PINIC ACID DIESTERS:
THEIR PREPARATION, PROPERTIES, AND LUBRICANT APPLICATIONS

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ABSTRACT

The preparation and properties are reported for a new class of diesters prepared from pinic acid and normal alcohols containing from 4 to 10 carbon atoms. These compounds compare favorably with the diesters of aliphatic dibasic acids and 2-ethylhexanol as regards V.I., pour point (or freezing point), volatility, and lubricity. Lubricating oil compositions have been developed which establish the suitability of the dialkyl pinates for a wide variety of applications. Excellent pinate-base greases have also been prepared with soap and other gelling agents. Mixtures of pinates with other types of esters, petroleum oils, polyethers, compatible silicones, and other synthetic oils can be used to formulate improved lubricant compositions.

The commercial development of pinic acid at low unit cost from α-pinene is eminently desirable as it is potentially available in large supply from turpentine—a native raw material. In addition to its use in synthetic lubricants, this dibasic acid has excellent possibilities for the synthesis of low-temperature plasticizers, polymers, resins, and fibers.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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INTRODUCTION

Aliphatic diesters are in increasing demand for the extreme low temperature lubrication of turbo-jet engines (18), instruments (6, 19), machine guns (7), and aviation and ordnance greases (21, 22, 23). Certain of these diesters are also useful as low-temperature plasticizers. A variety of end products compete for the dibasic acids, the branched-chain alcohols, and even the diesters themselves. Since 1942 the growing demand for diesters has made it desirable to increase the domestic supply of cheap dibasic acids suitable for the preparation of lubricants and low-temperature plasticizers. Products obtainable from native raw materials are especially desirable.

During a joint discussion on applications of terpene chemistry with representatives of the Southern Regional Research Laboratory (SRRL) of the Department of Agriculture, we pointed out the possibilities of using certain dibasic acids derivable from α-pinene, a major constituent of turpentine. The principal acids formed in the stepwise oxidation of α-pinene are shown below with structural formulae written to emphasize the analogy with an aliphatic dibasic acid:
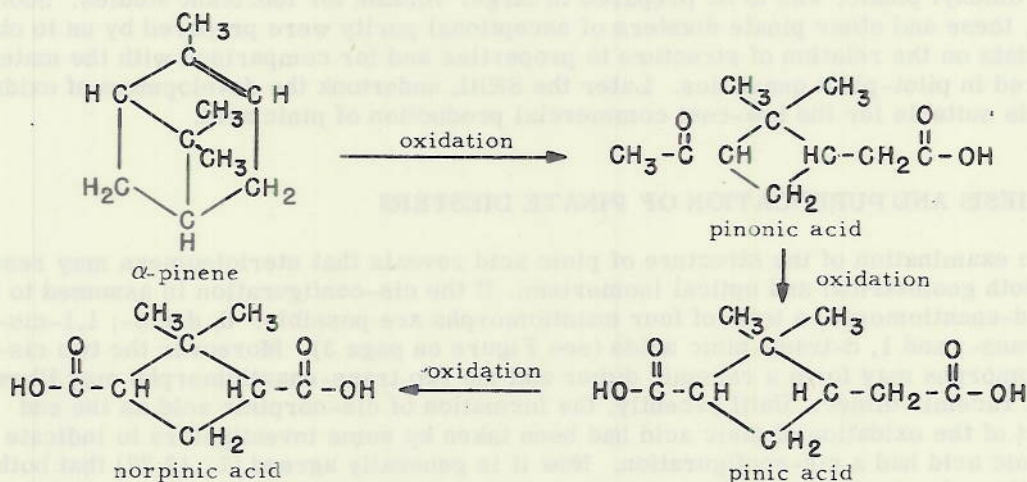
Although the earlier oxidation product, pinonic acid, appeared to be cheaper to produce than pinic acid, we did not expect it to be sufficiently oxidation stable for the intended uses. However, it was agreed that esters of this acid should also be prepared and studied. A plan was evolved for cooperative research in which the SRRL was to make the 2-ethylhexyl ester of pinonic acid and the corresponding diester of pinic acid for a preliminary study by us.

Early experiments demonstrated that both compounds had pour points below -56°F and viscosity indices (V.I.) of 60 and 86, respectively. Accelerated thermal oxidation tests using air at 125° and 150°C revealed that not only was the pinate diester the more stable, but that it was also more effectively stabilized by a good antioxidant like phenothiazine (7). Since the lesser resistance to oxidation manifested by the pinonates was caused by the keto group, it was concluded that the pinates were the more promising materials from which to develop stable lubricants. This does not imply that the pinonates may not be very useful for plasticizers or other applications.

Diesters containing cyclic groups have not found extensive use in low temperature lubricant applications because of either their large temperature coefficients of viscosity or their high freezing points (or pour points). Experience with such esters is based largely upon the phthalate esters and others prepared from alcohols containing phenyl or cyclohexyl groups. Since the cyclobutyl ring is much smaller than a 6-membered ring, its presence in the oil molecule should not cause such adverse effects on the combination of properties required of a low temperature oil (4, 25). We were confident that the dimethyl substituents on the cyclobutyl ring, which increase the asymmetry of the molecule, would act to prevent the close alignment of neighboring molecules and so produce very low freezing points. The presence in such compounds of four geometrical and optical isomers, which will be discussed subsequently, should cause an additional lowering of the freezing points. It has been demonstrated that branching near the center of the molecule is more effective in lowering the freezing point and has a less adverse effect upon V.I. than does branching near the end of the molecule (25). Diesters of pinic acid made with normal alcohols and especially the C_4 -C_{10} alcohols would have this type of configuration, and therefore, would be expected to have high viscosity indices, low freezing points, and lower viscosities at -40°F than the phthalates. Because of the similarity of these dialkyl pinates to other aliphatic dibasic acid esters used as low-temperature plasticizers, it was conjectured that such pinates should have interesting possibilities for this application.

