Some Higher Alkyl Naphthenates as Lubricating Oil for Fine Instruments

By Tsutomu KUWATA,[1] Shizuo NOGUCHI[2] and Hiroyasu ANDO[2]

(Received April 20, 1951)

Lower alkyl naphthenates, such as methyl or ethyl esters, have been known in detail, but as to the esters of higher fatty alcohols having more than eight carbon atoms no description has been found in the literature.

The present authors synthesized several higher alkyl esters of naphthenic acids and found that these new esters have suitable properties as lubricating oil for several fine instruments.

Synthesis of Higher Alkyl Naphthenates

Higher fatty alcohols used in the experiment are listed in Table 1. Refined naphthenic acids free from neutral oils, phenols, and other impurities are used for the study of characteristic properties of esters, and crude naphthenic acids contaminated with neutral oils, phenols, resinous substances and other impurities are employed for the estimation of commercial qualities of esters.

1. Refined naphthenic acids (R_ICOOH)derived from Niitu light machine oil distillates are light yellowish viscous liquid and have the following properties: b. p. 180-225°/9 mm.Hg (uncor.); d_4^{15} 1.0025; n_D^{15} 1.4896; acid value 223.6; av. mol. wt. calcd. 250.9.

2. Refined naphthenic acids ($R_{II}COOH$) produced in the refining of the same distillates are yellowish viscous liquid and have the following properties: b. p. 182-229°/9 mm.Hg (uncor.); d_4^{20} 0.9992; acid value 220.6; av. mol. wt. calcd. 254.3.

3. Crude naphthenic acids ($R_{III}COOH$)obtained by the distillation of the crude petroleum acids imported from abroad have approximately the following composition: Pure naphthenic acids (acid value, 227.1) 76%; phenols, neutral oils and other impurities 23%. The acids are brownish viscous liquid and have the following properties: b. p. 155-247°/9 mm.Hg (uncor.) ; d_4^{20} 0.9882 ; n_D^{20} 1.4957; acid value 192.6. Higher fractions (above 200°/5 mm.Hg) of the neutral oils contained

Table 1

Properties of Higher Fatty Alcohols Used

Alcohols	Materials	B. p. °C. (mm.Hg uncor.)	d_4^{20}	n_D^{20}	Hydroxyl value	Remarks
2-Ethylhexyl alcohol	Synthetic	182-183	0.8346	1.4316	—	—
n-Octyl alcohol	Reduction of coconut oil	191-196	0.8225	1.4298	429.8	B. p. (mainly) 193°
Decyl alcohol		120-125 (15)	0.8299	1.4356	353.8	B. p. (mainly) 122-123°/15 mm.Hg
Lauryl alcohol		143-148 (15)	—	—	295.0	M. p. 23.5-25.5°
Lauryl alcohol (industrial)		130-165 (15)	0.8273	1.4377	224.2	Solid. point 5.5°; Purity calcd. from H. V. 74.5%
Cetyl alcohol	Spermaceti	188-190 (15)	—	—	233.0	M. p. 49.0-50.5°
Oleyl alcohol	Sperm liquid alcohol	205-210 (13)	0.8505	1.4630	209.8	Iodine value 91.5
Sperm alcohol	Sperm oil	165-205 (13)	—	—	214.6	I.V. 45.2; av. mol. wt. calcd. from H. V. 261.4
Sperm liquid alcohol	*	80-260 (13)	0.8495	1.4604	204.5	I.V. 83.2; av. mol. wt. calcd. from H. V. 274.3

* Sperm liquid alcohol was prepared from sperm alcohol by separating the solidified substance in acetone solution at −3∼−7°; yield, 45.5% of sperm alcohol.

(1) Department of Applied Chemistry, the Faculty of Engineering, the University of Tokyo.

(2) Central Technical Laboratory, Nippon Oil Co., Ltd.

in the crude naphthenic acid amounted to 3.4% (in weight) and it is considered to be most probable that naphthenic esters prepared from the crude naphthenic acids contain the corresponding amount of hydrocarbon oil as impurity.

