United States Patent Office

2,864,828

Patented Dec. 16, 1958

2,864,828

ESTERS OF γ-(TETRAHYDRO-2-FURYL) ALKANOLS

Charles R. Russell, Peoria, and Lester E. Schniepp, Barrington, Ill., and Louis S. Hafner, Indian Head, Md., and Herbert E. Smith, Peoria, Ill., assignors to the United States of America as represented by the Secretary of Agriculture

No Drawing. Application June 11, 1957
Serial No. 665,104

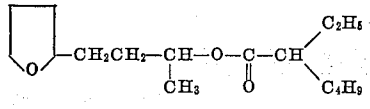
6 Claims. (Cl. 260—347.4)

(Granted under Title 35, U. S. Code (1952), sec. 266)

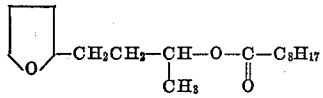
A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a continuation-in-part of application filed October 14, 1953, bearing Serial No. 386,140, now abandoned.

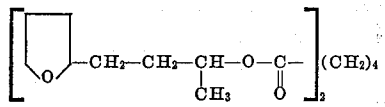
This invention relates to certain organic ester compounds, useful as low temperature lubricants, and selected from the group consisting of 4-(tetrahydro-2-furyl)-2-butyl 2-ethylcaproate having the formula



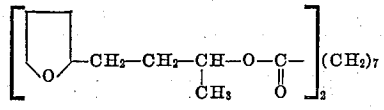
4-(tetrahydro-2-furyl)-2-butyl pelargonate having the formula



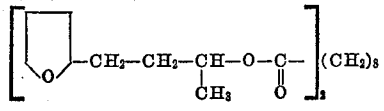
di-[4-(tetrahydro-2-furyl)-2-butyl] adipate having the formula



di-[4-(tetrahydro-2-furyl)-2-butyl] azelate having the formula



and di-[4-(tetrahydro-2-furyl)-2-butyl] sebacate having the formula



These compounds are liquids and remain so even at exceedingly low temperatures (low pour points), they are essentially non-volatile so that there is no evaporation of the liquids from lubricated bearings even when these are subjected to elevated temperatures, they are stable compounds and hence do not decompose when subjected to elevated temperatures as in overheated bearings or the like, and they exhibit superior lubricating activity over a wide temperature range as shown by their ASTM viscosity slopes and kinematic viscosity indexes. These properties make them admirably suitable as low temperature lubricants. They also find utility as plasticizers.

Data illustrating these properties is given in the following tables wherein Table I lists the boiling and pour points, Table II lists the viscosity-temperature characteristics of the esters, and Table III lists the use of some of the esters as plasticizers for polyvinyl chloride.

TABLE I

Boiling points and pour points of esters of 4-(tetrahydro-2-furyl)-2-butanol

Ester	Boiling Point		Pour Point or Melting Point, ° F.
	Temp., 0° C.	Pressure, μ/Hg	
2-Ethylcaproate	97	100	−84
Pelargonate	101	20	−88
Adipate	140	7	−62
Azelate	160	5	−60
Sebacate	180	5	[1] −42

[1] Compound crystallized and hence would not pour at the indicated temperature.

The high stability and low volatility of the compounds is illustrated by the following test data relative to the pelargonate ester:

Stability.—On heating at 212° F. with water, 0.18 milliequivalent of acid was liberated from 1 gram of the ester, and on heating in air for 158 hours at 150° F., 0.005 milliequivalent of acid was liberated from 1 gram of the ester.

Volatility.—For this test, a 1 gram sample of the pelargonate ester was placed in a ¾ inch by ¾ inch evaporating cup and placed in a forced-draft oven. It was found that a 1.1% loss in weight occurred on heating for 30 minutes at a temperature of 185° F.