In the next phase of the program the SRRL was asked to prepare small quantities of the n-amyl, n-hexyl, n-octyl, and 2-butoxyethyl diesters of pinic acid for further study by us. One ester, dihexyl pinate, was to be prepared in larger volume for lubricant studies. Soon afterwards, these and other pinate diesters of exceptional purity were prepared by us to obtain more data on the relation of structure to properties and for comparison with the materials prepared in pilot-plant quantities. Later the SRRL undertook the development of oxidation methods suitable for the low-cost commercial production of pinic acid.

SYNTHESIS AND PURIFICATION OF PINATE DIESTERS

An examination of the structure of pinic acid reveals that sterioisomers may result from both geometrical and optical isomerism. If the cis-configuration is assumed to be the d, d-enantiomorph, a total of four enantiomorphs are possible: d, d-cis-; 1,1-cis-; d, 1-trans-; and 1, d-trans-pinic acids (see Figure on page 3). Moreover the two cis-enantiomorphs may form a racemic dimer and the two trans-enantiomorphs may likewise form a racemic dimer. Until recently, the formation of cis-norpinic acid as the end product of the oxidation of pinic acid had been taken by some investigators to indicate that pinic acid had a cis-configuration. Now it is generally agreed (11,12,27) that both synthetic and natural pinic acids, as well as hydroxy pinic acid, have trans-configurations and that the change to the cis form occurs only at the last stage, when trans-hydroxypinic acid is oxidized to cis-norpinic acid.

The preparation of pure pinic acid free from racemic modifications has been described by Grandperrin (11). The acid obtained by the alkaline permanganate oxidation of d-α pinene was particularly resistant to cyclization and was therefore believed to be d-trans-pinic acid. Its properties are shown in Table 1. Small scale synthesis of pinic acid by the stepwise alkaline oxidation of pinene to pinonic acid and of pinonic acid to
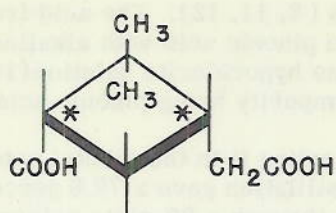
d,d-cis-pinic acid
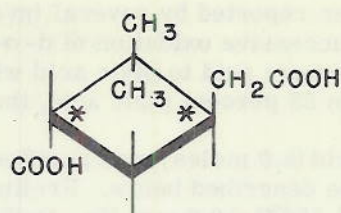
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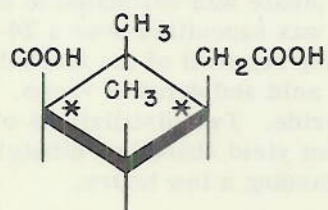
l,l-cis-pinic acid
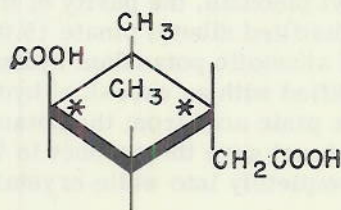
l,d-trans-pinic acid

racemic dimer

racemic dimer

*Asymmetric carbon atom

TABLE 1
Properties of Pinic Acid

Property	Found	Literature (11)
Melting Point °C	73-76[a]	74[a]
Boiling Point °C	185-187/1.0 mm Hg 163-165/0.2 mm Hg	185-186/2.0 mm Hg
Optical Rotation $[\alpha]_D^{20}$	-1.2 (chloroform, c = 4.10)[b]	-1.4 (chloroform, c = 9.7)[a]
		-1.9 (chloroform, c = 9.7)[c]
	-1.6 (water, c = 4.29)	-4 (water, c = 4.9)[c]
	6.6 (acetone, c = 7.60)	5 (acetone, c = 6.2)[c]
Neutralization Equivalent	93.10 (theory) 93.22 (found)	
Elemental Assay		
Calculated		
% C	58.05	
% H	7.58	
Found		
% C	58.09	
% H	7.84	

[a] After being distilled twice and worked on a clay plate

[b] c = g solute/100 ml solution

[c] After recrystallizing the redistilled acid from a mixture of
petroleum ether and diethyl ether

pinic acid has been reported by several investigators (8, 11, 12). The acid from SRRL was obtained by the successive oxidation of d-α-pinene to pinonic acid with alkaline permanganate solution, and of pinonic acid to pinic acid with alkaline hypochlorite solution(10). The crude acid assayed 80 to 85 percent pinic acid, the major impurity being pinonic acid.

The crude acid (8.0 moles) was purified by converting it to the dibutyl ester using the general procedure described below. Preliminary distillation gave a 79.0 percent yield of material; bp 180^0-186^0C/10.0 mm Hg. Redistillation through a 20-plate column yielded a product; bp 182^0-184^0C/10.0 mm Hg; n_D^{20} 1.4480; D_4^{20} 0.9710. On the assumption that the impurity was butyl pinonate, the purity of the dibutyl pinate was estimated to exceed 99.0 percent. The redistilled dibutyl pinate (5.00 moles) was saponified over a 24-hour period with an excess of alcoholic potassium hydroxide. After removal of the alcohols the reaction mixture was acidified with an excess of hydrochloric acid and dried in vacuo. Ether extraction separated the pinic acid from the potassium chloride. Two distillations of the acid from the ether extract gave the product in 74.8 percent yield (based on dibutyl pinate). The acid solidified completely into white crystals after standing a few hours.

On the basis of properties shown in Table 1, this acid is believed to be identical with the trans-pinic acid reported by other investigators (8, 11, 12, 26).

