temperature of the pyrolysis reaction. Table IV gives a list of those substances collected in a liquid air-cooled trap which could be detected and identified in the nitrogen 280 C-run of the pyrolysis of tall oil fatty acids with kraft lignin.

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Polyamine-Koch Acid Amides As Dispersants for Two-cycle Engine Oils

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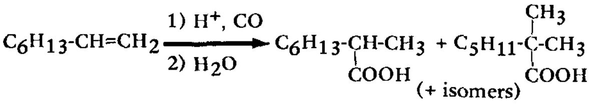
ABSTRACT

New ashless dispersants for two-cycle engine oils were developed from tetraethylenepentamine and C_{19}-C_{25} Koch acids. Engine tests showed these amides are excellent substitutions for the conventional isostearic acid-derived compounds.

INTRODUCTION

Prompted by a fluctuating supply of naturally derived isostearic acid, we have developed a product which can be used in its place in automotive applications. The route chosen to produce liquid isofatty acids in the C_{19} to C_{25} carbon number range involved the Koch reaction (1). These products are odd carbon number acids,



$$C_6H_{13}\text{-}CH{=}CH_2 \xrightarrow[\text{2) } H_2O]{\text{1) } H^+\text{, CO}} C_6H_{13}\text{-}\underset{\substack{|\\ COOH}}{CH}\text{-}CH_3 + C_5H_{11}\text{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ COOH}}{C}}\text{-}CH_3 \text{, } \quad \text{(+ isomers)} \qquad [I]$$

in contrast to the even numbered species from natural sources. Although most of the individual isomers of alkanecarboxylic acids in the C_{19} range and above are solids, a surprising liquid mixture of isomers is formed in the Koch reaction. Koch acids produced from higher olefins are mixtures of approximately equal amounts of secondary and tertiary alkanecarboxylic acids. With a C_{18} olefin feed, based on studies with model compounds, the product was expected to contain a total of 16 isomers. Secondary acids include x-carboxyoctadecanes, where x = 2-9; tertiary acids include x-methyl-x-carboxyheptadecanes, where x = 2-9. Isostearic acid, on the other hand, is believed to be an isomeric mixture of alkanecarboxylic acids with methyl group branching in the alkane chain, some *n*-alkanecarboxylic acids and smaller amounts of unsaturated acids. The average molecular weight (MW) of the mixture corresponds to a C_{18} carboxylic acid. Koch acids can replace isostearic acid in many applications. This paper describes the production of ashless dispersants for two-cycle engine oils from these new products (2).

EXPERIMENTAL

Apparatus and Analytical

Carbonylations were done in a 1-ℓ, 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie, PA). The autoclave was equipped with a cooling coil and was connected to a cylinder of CO, as well as temperature and pressure controllers and recording instruments. Olefins were introduced into the autoclave through the top using Milroy pumps. With solid olefins, C_{20} (mp 28.5 C) and C_{20}-C_{24} (mp 42-44 C), the addition lines were traced with steam lines. Product acids were analyzed by gas liquid chromatography (GLC) according to group types as trimethylsilyl (TMS) derivatives on a 2.5 ft x 1/8-in., 3% OV-1 column, programmed from 100-240 C at 4 C/min. *tert*-Carboxylic acids were the first to emerge from the column, followed by secondary acids. Olefins used were commercial samples. The carbon number distribution of internal C_{18} olefin was: C_{12}, 0.3%; C_{13}, 1.1%; C_{14}, 1.2%; C_{15}, 2.3%; C_{16}, 1.6%, C_{17}, 7.8%; C_{18}, 85.3%; and C_{19}, 0.4%; ave. MW = 247. Similarly, the composition of C_{20}-C_{24} α-olefin fraction was: C_{18}, 3.3%; C_{20}, 51.0%; C_{22}, 37.9%; and C_{24}, 7.8%; ave. MW = 295.

Carbonylation of 1-Octadecene.