Procedure.—The mixture of higher fatty alcohols, excess naphthenic acids, moderate quantity of xylene and conc. sulfuric acid is boiled in a flask fitted with reflux condenser and accessary which is widely used for measuring the water content in organic substance. When the volume of water distilled is constant, reactions are considered to be completed. The reaction products are washed with 0.5 *N* sodium hydroxide and then with distilled water and dried over sodium sulfate. After removing the solvent, the reaction products are distilled under reduced pressure in the presence of 1% anhydrous sodium carbonate or no additive. The data obtained are given in Table 2.

From these it is notable that under these experimental conditions esterification of naphthenic acids is carried out with satisfactory result. In the purification of the esters it is desirable to distil them under pressure as low as possible in order to avoid the increase of acid value.

General Properties of Higher Alkyl Naphthenates

The general properties of naphthenates are shown in Table 3. The increase of the carbon number of side chain attached to the carboxyl group reduces density, refractive index, and increases viscosity, and improves viscosity-temperature characteristics as evidenced by high value of kinematic viscosity index. The reaction of the esters is always neutral except those prepared from the crude naphthenic acids distilled with no additive. Corrosion test is good. Esters have the odor resembling to mineral oil, and not the characteristic unpleasant odor of naphthenic acids or lower alkyl naphthenates. The higher alkyl naphthenates are pale yellowish liquid, and the color of the oil may be greatly improved by the redistillation.

As may be seen from the fact that the esters prepared from crude naphthenic acids have properties as good as those from refined naphthenic acids, small amount of neutral oils included within the esters have no unfavourable influence upon the esters. But it is wiser to use crude naphthenic acids from kerosene or gas oil fractions as the starting materials, because the presence of high boiling neutral oil is apt to give dark color to the esters.

The data cited in table 3 indicate that the esters are mostly characterized by little change in viscosity with temperature, low viscosity and viscosity ratio, adequately low volatility, high flash point, and reliable resistance to heating. They spread on metal or glass surface far less extent than hydrocarbon oils. Though

Table 2

Synthesis of Higher Alkyl Naphthenates

Names	Naphthenic acids: Symbol	Naphthenic acids: g. mol	Alcohols, g. mol	Xylene, cc.	H_2SO_4, g.	Reaction time, hrs.	Reaction products, g.	Distil.* method	Esters: B. p. (°C./5 mm.)	Esters: Main** (°C./5 mm.)	Esters: Obtained, g.	Esters: Yield, % to alcohols
2-Ethylhexyl naphthenates	$R_{II}COOH$	0.39	0.3	350	7	2	95.0	×	200-240	200-220	84.3	77
n-Octyl naphthenates	$R_{II}COOH$	0.39	0.3	350	7	2	93.0	×	200-245	210-230	83.5	76
Decyl naphthenates	$R_{II}COOH$	0.26	0.2	250	5	2	72.1	×	200-255	220-240	63.4	81
Lauryl naphthenates	$R_{II}COOH$	0.39	0.3	400	8	2.5	117.0	0	210-265	240-260	99.1	78
Lauryl (industrial) naphthenates	$R_{III}COOH$	0.11	0.1	150	3	2	41.5	×	200-280	235-260	32.8	78
Cetyl naphthenates	$R_{I}COOH$	0.05	0.03	50	1	1.5	12.9	0	200-278	260-275	11.0	77
Oleyl naphthenates	$R_{I}COOH$	0.05	0.03	50	1	1.5	13.5	0	200-295	275-290	11.7	78
Sperm naphthenates	$R_{I}COOH$	0.05	0.03	50	1	1.5	13.6	0	200-291	270-290	11.4	77
Sperm liquid naphthenates	$R_{III}COOH$	(35.0) 0.10	0.1	150	3	4	45.9	0	200-300	285-300	34.9	69

* 0, No Additive; ×, in presenece of 1% anhydrous sodium carbonate.