Each alcohol used in the preparation of the various esters was distilled through a 20-plate spiral wire column. Their properties agreed with the best literature values. All of the esters of this report were prepared by a general procedure which involved refluxing a mixture of the appropriate alcohol with pinic acid in the presence of toluene and a small amount of p-toluenesulfonic acid monohydrate. Water formed during the reaction was removed azeotropically and collected in a calibrated water trap. Refluxing was continued until the formation of water ceased. Crude esters were recovered from the residual mixture by distillation through a 16-inch Vigreaux column at reduced pressure. Essential data on the preparation of the various pinate esters are given in Table 2. In all instances the distilled esters (water-white in color) were stripped through a helix-packed column

TABLE 2
Data on the Preparation of Pinate Diesters

Diester	Reactants grams moles		Reflux[a] Time (hrs)	Water (ml)		Boiling Point		Yield (%)
				Theory	Found	(^{0}C)	(mm Hg)	
Dibutyl pinate	55.6	0.75 butanol-1	3	10.1	10.8	126	0.4	93.0
	52.14	0.28 pinic acid						
Diamyl pinate	149.9	1.7 pentanol-1	4	25.2	26.5	150	0.4	90.0
	130.3	0.7 pinic acid						
Dihexyl pinate	235.0	2.3 hexanol-1	5	36.2	36.0	164	0.4	85.0
	186.2	1.0 pinic acid						
Diheptyl pinate	151.1	1.3 heptanol-1	3	18.3	18.3	178	0.4	95.8
	93.1	0.5 pinic acid						
Dioctyl pinate	247.4	1.9 octanol-1	4	28.8	28.8	192	0.4	85.5
	149.0	0.8 pinic acid						
Didecyl pinate	300.8	1.9 decanol-1	5	28.8	28.8	219	0.4	89.4
	149.0	0.8 pinic acid						
Bis (2-butoxyethyl) pinate	271.8	2.3 2-butoxy-ethanol	4	36.0	37.8	178-80	0.4	92.5
	186.2	1.0 pinic acid						

[a] Time required for removal of water

against a counter-flow of carbon dioxide gas (5 mm pressure, $100^\circ C$) (17) and then perco-
lated through "Florisil" and alumina to obtain the specially purified esters.

Physical and chemical constants of interest in the identification and characterization
of the various pinate esters are given in Tables 3 and 4. The surface tensions were meas-
ured by the ring method with Harkins and Jordan (14) corrections. The results are correct
within $\pm$ 0.3 percent. Attempts to obtain the saponification numbers of the esters using
ASTM Method D94-48T were unsatisfactory since the compounds were incompletely saponi-
fied (approximately 65 percent) in three hours. Refluxing for 8 hours resulted in about 80
to 95 percent saponification. Doubling the excess of alcoholic potassium hydroxide and
refluxing for 48 hours gave complete saponification; however the end points were obscured
by the presence of silicates from the glass vessel. The saponification numbers obtained
agreed with $\pm$ 1 percent of the theoretical.

Since the compounds synthesized were new, they were further identified by comparing
the calculated and observed molecular refractions and parachors. Excellent agreement
between the calculated and the observed refractions and parachors was obtained (see Table
4). That branching lowers both the molecular refraction and the parachor has been observed
by many investigators. The extent of this deviation depends on the class of compound and
the position of the branching. The small lowering observed on both the molecular refraction
and the parachor is consistent for the entire series of pinate esters and is evidently due to
the gem dimethyl branching on the cyclobutane nucleus. In going from dibutyl pinate to
didecyl pinate it is noteworthy that the observed increase of either the molecule refraction
or the parachor agrees very closely with increases calculated from either structural or
bond constants.

PROPERTIES OF PINIC ACID DIESTERS OF INTEREST IN LUBRICATION

Some of the properties of the pinates of special interest in the development of lubricants
are given in Table 5. Since minus $65^\circ F$ is the lowest temperature required in current mili-
tary specifications for lubricants, every pinate not having a freezing or a melting point was
subjected to storage tests of 72 hours duration at $5^\circ F$ intervals down to $-75^\circ F$. Only the
bis(2-butoxyethyl) and didecyl pinates could be made to crystallize. As was expected, the
dimethyl substituted cyclobutane ring in the pinic acid molecule hinders the close alignment
of neighboring molecules, and thus liquids with low freezing or pour points were obtained.
There was no important difference in the properties listed in Table 5 of the purified pinate
diesters prepared by us and the SRRL except that the bis(2-butoxyethyl) pinate of the SRRL
could not be made to freeze at $-50^\circ F$, but it failed to pour after 72 hours at $-75^\circ F$. From
these data it is evident that the pinates prepared from the normal alcohols C_4 through C_8
have sufficiently low freezing points (or pour points) to care for current requirements for
low-temperature lubricants.

There is a progressive increase in the viscosity of the normal pinate diesters with
increasing chain length, increasing from 7.1 cs. at $100^\circ F$ for the butyl to 20.9 cs. for the
decyl diester. The cyclobutane group adds to the over-all length of the pinate molecule in
its normal or "stretched out" configuration approximately the equivalent of two aliphatic
carbon atoms. As in our earlier work (4,25), the ether oxygen atom in each ester group
has been counted as one of the atoms in the principal chain. Thus, the total number of
atoms (Z) in the principal chain of the molecule of the pinates of Table 5 varies from
approximately 15 for the dibutyl ester to 27 for the didecyl ester. These pinate diesters
are in the same chain length and viscosity range as the aliphatic diesters made from
sebacic, azelaic, and adipic acids all of which are now in wide use in lubricant applications.