In a typical experiment, the autoclave was charged with 97% sulfuric acid (440 g) and pressured with CO to 92 atm. Temperature was kept at 15-20 C while 1-octadecene (222 g) was added to the autoclave over 3 hr; the reaction was continued for an additional 30 min. The product was hydrolyzed by adding reaction mixture to wet ice (1500 g) and the organic layer that formed upon standing was transferred to a separatory funnel and washed three times with an almost equivalent volume of hot 15% sodium chloride solution. Distillation using a 12 in x 3/4-in od column packed with stainless steel rings produced 199.2 g of acids, bp 200-205 C at 1.5 mm of Hg, neq = 312. "Vacuum distillation at 10 mm Hg (% distilled at temperature C): IBP, 221; 5-20, 222; 30-50, 223; 60-80, 224; 90, 226; end, 227." Reactions with other feeds were carried out under comparable conditions.

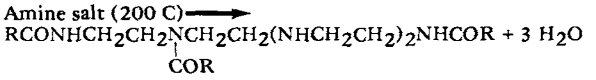
Preparation of Polyamides

A total of 1107 g (26.33 amine equivalent) of commercial tetraethylenepentamine was charged into a 12-1, round-bottomed flask equipped with a thermometer, a probe to control and record temperature, a nitrogen inlet and a take-off condenser. The amine was heated under nitrogen to 125 C and C_{19} Koch acids (5079 g; 16.28 mol) were added continuously over 2.5 hr with stirring and with temperature maintained at 125-140 C. After the addition of acids was completed, the reaction temperature was raised to 150 C for 1 hr, and then to 195 C for 3 hr at atmospheric pressure and ca. 50% of the theoretical amount of water was collected. The reaction was then continued at 195 C and 20-30 mm of Hg for 2 hr, then at 5 mm of Hg for 7 hr, after which no further reaction was evident. A total of 254 g of water was collected, corresponding to 87% of the theoretical amount expected according to equation III. Analysis showed: 76.29% C, 12.76% H, 5.88% N, and 5.07% O (by difference); specific gravity (15.5/15.5 C), 0.9226; MW, 935 (vapor pressure osmometry). The infrared (IR) spectrum showed typical amide bands at 3300 (m) and 1640 (s) cm^{-1} of the type $RCONHR^1$, and a weak band at 1700 cm^{-1} for the unreacted COOH group. The ^1H-nuclear magnetic resonance (NMR) spectrum (acetone-d_6, TMS) was identical to the spectrum of C_{19} Koch acids, with additional low intensity peaks at 2.43 and 2.7 ppm (CH_2NR_2 and CH_2NHR), and at 3.23 and 3.53 ppm (CH_2NHCOR^1 and CH_2NRCOR^1), respectively. A small peak was also evident at 8.3 ppm for the amide proton ($RCONHR^1$). The protons in the 0.5 to 2.2 ppm range comprised 85% of the total. The ^{13}C-NMR spectrum contained typical amide carbonyl bands in the range of 170 to 178 ppm (CONHR and $CONR_2$), but no peaks for the imidazole structures. The spectrum had only a small peak for the free carboxyl carbonyl at 181 ppm, indicating that most acids had reacted and that some product was present as amine carboxylate on the basis of a 182.7 ppm band.

RESULTS AND DISCUSSION

Isostearic acid is used in the preparation of polyamides which have use as pour point depressants, detergents and ashless dispersants for two-cycle outboard engine oils. For example, Benoit (3) reported on the reaction of isostearic acid with tetraethylenepentamine to produce the corresponding polyamide. For optimal performance as an ashless dispersant in a two-cycle engine oil, 1 mol of the pentamine is generally reacted with ca. 3 mol of acid to produce a random mixture of polyamides with an ave. MW of ca. 1000 (equations II and III):

$$3\ RCOOH + H_2N(CH_2CH_2NH)_4H \longrightarrow \text{Amine salt} \qquad [II]$$



$$\text{Amine salt (200 C)} \longrightarrow RCONHCH_2CH_2\underset{\displaystyle COR}{\underset{|}{N}}CH_2CH_2(NHCH_2CH_2)_2NHCOR + 3\ H_2O \qquad [III]$$

(R = typically C_{17} isomerized alkyl radical)