TABLE II

Viscosity temperature characteristics of esters of 4-(tetrahydro-2-furyl)-2-butanol

Ester	Viscosity		A. S. T. M. Slope	Kinematic Viscosity
	210° F.	100° F.		
2-Ethylcaproate	1.84	6.78	.882	
Pelargonate	2.01	6.45	.784	109.1
Adipate	4.56	23.18	.720	126.8
Azelate	5.68	31.00	.694	133.1
Sebacate	6.17	31.23	.648	147.8

TABLE III

Physical properties of polyvinyl chloride (Geon 121) films plasticized with esters of 4-(tetrahydro-2-furyl)-2-butanol; 60 parts polyvinyl chloride, 40 parts ester

Ester	M	T	E	S	Low Temp. Flexibility, ° F.				Appearance of Film		
					−40	−50	−60	−70	Clarity	Color	Odor
Pelargonate	1,060	2,445	290	45	P	P	P	P	Clear	None	None.
Adipate	630	1,700	300	30	P	P	P	P	do	do	Very slight.
Dioctyl phthalate (Control)	745	2,070	320	50	P	P	P	F	do	do	None.

M=Modulus at 100 percent elongation, p. s. i.
T=Tensile strength, p. s. i.
E=Percent elongation at break.
S=Percent set at break.
P=Passed.
F=Failed.

The γ-(tetrahydro-2-furyl)-alkanols used as starting materials in this invention, and methods for their preparation, are disclosed in a paper by C. R. Russell, K. Alexander, W. O. Erickson, L. S. Hafner, and L. E. Schniepp, published in Jour. Am. Chem. Soc., 74, 4543 (1952).

Our esters may be prepared by esterifying the required alkanol with the appropriate acylating agent. The process which we have employed, in most cases, has been to heat the reactants, dissolved in an inert non-aqueous solvent such as benzene, in the presence of a catalytic amount of an acidic catalyst such as p-toluenesulfonic acid. The course of the esterification may be followed by separating the water of reaction in such a manner as to enable observation of its rate and quantity. In general, the esters may be purified by distillation using conventional columns for the more volatile esters and molecular stills for those having higher boiling points.

Other physical properties of the esters and the methods by which they may be prepared are given hereafter, Table IV listing these properties.

PREPARATION OF ESTERS

General procedure.—To 200 ml. of benzene containing 2 g. of p-toluene sulfonic acid were added the tetrahydrofuryl alkanols and acids as indicated in the table. The reaction mixture was heated at reflux until water ceased to collect in the separating device attached between the flask and reflux condenser, after which period, the reaction mixture was cooled and 400 ml. of benzene added. The benzene solution was extracted with cold 5 percent sodium hydroxide in an amount slightly less than that calculated as necessary for the removal of excess acid and catalyst. The remaining acid was removed with 5 percent sodium bicarbonate solution, the benzene layer washed with water until neutral, and dried over anhydrous magnesium sulfate.

Butanol was added during the extraction of a number of the higher molecular weight esters to break up the emulsions which formed.

The dry benzene solutions of the esters were filtered and the solvent removed on a steam bath under reduced pressure. The crude esters were then purified by the methods indicated in the table. All of the esters which were distilled on the falling-film still were degassed for 1 to 2 hours at 125° C. at .01 to .05 mm. before placing them on the still.

The yields recorded in Table IV, hereafter, are based on those fractions of the once-distilled esters having a degree of purity in excess of 95 percent, as determined by the saponification equivalent and the free acid content.

TABLE IV

Esters of γ-(tetrahydro-2-furyl)-2-butanol

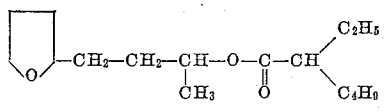
Ester of 4-(Tetrahydro-2-furyl)-2-butanol	n	Acid, moles	THF-Alkanol, moles	Time, hrs.	Yield,[a] Percent	Method of Purification	Properties of Purified Esters			
							Distillation		n_D^{25}	d_4^{20d}
							Temp., °C.[b]	Pressure, μ Hg[c]		
2-Ethylcaproate	1	0.85	0.6	107	38	(f i f)	97	100	1.4437	0.912
Pelargonate	1	0.75	0.5	25	64	(i g)	101	20	1.4480	0.912
Adipate	2	0.50	1.25	7	58	(h)	140	7	1.4627	1.025
Azelate	2	0.05	1.25	48	36	(h)	160	5	1.4638	1.011
Sebacate	2	0.50	1.25	12	63	(h h)	180	5	1.4631	0.997

