New Diffusion Pump Oil—Higher Monoalkyl-naphthalenes.

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Introduction. C. R. Burch[1] who first used organic liquid, in place of mercury, for diffusion pump medium obtained the vacuum of 10^{-6} mm-Hg, using a special fraction of lubricating oil of paraffin series and no cooling trap. Hickman and his collaborators[2] reported later that esters of phthalic acid or sebacic acid have suitable properties as diffusion pump oil and obtained the high vacuum of 1×10^{-7} mm-Hg by using octyl phthalate (Octol) and octyl sebacate (Octoils). Sagane, Haruta and others[3] have tested a synthetic oil, "Kao" oil, which was prepared from olefine hydrocarbons derived from higher fatty acids using aluminium chloride as a polymerization catalyst and showed the oil to be as good as Apiezon B or Octoil S in regard to vacuum and stability when used as diffusion pump oil.

One of the present authors (T. Kuwata) has found a new synthetic method of preparing higher alkyl-naphthalenes from higher alcohols and naphtahlene by the dehydrating and alkylating action of Japanese acid clay.[4] The process is relatively simple and gives good yield of condensate. For example, when 250 g. of cetanol and 100 g. of naphthalene were heated in the presence of 75 g. of activated Japanese acid clay, eliminatoin of water began at the neighbourhood of 190°C. The heating was continued at 190–210°C. until the evolution of water vapour ceased, the catalyst was filtered off, and then the resultant oil was distilled under reduced pressure, obtaining 260 g. of the produc of which ca. 45% were monoalkyl-naphthalene and 35% were dialkyl-naphthalene with small amount of tri-derivative. The saturated paraffin hydrocarbon containing no naphthalene ring amounted to ca. 10% of the product.

The present report concerns the properties of some of higher alkyl-naphthalenes, such as monododecyl, monotetradecyl, monohexadecyl and monooctadecyl-naphthalenes obtained by the process above mentioned.

Preparation and Properties of Monoalkyl-naphthalenes. 20 kg. of crude higher alcohols (Sp. v. 9.6, Ac. v. 212.5), which were prepared by the catalytic reduction of cocoanut oil, were rectified under reduced pressure using a column 1 m. long filled with Stedman's wire gauze corn, and pure dedecyl alcohol was obtained. The higher fraction was changed into acetic ester, and repeating its fractional distillation, pure acetic ester of tetradecyl alcohol was obtained. Pure hexadecyl and octadecyl

(1) C. R. Burch, *Proc. Roy. Soc.*, A, **23** (1929), 271.
(2) Hickman, *Frank. Inst.*, **321** (1946), 381.
(3) Sagane etc., *Kagaku*, **14** (1944), 315.
(4) T. Kuwata *J. Chem. Soc., Japan, Ind. Section*, **52** (1949), 146.

alcohols were prepared by the repeated fractionation of 3 kg. of crude cetanol (Sp. v. 0.5, Ac. v. 186).

The higher alcohols thus obtained had the following properties.

Table 1. Properties of Pure Higher Alcohols and their Acetic Esters.

		Dodecyl alcohol	Tetradecyl alcohol	Hexadecyl alcohol	Octadecyl alcohol
Acetate	Boiling point (°C/mm.)	—	129-131/1	147-150/1	166-168/1
	Sp. v. obs.	—	220.1	199.5	178.8
	calc.	—	219.0	199.0	179.6
	M. p. obs.	—	—	21.5-22.0	30.0-30.5
	lit.	—	—	22.7	31
Free alcohol	B. p. (°C/mm.)	110-112/1	125-126/1	142-144/1	159-161/1
	Ac. v. obs.	241.9	219.8	199.2	179.1
	cal.	243.8	219.0	199.0	179.6
	M. p. obs.	24.5-25.0	37.0-35.5	48.5-49.5	58-59
	lit.	24	38	50	59

The dehydrating condensation of these alcohols with naphthalene was carried out at 200°C. for 60 minutes. The resulant product was purified by the fractional distillation under the pressure of 1×10^{-2} mm-Hg and then 5×10^{-3} mm-Hg. The properties of monoalkly-naphthalenes thus obtained were shown in Table 2.

Table 2. Properties of Higher Monoalkyl-naphthalenes.

		Dodecyl-naphthalene	Tetradecyl-naphthalene	Hexadecyl-napnthalene	Octadecyl-naphthalene
Boiling pt. (1 mm-Hg)		180-182°C.	198-200°C.	212-214°C.	226-228°C.
Specific gravity (30°/4°)		0.9107	0.9055	0.8991	0.8942
Refractive index (30°/D)		1.5262	1.5240	1.5219	1.5192
Specific refraction (r_D^{30})		0.3371	6.3379	0.3392	0.3395
Mol refraction	obs.	99.61	108.80	118.48	127.73
	calc.	99.06	106.30	115.43	123.67
Mol. weight	obs.*	295	322	349	376
	calc.	296	324	352	379
Solidifying pt.		-42°C.	—	—	-16°C.
Viscosity (S. U. S.)	210°F	37.0	39.4	41.7	44.6
	100°F	90.0	113.5	140.5	173 9
Viscosity index		6.16	50.5	74.1	97.6
Elementary analysis C %	obs.	88.82	89.42	88.36	88.13
	calc.	89.11	88.82	88.56	88.35
H %	obs.	10 87	11.46	11.47	11.70
	calc.	10.88	11.18	11.44	11.67

* Cryoscopic method.

The values cited in Table 2. differ from those reported by Mikeska and his collaborators,[5] i. e. n-octadecyl-naphthalene of Mikeska melted at 51–52°C. and had viscosity index of 144. The constitution of monoalkyl-naphthalenes of the present authors has not yet been confirmed, but they may be assumed to be 2-naphthyl alkanes.

Vacuum Test of Monoalkyl-Naphthalenes. The vacuum test of the oil was carried out by the diffusion oil pump of Hickman type. The pump was charged with the testing oil and put on action for 5–6 hours, and then heating was controlled at the intervals of 30 minutes so as to obtain the optimum vacuum which was measured by ionization gauge. The data are shown in Table 3.

In order to test the oxidation stability of the oils, the air was introduced into the acting pump, continuing the heating until the pressure dropped to atmospheric pressure. After the lapse of 2 minutes, the pump was put again on action, and the restoration time and maximum attainability of vacuum were observed. On repeating the same process for 4 times, the "Kao" oil showed the evident deterioration, while alkyl-naphthalenes rather shortened the restoration time and increased the maximum vacuum.

Table 3. The Highest Attainability of Vacuum.

Monododecyl-naphthalene	2.1×10^{-6} mm-Hg
Monotetradecyl-naphthalene	5.2×10^{-6} ,,
Monohexadecyl-naphthalene	4.5×10^{-6} ,,
Monooctadecyl-naphthalene	1.2×10^{-5} ,,
"Kao" oil	3.0×10^{-6} ,,

Among the alkyl-naphthalenes used in the present studies, monododecyl-naphthalene was the most excellent as diffusion pump oil in regard to the action of the pump at relatively low temperature and the attainability of high vacuum.

Summary. Some monoalkyl-naphthalenes were prepared by the condensation of naphthalene and respective alcohols using activated Japanese acid clay as a condensing catalyst. The constitution of the alkyl-naphthalenes was assumed to be 2-naphthyl alkanes. The alkyl-naphthalenes were shown to be usable as good diffusion pump oil. The oils were very resisting for oxidation.

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(5) Mikeska etc., *Ind. Eng. Chem.*, **29** (1937), 970.