The same reference states that preferred carboxylic acids lie in the C_{16} to C_{20} carbon number range. They can be linear or branched, or mixtures of both, like those obtained by the hydroformylation of olefins, followed by their oxidation. Initially it was not known whether Koch acids, containing substantial amounts of *tert*-alkanecarboxylic acids (neo structures), would satisfactorily react with the pentamine, or whether the amide product would make a good additive. Although the Koch reaction has been known since the 1950s (1), no work with the higher MW isofatty acids (4) had been reported. The presence of *tert*-alkanecarboxylic acids in the product may have discouraged work in this area since neo acids are the least reactive type of carboxylic acids known. The physical properties of C_{19}, C_{21} and C_{21}-C_{25} mixtures of Koch acids used in our work are shown in Table I. Among these acids, the C_{19} and a C_{21}-C_{25} product mixture are considered the most promising because of the commercial availability of their starting materials. The preparation of polyamides from Koch acids and tetraethylenepentamine is shown in Table II.

Analysis of product by ^{13}C-NMR showed only amidation reaction, but no imidazole ring formation. Analysis also indicated that almost no free carboxylic acids were formed, but that some of the product still appeared as amine carboxylate. This is attributed to a very unreactive component of the Koch acid mixture which apparently does not undergo amidation reaction even under forcing conditions.

To determine whether polyamides from Koch acids and tetraethylenepentamine are effective dispersants for two-cycle engine oils, Mercury 100 and 50 horsepower outboard engines were tested, following conditions specified by the Boating Industry Association (BIA). A gasoline-to-lubricant

TABLE I

Physical Properties of Koch Acids

Properties	C_{19} Koch acids (from α-C_{18})	C_{19} Koch acids (internal C_{18})	C_{21} Koch acids	C_{21-23} Koch acids	Isostearic[a] acid (871)
Specific gravity, 15.5 C	0.8820	0.8789	0.8803	0.8789	0.8970
Viscocity at 98.9 C, cs	7.89	6.77		9.00	53.5 (25 C)
135.0 C	3.44	3.32		4.25	
148.9 C	2.77	2.66		3.39	
Iodine number, cg/g	1.2	4.2	2.0	1.4	10 (max)
Saponification number, mg/KOH/g	187	175	185	165	180
Neutral equivalent, g/equiv.	313	310	333	356	315
Titer test, C	1.2	6.3		12.9	10 (max)
Lovibond color (before and after heating)					
Red	0.6 3.3			1.1 3.8	1.9 15.0
Yellow	3.5 20.0			4.5 20.0	11.0 40.0
Neutral	0.5 0.5			0.5 0.5	0.5 0.5
Gardner color	1			1	
Boiling point, C	200-205 (1.5 mm)	200-205 (1.5 mm)	210 (1.2 mm)	220-230 (1 mm)	
Refractive index, $n_D^{27.5}$	1.4512	1.4507	1.4528	1.4536	1.4603 (25)
Ratio of sec/tart acids	47/53	51.3/48.7	43.7/56.3		

[a] Properties taken from Technical Bulletin 242B, Emery Industries, Inc., or determined in this laboratory.

TABLE II

Polyamides of Tetraethylenepentamine and Koch Carboxylic Acids

					Product analysis			
					N			
Exp. no.	Koch acids	Acid/amine (molar ratio)	Temp., C	Rxn time, hr	Total (%)	Basic (%)	Free base, meq/g (to pH 3)	Total acid no. (ASTM D664)
1	C_{19}	3.09	195	12.5[a]	5.88	3.65	2.03	56
2	C_{21}-C_{25}	3.23	195	9.0	4.80	2.72	1.48	55
3	Commercial isostearic acid (871)	3.00	195	7.0	6.30	2.34	ND[b]	ND

[a] First two or three hr at atm pressure; remainder at 30 mm of Hg or lower.
[b] ND = not determined.

ratio of 50:1 was used in these tests. Data in Table III on the formulation of our lubricants and engine test data indicate excellent performance with our product was achieved. Prior to this work, the only oils that have passed the standardized engine tests specified by the BIA are those employing an ashless dispersant additive package based on isostearic acid. BIA certified a lubricant containing the Koch acid polyamide for Service TC-W in 1978, following successful completion of the prescribed test procedure at the Southwest Research Institute. These tests include the following procedures: (a) an accelerated lubricity test run at high speed and using a fuel-to-lubricant ratio of 150:1; (b) a general performance test running 21 hr at the recommended fuel-to-lubricant ratio of 50:1, and (c) an accelerated preignition test running 98 h at a rich fuel-to-lubricant ratio of 24:1.