TABLE 3
Structure and Analysis of Pinate Esters

Compound	Structure	Empirical Formula	Molecular Weight (Theory)	Boiling Point (°C)	(mm Hg)	Specific Rotation $[\alpha]_D^{20}$	Carbon, percent Calc.	Found	Hydrogen, % Calc.	Found	Neut. No.
Dibutyl pinate		$C_{17}H_{30}O_4$	298.41	126	0.4	-0.28	68.42	68.56	10.13	10.36	<0.05
Diamyl pinate		$C_{19}H_{34}O_4$	326.46	150	0.4	-1.03	69.90	69.92	10.50	10.14	<0.05
Dihexyl pinate		$C_{21}H_{38}O_4$	354.51	164	0.4	-0.58	71.14	71.50	10.81	10.71	<0.05
Diheptyl pinate		$C_{23}H_{42}O_4$	382.57	178	0.4	-0.19	72.20	72.26	11.07	11.01	<0.05
Dioctyl pinate		$C_{25}H_{46}O_4$	410.62	192	0.4	-0.39	73.12	73.07	11.29	11.07	<0.05
Didecyl pinate		$C_{29}H_{54}O_4$	466.72	219	0.4	-0.13	74.63	74.69	11.66	11.48	<0.05
Bis(2-butoxyethyl) pinate		$C_{21}H_{36}O_6$	386.51	178	0.4	-1.22	65.25	65.28	9.91	9.85	<0.05

TABLE 4
Molecular Refractions and Parachors of the Pinate Esters

Compound	Index of Refraction n_D^{20}	Density 20°C g/ml	Surface Tension 20°C dynes/cm	Molecular Refraction M_R			Parachor P		
				Calculated[a]		Found	Calculated[a]		Found
				Structural	Bond		Structural	Bond	
Dibutyl pinate	1.4478	0.9702	30.49	82.37	82.54	82.30	736.6	735.4	722.7
Diamyl pinate	1.4498	0.9578	30.40	91.66	91.83	91.56	816.6	815.4	800.4
Dihexyl pinate	1.4512	0.9468	30.73	100.95	101.13	100.86	896.6	895.4	881.4
Diheptyl pinate	1.4525	0.9380	30.96	110.23	110.42	110.13	976.5	975.4	962.3
Dioctyl pinate	1.4540	0.9313	31.10	119.52	119.72	119.42	1056.4	1055.4	1041.3
Didecyl pinate	1.4562	0.9198	31.58	138.09	138.31	137.98	1216.4	1215.4	1203.1
Bis(2-butoxy-ethyl) pinate	1.4514	0.9981	32.20	104.47	104.70	104.44	936.4	935.6	926.7

a Calculated from Vogel's structural constants and from Vogel's bond constants of References (28), (29), (30), (31).

The temperature coefficient of viscosity decreases with increasing chain length if the molecular chain is flexible (25). Thus the Dean and Davis V.I. increases from 97 for the dibutyl ester to 158 for the didecyl ester and the ASTM viscosity-temperature slope decreases from 0.77 to 0.67. As the molecular cross section remains constant while the length increases in going to the higher homologues, the V.I. should increase, since the ratio of breadth to length decreases. Because bis(2-ethylhexyl) pinate contains two ethyl side-chains which increase the effective cross section of the molecule, it is considerably more viscous than dihexyl pinate and has a smaller V.I. Like the aliphatic diester (1,4), the pinate diesters made from primary alcohols exhibited essentially linear graphs of viscosity vs. temperature on ASTM Chart D341 of log log viscosity vs. log temperature. The graphs of bis(2-butoxyethyl) pinate curved away from the temperature axis at subzero temperatures.

Both bis(2-butoxyethyl) and diheptyl pinate have 21 atoms in the principal chain of the molecule and they also have essentially the same molecular cross section. They differ only in that two methylene groups in the heptyl ester have been replaced by ether oxygen atoms. As would be predicted from a comparison of dialkyl ethers and alkanes (25), the 2-butoxyethyl diester is the less viscous at high temperatures and has the greater ASTM Slope. The viscosity of bis(2-butoxyethyl) pinate at subzero temperatures is greater than would be predicted from its ASTM Slope (100° to 210°F) as the graph curves upward. The upward curvature of the graph is possibly a manifestation of association.

In many applications the relubrication intervals are governed by the volatility of the lubricant, and hence the oil used should be as low in volatility as possible consistent with the other characteristics required. In the last column of Table 5 are given the weight losses at 210°F in 22 hours measured by ASTM Method D972-48T which is a measure of the volatility. The diamyl and dibutyl pinates had weight losses of 1.8 percent and 4.5 percent, respecitvely, while all the other pinates examined had values of less than 1 percent.

Properties of the dialkyl pinates are compared with those of the 2-ethylhexyl diesters of aliphatic acids in Table 6. These two series of esters have equal values of Z for comparable molecular weights. It is evident from this table that for a given value of Z the pinates though more viscous have ASTM Slopes and V.I.'s equivalent to those of the 2-ethylhexyl diesters of aliphatic acids. Conversely, at the same 100°F reference viscosity, the pinate esters have lower molecular weights but the ASTM Slope and V.I. are comparable to those of the aliphatic diesters. That the dialkyl pinates have viscosity-temperature properties equivalent to those of the analogous 2-ethylhexyl diesters of aliphatic acids may also be shown graphically by plotting the ASTM Slope vs. 100°F viscosity. A single smooth curve can be drawn through the points for both esters. This curve is approximately parallel to, but displaced above, the curve for the n-alkanes as would be expected (25) from the branched structure of the diesters.

The dialkyl pinates have larger rates of evaporation than do similar viscosity diesters of aliphatic dibasic acids, but, as expected, the evaporation rates and boiling points of comparable molecular weight diesters are nearly the same. The freezing or pour points of the dialkyl pinates prepared from normal alcohols containing less than 10 carbon atoms are below -75°F (see Table 4). In this respect the pinates are equal or superior to the 2-ethylhexyl esters of aliphatic dibasic acids.

Nearly all lubricants must have good resistance to atmospheric oxidation at temperatures of at least 100° to 125°C. Since few organic liquids are sufficiently stable at higher temperatures, it is necessary to require that they exhibit good response to antioxidant additives. Accelerated dynamic oxidation tests in glass systems containing copper, aluminum, and steel catalysts (1,24) were made on the pinates both with and without the addition of an antioxidant. The extent of oil deterioration and the formation of harmful products was followed by measurements of viscosity and neutralization number, and by observing the deposits and the corroded condition of the metals present. The results are summarized in Table 7. As was to be

TABLE 5

Physical Properties of Some Pinate Diesters

Identification	Z	Viscosity, cs. at °F							Dean & Davis V.I.	ASTM Slope -65° to 210°F	Pour Point b °F	Evaporation Loss c (Wt. %)
		210	130a	100	0	-20	-40	-65				
Dibutyl pinate	15	2.08	4.6	7.10	79.2	183.5	532.	2945.	97	0.77	<-90	4.5
Diamyl pinate	17	2.45	5.7	8.90	124.0	295.a	972.	5617.	109	0.76	<-75	1.8
Dihexyl pinate	19	2.76	6.6	10.28	149.4	360.a	1136.	6480.	124	0.74	<-75	0.3
Bis(2-ethylhexyl) pinate d	19	3.67	10.3	18.51	569.1	2000.a	10650.	100000.a	86	0.78e	-65	<0.1
Diheptyl pinate	21	3.22	7.9	12.65	192.0	479.	1437.	8540.	138	0.71	<-75	0.1
Bis(2-butoxyethyl) pinate	21	2.96	7.5	11.83	238.5	690.a	2995.	---	116	0.74f,g	-50h	<0.1
Dioctyl pinate	23	3.62	9.1	14.83	246.7	600.a	1882.	11300.	148	0.70	<-75	0.1
Didecyl pinate	27	4.67	12.5	20.94	395.3	1000.a	3375.	---	158	0.67	+23h	<0.1

a Interpolated or extrapolated

b After 72 hours storage

c ASTM Method D-972-48T at 210°F

d SRRL preparation

e ASTM Slope – 40° to 210°F

f ASTM Slope 100° to 210°F

g Graph curves

h Melting Point

z = Atoms in Main Chain

TABLE 6

Comparison of Properties of Some Dialkyl Pinates with the
Diesters of 2-ethylhexanol and Aliphatic Acids

	Empirical Formula	Mol. Wt.	Z	Viscosity, cs. at °F					Dean & Davis V.I.	ASTM Slope[a]	Freezing or Pour Point °F	Evaporation Loss[b] Wt. %
				210	100	0	-40	-65				
Diamyl pinate	$C_{19}H_{34}O_4$	326.4	17	2.45	8.90	124.	972	5620	109	0.77	<-75	1.8
Bis(2-ethylhexyl) glutarate	$C_{21}H_{40}O_4$	356.5	19	2.17	7.40	94.7	715	4200[c]	106	0.80	<-75	--
Dihexyl pinate	$C_{21}H_{38}O_4$	354.5	19	2.76	10.3	149.	1136	6480	124	0.74	<-75	0.3
Bis(2-ethylhexyl) adipate	$C_{22}H_{42}O_4$	370.5	20	2.38	8.22	107.	807	5000[c]	121	0.77	<-75	0.2
Bis(2-ethylhexyl) pimelate	$C_{23}H_{44}O_4$	384.6	21	2.65	9.28	122.	878	5300[c]	137	0.74	<-75	0.2
Diheptyl pinate	$C_{23}H_{42}O_4$	382.6	21	3.22	12.6	192.	1437	8540	138	0.71	<-75	0.2
Bis(2-ethylhexyl) azelate	$C_{25}H_{48}O_4$	412.5	23	3.06	11.4	156.	1190	6900[c]	146	0.72	<-75	<0.1
Dioctyl pinate	$C_{25}H_{46}O_4$	410.6	23	3.62	14.83	246.7	1882	11300	148	0.70	<-75	<0.1
Bis(2-ethylhexyl) sebacate	$C_{26}H_{50}O_4$	426.6	24	3.32	12.6	187.	1410	8300[c]	154	0.71	-67	<0.1

[a] ASTM Slope -65° to 210°F

[b] ASTM Method D972 at 210°F

[c] Extrapolated

Z Number of atoms in principal chain

expected, the uninhibited liquids oxidized in 24 hours at 125°C. Only the esters of butyl alcohol and of 2-butoxyethanol-1 yielded highly corrosive products. It is concluded that in resistance to thermal oxidation at these temperatures the pure diesters of pinic acid are comparable to the pure aliphatic diesters of adipic, azelaic, and sebacic acids as shown by a comparison with bis(2-ethylhexyl) sebacate (23).

To obtain information as to whether the pinate diesters were responsive to the same types of antioxidants as the aliphatic dibasic acid esters, the effect of several different antioxidants was investigated in dihexyl pinate. These were: dilauryl selenide, 4-tert. butyl, 2-phenylphenol, phenothiazine, and a combination of the last two compounds. The results of these experiments are shown in Table 7. As in previous work (24), the induction period was taken as the time at which the rate of increase per hour of the neutralization number for the volatile acids become 0.05. All three antioxidants stabilized dihexyl pinate at 125°C for more than 500 hours according to this criterion. The phenolic inhibitor did not, however, prevent the formation of corrosive materials as evidenced by the etching of the copper specimen and the green color of the oil. At 163°C, the phenolic antioxidant was ineffective in dihexyl pinate, the induction period being less than 24 hours. A similar ineffectiveness has been observed for the same compound in aliphatic diesters at temperatures above 125°C. Both dilauryl selenide and phenothiazine were very much more effective antioxidants at 163°C, the latter being the better. Though some insoluble deposits were formed during the longer test with phenothiazine there was no evidence of corrosive products as was observed with the dilauryl selenide. When a combination of phenothiazine and 4-tert. butyl, 2-phenylphenol was used as an antioxidant, the induction period was only 48 hours and the copper specimen was badly etched after 168 hours. This indicates that the addition of the latter reduces the effectiveness of phenothiazine as an antioxidant.

Consequently, phenothiazine was selected as the antioxidant for use in the comparative studies of the different pinate diesters. Weight concentrations of 0.07 weight percent were employed in the 168-hour tests at 125°C and 0.50 weight percent at 163°C. From the results in Table 7 it is apparent that phenothiazine is equally effective in all of the pinate diesters as well as in bis(2-ethylhexyl) sebacate.

Lubricant compositions often contain rust-inhibiting agents to prevent the rusting of ferrous metal parts during storage and operation. It has been shown (2,3) that the effectiveness of a given molal concentration of a polar-type rust inhibitor in any oil will decrease as its oil solubility increases. Some commonly used rust inhibitors were studied in the pinate diesters using the static-water-drop test (3) at 140°F. Sorbitan mono-oleate, glycerol mono-oleate, high molecular weight zinc naphthenate, barium naphthenate, barium petroleum sulfonate, and barium dinonylnaphthalenesulfonate effectively prevented the rusting of the steel specimen for a week under the test conditions. As was expected, a slightly larger concentration of each rust inhibitor was required because of the somewhat greater solvent power of the pinates over the aliphatic diesters made from adipic, azelaic, or sebacic acids.

Measurements of the friction-reducing properties of the pinates were made with a Bowden "stick-slip" machine modified and operated as described in an earlier publication (5). The static coefficient of friction of steel on steel lubricated with dihexyl pinate was 0.20 at 20°C. When the temperatures were increased up to 150°C, no significant change in the static or kinetic coefficients of friction were found. These values are essentially the same as those previously reported for the aliphatic diesters (5). Like mineral oils and the other diesters, the pinates can be fortified with commonly used wear preventives.

TABLE 7
'Oxidation Characteristics and Antioxidant
Efficiency in Pinate Diesters

Identification	Antiox. Wt. %	Temp. °C	Test Period Hours	Induction Period Hours	Viscosity Increase at 100°F %	Neut. No. Increase		Wt. Change Mg	
						Volatile	Nonvolatile	Steel	Copper
Dihexyl pinate	0.25[a]	125	504	>504	14.	4.7	2.4	+0.1	-4.9
	0.07[b]	125	504	>504	7.4	2.6	1.5	<-0.1	-0.3
	0.07[c]	125							
	1.00[a]	163	168	<24	390.	41.	34.	<-0.1	-56.
	0.50[b]	163	168	168	-3.7	4.7	17.	<+0.1	-2.2
	0.50[c]	163	288	288	61.	5.5	22.	+0.8	+1.3
	0.60[d]	163	168	48	24.	19.	3.4	+0.2	-9.5
Dibutyl pinate	Nil	125	168	<24	16.	46.	38.	<+0.1	-5.3
	0.07[c]	125	168	>168	2.5	0.45	0.09	+0.1	-0.1
Diamyl pinate	0.07[c]	125	168	>168	2.2	0.45	0.03	<+0.1	<-0.1
	0.50[c]	163	168	>168	5.4	1.7	0.41	+0.2	+0.2
Dihexyl pinate	Nil	125	168	<24	820.	51.	77.	<-0.1	-0.1
	0.07[c]	125	168	>168	1.8	0.22	0.03	<+0.1	<-0.1
	0.50[c]	163	168	>168	3.9	1.1	0.45	+0.1	+0.2
Diheptyl pinate	Nil	125	168	<24	1400.	78.	92.	-0.1	<-0.1
	0.07[c]	125	168	>168	0.4	0.28	0.02	<+0.1	-0.1
	0.50[c]	163	168	>168	3.3	1.2	0.50	+0.2	+0.2
Dioctyl pinate	Nil	125	168	<24	1200.	74.	84.	<-0.1	<-0.1
	0.07[c]	125	168	>168	1.5	0.19	0.01	<+0.1	<-0.1
	0.50[c]	163	168	>168	4.6	1.2	0.45	+0.2	+0.2
Didecyl pinate	Nil	125	168	<24	820.	36.	64.	<+0.1	<-0.1
	0.07[c]	125	168	>168	1.4	0.22	0.02	<+0.1	<-0.1
	0.50[c]	163	168	>168	4.1	0.90	0.53	+0.1	+0.2
Bis(2-butoxyethyl) pinate	Nil	125	168	<24	3700.	75.	68.	+0.1	-2.3
	0.07[c]	125	168	>168	1.0	.38	.26	<+0.1	-0.1
	0.50[c]	163	168	>168	3.3	2.4	1.2	+0.2	40.1
Bis(2-ethylhexyl) pinate[e]	0.50[c]	150	168	>168	1.7	1.3	0.50	+0.2	+0.1
Bis(2-ethylhexyl) sebacate	Nil	125	168	<24	375.	67.	58.	+0.1	-3.5
	0.07[c]	125	168	>168	<1.	0.17	0.12	-0.1	<-0.1
	0.50[c]	163	168	>168	<1.	0.28	1.0	+0.3	+0.2