** "Main" means the range of temperature in which more than 80% (in weight) of the esters are distilled.

Table 3

General Properties of Higher Alkyl Naphthenates

Esters	Color (union)	d_4^{25}	n_D^{25}	Saponification number	Acid value: Non treating	Acid value: After heating	Iodine value	Solid. point, °C.	Flash. point,** °C.	Volatility,*** %	Heating†: Ppt.	Heating†: Color (union)	Kinematic viscosity (cst)††: Non treating 30°C.	50°C.	100°F.	After ht. 210°F.	After ht. 50°C.	Viscosity ratio (50°C.)	Kinematic viscosity index
2-Ethylhexyl naphthenates	1	0.9306	1.4745	140.5	1.1	1.1	0.5	−47	196	0.017	None	3½	29.85	13.38	21.47	3.74	13.52	1.00	43
n-Octyl naphthenates	1½	0.9266	1.4721	144.8	0.9	1.2	0.8	−52	198	0.026	〃	2½	21.82	10.70	16.14	3.44	10.79	1.00	95
Decyl naphthenates	1½	0.9205	1.4719	120.7	2.7	2.9	1.2	−43	197	0.025	〃	2½-3	25.64	12.40	18.88	3.85	12.45	1.00	106
Lauryl naphthenates	1	0.9139	1.4707	113.2	0.3	0.9	1.0	−45	210	0.012	〃	2-2½	30.15	14.15	23.36	4.53	15.15	1.07	122
Lauryl (industrial)* naphthenates	1½	0.9152	1.4747	111.8	0.0	<0.1	2.9	−45	207	0.028	〃	2½-3	31.92	14.97	23.31	4.46	15.13	1.01	116
Cetyl naphthenates	1-1½	0.9077	1.4605	105.8	2.2	2.3	2.4	−10	215	0.026	〃	1-½	42.36	17.65	30.49	5.66	20.46	1.11	136
Oleyl naphthenates	1½	0.9087	1.4653	100.5	2.7	2.8	36.6	−40	193	0.016	〃	1½	45.38	21.11	32.84	6.10	22.78	1.03	138
Sperm naphthenates	1½-2	0.9071	1.4633	105.4	1.6	1.8	20.2	−16	220	0.005	〃	1½-2	47.03	21.63	33.96	6.24	22.93	1.06	138
Sperm liquid* naphthenates	1½	0.9064	1.4733	100.9	0.0	<0.1	41.9	−32	198	0.023	〃	3	38.33	18.12	28.07	5.40	18.73	1.03	138

* The distillate was washed with alkali solution in order to remove the acidic substances produced by thermal decomposition of crude naphthenates.

** Determined with Pensky-Martens closed tester.

*** Per cent loss of weight in 5 hr. at 98° in a convection type oven.

† Observed after 6 hr. at 140° in a convection type oven.

†† Determined with modified type of Ostwald viscometer.

cetyl and sperm naphthenates have high solid points, esters of higher saturated alcohol having not more than twelve carbon atoms have low solid points below −40°. On comparing the two isomers, 2-ethylhexyl and *n*-octyl esters, the former has higher boiling point, higher viscosity, and smaller viscosity index than the latter. The higher solid point of the former may be accounted for low temperature viscosity relationship.

It seems unavoidable that acid value of the distillate slightly increases during distillation under pressure as low as 5mm. In order to obtain fractions of lower acid value it may be necassary to distil the esters under high vacuum as far as possible. The presence of small quantities of anhydrous sodium carbonate may decrease acid value, though not to a satisfactory extent.

Considering from these properties, the esters of naphthenic acids above mentioned are almost comparable in lubricating quality to the lubricants hitherto known with the exception of cetyl esters. Some esters, lauryl naphthenates may be expected to be available for the lubrication of watch, clock, and other delicate machinery of fine instruments.

Conclusion

2-Ethylhexyl, *n*-octyl, decyl, lauryl, cetyl, oleyl and sperm esters of pure naphthenic acids and lauryl (industrial) and sperm liquid esters of crude naphthenic acids are synthesized.

As the result of experiments it was found that higher fatty alkyl esters of naphthenic acids possess the most excellent qualities as lubricating fluids for delicate machinery of fine instruments; *i. e.*, pale yellowish color, low viscosity, low evaporation rate, low solid point, high flash point, high kinematic viscosity index, high thermal stability, and slow spreading velocity on metal or on glass surface.

Department of Applied Chemisty, the Faculty of Engineering, the University of Tokyo, Tokyo