We also subjected polyamides from tetraethylenepentamine and C_{19} as well as C_{21}-C_{25} Koch acids to the Alcor Deposition test for thermal and oxidative stability and compared their performance to that of the isostearic acid-derived polyamide. The Alcor Deposition test uses a commercially available apparatus which circulate aerated test fluid through the annular space between an electrically heated tube and concentric housing. A filter screen is included in the circulation system. A deposit rating is calculated from deposit weights on the heater tube and filter. Formulation and test results of the Alcor Deposition test are shown in Table IV. Low deposit weights and relatively small changes in neutralization number and viscosity of the lubricant during the testing are good indicators of the resistance of Koch acid-derived polyamides toward degradation.

TABLE III

Formulation and Engine Performance of Polyamides Derived from C_{19} Koch Acids and Tetraethylenepentamine

Lubricating composition, % by volume		
Neutral mineral oil (600 SUS at 37.8 C; 68.7 SUS at 98.9 C)		60.6
Bright stock (2572 SUS at 37.8 C; 155 SUS at 98.9 C)		10.0
Stoddard solvent		20.0
Polyamide of tetraethylenepentamine and C_{19} Koch acids		9.4
Inspection		
Gravity, API		31.3
Viscosity, SUS seconds		
at 37.8 C		169
at 98.9 C		46.1
Viscosity index		126
Flash point, P-M, C		58.9
Pour point, C		-37.2
Outboard engine test conditions		
Engine Horsepower	100	50
Test duration, hr	100	100
Fuel: regular gasoline, ml/gal TEL	3.0	2.5
Gasoline-to-oil ratio	50:1	50:1
Test results		
Average piston skirt rating (10 is clean)	8.0	8.8
Average piston ring sticking rating		
Top (10 is free)	7.0	10.0
Others (10 is free)	10.0	10.0
Average piston ring weight loss, mg	68.7	71.9
Combustion chamber deposits, wt., g	12.92	light to medium
Piston or cylinder wall scuffing	none	none
Number of instances of preignition	none	none
Condition of bearings, pitting	none	none
Spark plug failures	0	1

TABLE IV

Formulation and Test Results of the Alcor Deposition Test of Polyamides Derived from Koch and Isostearic acids

Test conditions:	Lower tube temp., C	260
	Oil-in temp., C	150
	Cabinet temp., C	93.3
	Air flow, cc/min	1,000
	Test duration, hr	24

Lubricating composition, % by volume			
Neutral mineral oil (600 SUS at 37.8 C; 68.7 SUS at 98.9 C)	78.3	78.3	78.3
Bright stock (2572 SUS at 37.8 C; 155 SUS at 98.9 C)	12.7	12.7	12.7
Polyamide of tetraethylenepentamine and			
C_{19} Koch acid	9.0		
C_{21-25} Koch acids		9.0	
Isostearic acid			9.0
Test results			
Critical temp., C	285	301.7	304.4
Deposits rating	37.3	17.6	26.0
Tube deposits, mg	26.5	20.3	15.0
Filter deposits, mg	47.2	36.3	1967
Oil consumption, ml	40	20	30
Overall rating (0 is clean)	55	37	1004
Inspection			
Viscosity, SUS (37.8 C), initial	812	802	854
24 hr	982	954	1058
Increase %	20.9	18.9	23.9
Total acids initial	5.3	3.0	0.57
24 hr	6.0	4.5	2.80
Change	+ 0.7	+ 1.5	+ 2.23

Addition of 9% by volume of a C_{19} Koch acid derived polyamide of tetraethylenepentamine to a base oil (gravity, API, 28.2; viscosity, SUS, 700 [37.8 C] and 74.6 [98.8 C]; pour point, -15 C) lowered its pour point to -24.7 C. This shows the multifunctional nature of the new additive.

ACKNOWLEDGMENT

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