0.9	0.6	1.2	0.9	0.9	0.7
Other acids	9.4	8.9	8.8	12.5	10.7	15.3
Unsaponifiables, total	25.3	30.8	28.2	31.8	28.6	36.0
Low molecular wt.	14.6	12.3	14.1	24.7	17.7	24.0
High molecular wt.	10.6	11.5	14.1	7.1	10.9	12.0

TABLE III

Main Fatty Acid, Resin Acid and Low Molecular Weight Unsaponifiable Constituents of Three Original (B_1 - D_1) and Treated (B_2 - D_2) Tall Oil Pitch Grades (wt % of Pitch)

Constituents[a]	B_1	B_2	C_1	C_2	D_1	D_2
Free acids						
Oleic	0.5	0.7	+[b]	+	+	+
Pimaric	0.5	0.6	+	+		
Isopimaric	0.7	0.6	0.6	0.5	+	+
Palustric	0.6	0.6	+	+		+
Dehydroabietic	3.5	3.7	3.2	2.6	1.9	1.9
Abietic	4.4	3.7	2.9	3.2	1.9	2.3
Esterified acids						
Palmitic	+	+	+	+	+	+
Oleic	4.8	5.4	4.6	6.1	3.6	5.0
Linoleic	1.8	2.1	2.2	2.4	2.4	2.6
Conj. Linoleic (trans-trans)	0.8	0.9	0.7	1.2	0.8	0.8
Dehydroabietic	+	+	+	+	+	+
Unsaponifiables						
Unident. diterpene alcohol	0.5	0.6				
Pimarol	+	0.6	0.7	0.5	0.7	1.0
Isopimarol			+			
Docosanol	0.8	0.9	0.8	1.2	0.6	0.8
Tetracosanol	0.7	0.8	0.7	1.1	0.6	0.8
Dehydrated β-sitosterol	1.0	1.3	+	0.7	0.5	0.9
Campesterol	0.6	0.7	0.7	0.6	0.7	0.9
β-sitosterol	4.6	5.3	5.6	5.7	6.4	7.0
Sitostanol	1.3	1.5	1.3	1.8	1.8	2.0
Betulinol	0.6	0.5	0.8	0.5	0.9	1.1

[a] All constituents amounting to more than 0.5 wt% on the pitch samples listed.

[b] + = Amounts of 0.2 - 0.5 wt % of pitch.

D_2) TOP grades. The characteristic feature of all investigated samples is the notable amount of high molecular weight components which were not eluted from the gas chromatographic column under used conditions. Approximately 60% of the weight fraction in the original TOP consists of high molecular weight components of which about half were acidic components. The presence of functional groups such as hydroxy and keto groups in the high molecular weigh fraction of the free and esterified acids of tall oil has been shown previously (6).

In the treated TOP samples B_2, C_2 and D_2, the free acids decrease by 3.4%, 10.9% and 11.7%, respectively. In all investigated samples, the resin acid content decreases, which indicates the removal of solid resin compounds during the refining process. This has a bearing on the lowering of the softening point of the treated samples as is shown in Table I.

Table III gives an example of the main fatty acid, resin acid and low molecular weight unsaponifiable constituents in the original (B_1 - D_1) and treated (B_2 - D_2) TOP samples. The variations in the content of these compounds between investigated samples point out the heterogeneous structures of TOP grades. The presence of betulinol in all Finnish TOP grades indicates the use of birch in the pulping of wood. In the treated TOP samples there can be seen only small variations in the amounts of low molecular weight components when compared with those of the original ones.

The composition of TOP fraction insoluble in n-hexane is seen in Table IV. The acid number of this fraction was found to be 84. Considering the composition of this fraction in connection with the acid number, it can be concluded that the enrichment of the acidic components takes place especially in those of high molecular weight species. The total content of the high molecular weight components amount to 91.5% indicating the selectivity of n-hexane on

TABLE IV

Composition of TOP Fraction[a] Insoluble in n-Hexane

Constituents	Wt % of fraction
Free acids, total	83.9
Fatty acids	0.7
Resin acids	2.1
Other acids	81.1
Esterified acids, total	10.6
Fatty acids	2.5
Resin acids	0.4
Other acids	7.7
Unsaponifiables, total	5.5
Low molecular weight	2.8
High molecular weight	2.7

[a] Separated from sample C_1.

TABLE V

Grading of the Color of TOP during Refining[a]

Sample	A	B	C	D
A_1	3	3	1	
B_1	1	1	0	
C_1	2	1	0	
D_1	2	1	0	
E_1	2	2	1	
F_1	2	2	2	1

[a] Explanations: A = color of the original TOP; B = color of TOP after treatment with n-hexane; C = color of TOP after the subsequent treatment with SiO_2-activated carbon blend; D = color of TOP after the 2nd treatment with SiO_2-activated carbon blend.

the removal of compounds which were not eluted from the gas chromatographic column. The dark color of this fraction indicates that a part of the colored compounds may be removed from TOP by n-hexane.

To determine the effect of both n-hexane and the subsequent SiO_2-activated carbon treatment on the color of TOP, 0.1 mm thick films were drawn on the glass plates. The visual observations on the color of the films were graded according to the following scheme: 0 = colorless, 1 = light yellow, 2 = yellow, and 3 = light brown. The results are seen in Table V.

It can be seen from Table V that samples B_1, C_1 and D_1 respond well to the refining treatments giving colorless films. In sample F_1 two treatments with SiO_2-activated carbon blend is required for color change owing to the presence of impurities as shown previously. In samples A_1 and E_1 light yellow color persisted after treatment.

On the basis of the results, it can be concluded that TOP may be decolorized by using solvent extraction in combination with SiO_2-activated carbon blend treatment. This result is of practical importance in making derivatives of refined TOP for further uses such as coatings and other applications. The light yellow color left behind in some TOP grades after refining may not restrict its use as an ingredient in coating formulations.

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