[a] 4-tertiary butyl 2-phenylphenol

[b] Dilauryl selenide

[c] Phenothiazine

[d] 0.35 wt. % phenothiazine and 0.25 wt. % 4-tert. butyl 2-phenylphenol

[e] SRRL preparation

METALS	Appearance			Appearance of Oil
/sq cm Dural	Steel (cold rolled) C. R. S.	(Electrolytic) Copper	(24ST) Dural	
<+0.1	Discolored	Etched	No change	Green - clear
<-0.1	Discolored	Light lacquer	No change	Yellow - clear
<-0.1	Discolored	Etched	No change	Green - opaque
<+0.1	Discolored	Etched	No change	Brown - clear
+1.0	Heavy deposit	Heavy deposit	Heavy deposit	Red - clear
+0.1	Light deposit	Etched	Light deposit	Opaque
<+0.1	Discolored	Etched	No change	Green - turbid
<+0.1	Light peacock colors	Peacock colors	Light peacock colors	Red - clear
<+0.1	Peacock colors	Peacock colors	Light peacock colors	Red - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
<+0.1	Light peacock colors	Discolored	Light peacock colors	Yellow - clear
<+0.1	Peacock colors	Peacock colors	Light peacock colors	Red - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
<+0.1	Light peacock colors	Discolored	No change	Yellow - clear
<+0.1	Peacock colors	Peacock colors	Peacock colors	Red - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
<+0.1	Light peacock colors	Discolored	No change	Yellow - clear
<+0.1	Light peacock colors	Peacock colors	Light peacock colors	Red - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
<+0.1	Light peacock colors	Discolored	No change	Yellow - clear
<+0.1	Peacock colors	Peacock colors	Light peacock colors	Red - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
<-0.1	No change	Etched light deposit	No change	Yellow - sludge
<+0.1	Peacock colors	Peacock colors	Light peacock colors	Red - clear
<+0.1	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear
+0.3	Medium lacquer	Etched	Medium lacquer	Opaque
<-0.1	Discolored	Brassy color	No change	Brown - clear
+0.2	Brown lacquer	Brown lacquer	Brown lacquer	Dark red - clear

LUBRICANT COMPOSITIONS

Recently a new specification, MIL-L-7808 (18) was issued covering an improved aircraft gas-turbine oil. Although the composition of the oil is not limited, reference oil bis(2-ethylhexyl) sebacate containing 5 weight percent tricresyl phosphate as an antiwear agent, 0.5 percent of phenothiazine, and 0.001 percent silicone antifoam agent) is cited in the specification to provide a basis for settling future questions on properties or performance requirements. Both dihexyl and diheptyl pinate oil compositions were prepared containing the same concentration of additives as the reference oil of MIL-L-7808. Their properties are compared in Table 8 with the specification requirements. It is evident that the diheptyl pinate composition is satisfactory, but that a composition based on dihexyl pinate has a slightly lower viscosity at 210°F than the specification requirement. A small amount of a more viscous oil (e.g., 35 weight percent of either diheptyl pinate or bis(2-ethylhexyl) sebacate will increase the viscosity at 210°F to the required value without exceeding the -65°F maximum.

TABLE 8
Properties of Some Pinate Diester
Compositions of Promise as Gas Turbine Oils

	Dihexyl Pinate Composition	Diheptyl Pinate Composition	Specification MIL-L-7808
Viscosity, cs. at 210°F	2.80	3.18	3.0 (min)
Viscosity, cs. at 100°F	10.98	12.93	11.0 (min)
Viscosity, cs. at -65°F	9500.	12570.	13000. (max)
Pour Point °F	<-75.	<-75.	-75. (max)
Low Temperature Stability, °F 120 Hour Storage	<-75.	<-75.	-65. (max)
Flash Point °F	385.	410.	385. (min)

The same two pinate esters also are useful in formulating lubricants for various instruments and small mechanisms. Oil compositions for such applications covered by specifications MIL-O-6085 (19) and 14-0-20 (Ord) (6) differ from the previously mentioned aircraft gas-turbine oil compositions in that a rust inhibitor is required, and the tricresyl phosphate antiwear agent is not needed. Dihexyl and diheptyl pinate oil compositions were prepared with 3 weight percent barium dinonylnaphthalenesulfonate as the rust inhibitor and 0.35 percent phenothiazine as the antioxidant. Both compositions comply with the requirements of the above specifications.

Many types of equipment used in the Arctic need to be lubricated with low pour point, high V.I. oils. A synthetic oil made up by us largely of bis(2-ethylhexyl) adipate was used with unqualified success at Point Barrow, Alaska as an automotive crankcase oil during the two Arctic winters of 1947 and 1948 (15). A blend of mineral oil with synthetics and additives is now in use for such applications (19). Suitable lubricants of this type may be prepared from diesters of polyethers. The low viscosities of these oils at subzero temperatures permits engine starting without the use of external aids. The behavior of dihexyl pinate containing 0.35 percent phenothiazine as a crankcase oil was observed in a small scale, one-cylinder 2.5 h.p., air-cooled gasoline engine (Onan Type 10-LS) fitted with

aluminum pistons. In preliminary engine tests at 1800 rpm at full load and a sump temperature of 125°, dihexyl pinate behaved like the analogous composition based on bis(2-ethylhexyl) sebacate. Although the rate of oil consumption in runs lasting 100 hours was somewhat greater, 16 cc/hour as compared to 10 cc/hour, it was not unexpected because of the difference in viscosities (2.76 vs. 3.32 cs. at 210°F). A slightly greater tendency for the pinate oil to form engine lacquer was discerned. It is concluded that the dialkyl pinates are promising lubricants for use in whole or in part in formulating gasoline-engine lubricant oils.

Stable lubricating greases suitable for use over a wide range of temperatures have been made from the dialkyl pinates. Data are given in Table 9 for the composition and properties of typical lithium soap and copper phthalocyanine greases made from dihexyl pinate and dioctyl pinate by the methods of preparation and measurement described in previous publications of this laboratory (9, 13). These soap greases are suitable for application in the temperature range -65°C to 125°C. Copper phthalocyanine greases are effective over the same range and with suitable antioxidants, such as dilauryl selenide or phenothiazine, can be used up to 150°C. Grease (No. 5), made with copper phthalocyanine and bis(2-ethylhexyl) sebacate, was included in Table 9 in order to permit a comparison of the behavior of a similar grease (No. 4), made from dihexyl pinate. Evidently, the oxidation stability of the grease No. 4 is only slightly less than that of No. 5. Bomb oxidation runs were made at 150°C on these two greases using an initial oxygen pressure of 110 psi, and the bomb-pressure decreases in the first 24, 48, 72, and 96 hours were 2, 5, 11, and 18 psi, respectively. Hence, the dihexyl pinate greases are comparable in oxidation stability with those made from bis(2-ethylhexyl) sebacate. It can be concluded that dihexyl, diheptyl, and dioctyl pinates are as satisfactory for the production of lubricating greases as are those made from open-chain dicarboxylic acids. It is obvious that lithium soaps of other acids can be used as gelling agents instead of stearic acid by simply altering the concentration needed to obtain the desired grease consistency. Since the sodium, calcium, and barium soaps of the fatty acids have been used successfully to make useful lubricating greases from aliphatic diesters such as adipates, azelates, and sebacates, they may also be used for that purpose in gelling the dialkyl pinates.

RELATED NEW DIESTERS

Apart from pinic acid, several cyclobutanedicarboxylic acids may be of future interest in the preparation of diesters for lubricant applications. Related acids derived from natural products include such compounds as norpinic acid, homopinic acid, norcaryophyllenic acid, caryophyllenic acid, and homocaryophyllenic acid. In addition to these materials, 1,2-cyclobutanedicarboxylic acids, with or without alkyl substituents in the 3 and 4 positions, may be synthesized by a simple method described by Jahn (15). Because of the simple relations between molecular structure, viscometric properties, and freezing point pointed out here and in our earlier publications (1, 4, 25) on aliphatic esters and ethers, it is obvious that each mole of pinic acid could be reacted with two moles of an aliphatic glycolether to make high V.I. liquid lubricants. Also, each acid group of the pinic acid could be reacted with a glycol and the resulting product esterified by reacting the terminal hydroxyl group with an aliphatic (or other) monocarboxylic acid. In short, a variety of ways are evident for making high V.I. "oils" from pinic acid limited only by the economics of supply and the demand for synthetic liquids of such viscosities.

CONCLUSIONS

The preparation and physical properties are reported for a new class of diesters made from pinic acid and the normal alcohols containing from 4 to 10 carbon atoms. These

TABLE 9

Composition and Properties of Typical Pinate Greases

Code	Grease Composition (Wt. %)	Micro-penetration[a]	After 50 Hours at 100°C[b]		After 168 Hours at 150°C[c]		Oxidation Bomb Pressure Drop[d] (psi at 100°C)	
			Bleeding (Wt. %)	Evaporation (Wt. %)	Bleeding (Wt. %)	Evaporation (Wt. %)	After 100 Hours	After 300 Hours
1.	14.0 Lithium stearate 1.0 Sorbitan mono-oleate 0.2 4-tert. Butyl-2-phenylphenol 84.8 Dihexyl pinate	100.	4.7	0.62	--	--	10.	30.
2.	14.0 Lithium stearate 1.0 Sorbitan mono-oleate 0.1 4-tert. Butyl-2-phenylphenol 1.0 Dilauryl selenide 83.9 Dihexyl pinate	190.	--	0.62	--	--	1.	4.
3.	16.25 Lithium stearate 1.25 Sorbitan mono-oleate 0.10 4-tert. Butyl-2-phenylphenol 82.4 Dihexyl pinate	46.	--	0.62	35.	29.	7.	22.
4.	24.0 Copper phthalocyanine 1.0 Dilauryl selenide 75.0 Dihexyl pinate	201.	3.4	0.60	9.0	23.	0.	2.
5.	24.0 Copper phthalocyanine 1.0 Dilauryl selenide 75.0 Bis(2-ethylhexyl) sebacate	216.	2.5	0.47	8.3	7.0	0.	0.

[a]Kaufman micropenetration after 10 passes through Hain microworker using 60-mesh screen

[b]Test methods as per specification AN-G-3a

[c]Procedures given in Reference 9

[d]Using Norma-Hoffmann bomb test; 110 lb/sq inch initial pressure of oxygen

compounds compared favorably with the diesters of aliphatic dibasic acids and 2-ethylhexanol as regards V.I., pour point (or freezing point), volatility, and lubricity. Pinates were readily inhibited against oxidation and corrosion by typical oil additives. Lubricating oil compositions were developed which establish the suitability of the dialkyl pinates for a wide variety of applications. Excellent pinate-base greases were also prepared with soap and other gelling agents.

Since the dialkyl pinates and certain analogous types of compounds have been established as valuable lubricants, any one or mixture can be used as the base liquid for the manufacture of improved lubricating oils, hydraulic fluids, or greases. Also they can be mixed with other types of esters, with polyethers, with compatable silicones, or with mineral oils to formulate improved lubricants.

The commercial development of pinic acid at low unit cost from α-pinene is eminently desirable as it is potentially available in large supply from turpentine, a native raw material. In addition to its use in synthetic lubricants, this dibasic acid has excellent possibilities for the synthesis of low-temperature plasticizers, polymers, resins, and fibers.

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