Ester of 4-(Tetrahydro-2-furyl)-2-butanol	Properties of Purified Esters									
	M_D^{20e}		Saponification equiv.		Free Acid, Percent	Empirical Formula	Analyses			
							Carbon		Hydrogen	
	Calcd.	Found	Calcd.	Found			Calcd., Percent	Found, Percent	Calcd., Percent	Found, Percent
2-Ethylcaproate	77.25	78.83	270.4	275.3	0.03	$C_{16}H_{30}O_3$	71.06	71.2	11.18	11.2
Pelargonate	81.87	83.54	284.4	282.3	0.10	$C_{17}H_{32}O_3$	71.78	71.3	11.34	11.2
Adipate	106.1	107.2	199.2	204	0.68	$C_{22}H_{38}O_6$	66.30	66.2	9.61	9.7
Azelate	120.0	120.3	220.3	217	0.80	$C_{25}H_{44}O_6$	68.14	67.4	10.06	10.1
Sebacate	127.6	125.8	227.3	228.3	0.70	$C_{26}H_{46}O_6$	68.69	68.4	10.20	10.3

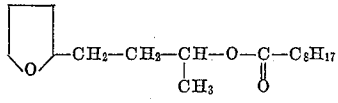
[a] Calculated on the basis of the once-distilled product having an analytical purity of 95+%.
[b] Observed on final distillation, temperature of hot finger in the falling-film still; vapor temperature in all other distillations.
[c] Measured by McLeod and calibrated thermocouple gauges attached between the still head and solid CO_2 cooled trap.
[d] Measured by Fischer-Davidson gravitometer.
[e] Calculated from n and d values determined at 20° C.
[f] Fractionated through a jacket-heated 3-foot packed column.
[g] Low boiling impurities removed on alembic flask still by protracted heating just under the boiling point at low pressures.
[h] Distilled on falling-film still.
[i] Fractionated through jacket-heated 14-inch packed column.
[j] Distilled from alembic flask still.

We claim:

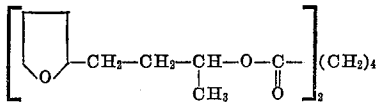
1. 4(tetrahydro-2-furyl)-2-butyl 2-ethylcaproate having the formula



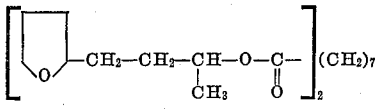
2. 4-(tetrahydro-2-furyl)-2-butyl pelargonate having the formula



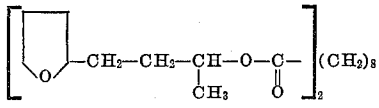
3. Di-[4-(tetrahydro-2-furyl)-2-butyl] adipate having the formula



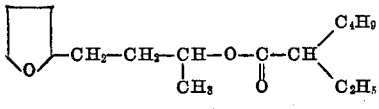
4. Di-[4-(tetrahydro-2-furyl)-2-butyl] azelate having the formula



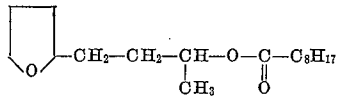
5. Di-[4-(tetrahydro-2-furyl)-2-butyl] sebacate having the formula



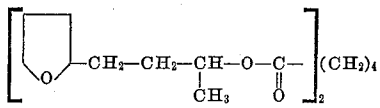
6. A compound selected from the group consisting of 4-(tetrahydro-2-furyl)-2-butyl 2-ethyl caproate having the formula



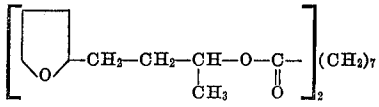
4-(tetrahydro-2-furyl)-2-butyl pelargonate having the formula



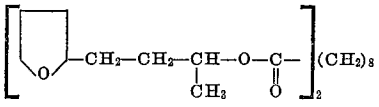
di-[4-(tetrahydro-2-furyl)-2-butyl] adipate having the formula



di-[4-(tetrahydro-2-furyl)-2-butyl] azelate having the formula



and di-[4-(tetrahydro-2-furyl)-2-butyl] sebacate having the formula



References Cited in the file of this patent

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OTHER REFERENCES

Chem. Abstracts, vol. 42, p. 5861a (1942).

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,864,828 December 16, 1958

Charles R. Russell et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 3 and 4, Table IV, third column thereof, opposite "Azelate", for "0.05" read -- 0.50 --.

Signed and sealed this 7th day of April 1959.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents