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3,544,614
COMPLEX ESTERS PRODUCED BY REACTING A
DICARBOXYLIC ACID, A POLYHYDRIC ALCO-
HOL AND BORIC ACID
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6 Claims

ABSTRACT OF THE DISCLOSURE

Complex esters for use as lubricants and to impart
desirable rust inhibiting films on metallic surfaces, such
as those of wire, rods, strips, webs and plates, by way
of example, as produced by compositions of matter com-
posed of various combinations of di- and poly-basic car-
boxylic acids, polyhydric alcohols, borates and phos-
phates, particularly in the equivalent weight ratios set
out in the specification.

This invention relates to the production and use of
complex esters and more particularly to the production
and use of complex esters which may be employed, for
example, as lubricants for metallic surfaces and which
lubricants have dual functions since they possess rust-
inhibiting characteristics.

The complex esters of this invention are produced by
various combinations of di- or poly-basic carboxylic acids,
polyhydric alcohols, borates and phosphates.

Normal dibasic esters commonly employed as lubri-
cants suffer from the disadvantages of lacking rust-in-
hibiting properties.

An important object of this invention is to provide
lubricants for metallic surfaces containing complex esters
synthesized from compositions of matter including, for
example, boric acid, which lubricants actually impart
rust inhibiting properties to films of the lubricants spread
upon the surfaces of the metals.

Lubricants for metallic surfaces, which lubricants in-

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clude synthetic esters produced by the employment of
some acids, sometime contain additives, which have no
part in the synthesizing of the esters and have no lubri-
cating characteristics but are rust or corrosion inhibitors,
pure and simple.

Another important object of this invention is to pro-
vide complex ester-containing lubricants with the dual
function of inhibiting formation of rust. These esters are
synthesized from at least one constituent which would be
regarded generally as not suitable for rust inhibiting pur-
poses, and may actually be regarded as having corrosive
properties. However, when employed as detailed herein,
the resulting complex esters do inhibit formation of rust.

Other objects and advantages of the invention will be
apparent during the course of the following detailed de-
scription of the invention.

In this disclosure, new, unique, and useful complex
esters have been prepared by combining, for example:

(a) Boric acid, a polyhydroxylic alcohol, and a satu-
rated or unsaturated aliphatic dicarboxylic acid or an-
hydride.

(b) Boric acid, a polyhydroxylic alcohol, and an aro-
matic dicarboxylic acid or anhydride.

(c) Boric acid, an alkylolamine, and a saturated or
unsaturated aliphatic dicarboxylic acid or anhydride.

(d) Orthophosphoric acid, a polyhydroxylic alcohol,
and a saturated or unsaturated aliphatic dicarboxylic
acid or anhydride.

(e) Orthophosphoric acid, a polyhydroxylic alcohol,
and an aromatic dicarboxylic acid or anhydride.

The polyhydroxylic alcohols include the glycols, triols,
tetrols, and hexols, and encompass the entire general
family of polyhydroxylic alcohols. The concepts of (a),
(b), (c), (d), and (e) in the preceding paragraphs
apply to the entire family of polyhydroxylic alcohols
and are not limited to these examples specifically cited.
Among the particularly suitable specific polyhydroxylic
alcohols are glycerin ethylene glycol, hexylene glycol,
polyethylene glycols, pentaerythritol, sorbitol, and 2,4,
7,9-tetramethyl-5-decylene-4, 7-diol.

Typical examples of formulations for the preparation
of new, unique and useful complex esters of this inven-
tion are as follows:

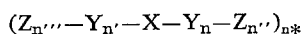
Example	Starting ingredients	Weight, grams	Mole ratio	Hours heated at 110° C.	Acid value calc.	Acid value observed
I.	Boric acid	22.8	1.00			
	Glycerin, U.S.P.	69.0	1.96			
	Sebacic acid	146.0	1.89	300	200	125
II.	Boric acid	22.8	1.00			
	Glycerin, U.S.P.	69.0	1.96			
	Azelaic acid	136.0	1.89	300	210	125
III.	Boric acid	22.8	1.00			
	Glycerin, U.S.P.	69.0	1.96			
	Azelaic acid	68.0	0.98	300	226	146
	Phthalic acid	60.0	1.10			
IV.	Boric acid	30.2	1.00			
	Glycerin, U.S.P.	92.0	2.05			
	Phthalic anhydride	89.0	1.10	300	179	195
V.	Boric acid	20.0	1.00			
	Ethylene glycol	62.0	3.09			
	Azelaic acid	90.0	1.48	300	188	30
VI.	Boric acid	20.0	1.00			
	Hexylene glycol	88.6	3.09			
	Azelaic acid	94.0	1.54	150	217	208
VII.	Boric acid	30.9	1.00			
	Pentaerythritol	136.0	2.00			
	Sabacic acid	100.0	1.00	150	136	154
VIII.	Boric acid	12.5	1.00			
	60% sorbitol	85.0	1.62			
	Azelaic acid	50.0	1.31	300	203	195
	Phthalic acid	40.0	1.33			
IX.	85% phosphoric acid	19.0	1.00			
	200 MW polyethylene glycol	110.0	3.00			
	Phthalic anhydride	46.0	1.50	300	75	114
	85% phosphoric acid	43.3	1.00			
X.	Glycerin, U.S.P.	69.0	2.00			
	Azelaic acid	68.0	0.96	150	196	268
	Phthalic anhydride	60.0	0.96			

Example	Starting ingredients	Weight, grams	Mole ratio	Hours heated at 110° C.	Acid value calc.	Acid value observed
XI	Boric acid	30.9	1.00			
	Diethanolamine	106.0	2.01	300	170	120
	Azelaic acid	141.0	1.50			
XII	Boric acid	30.9	1.00			
	Triethanolamine	101.0	0.677	300	210	160
	Azelaic acid	141.0	1.50			
XIII	Boric acid	18.0	1.00			
	Glycerin, U.S.P.	63.0	2.35	300	195	180
	Maleic anhydride	54.0	1.88			
XIV	Boric acid	5.0	1.00			
	Surfynol 475	100.0	1.37	300	96	26
	Sebacic acid	35.0	2.14			

The above-named ingredients may be introduced to a rotary-blades mixer and thoroughly mixed together, or otherwise thoroughly mixed together in any conventional way.

The 60% sorbitol of Example VIII is an aqueous solution of 60% by weight sorbitol and 40% by weight water; the phosphoric acid of Example X is an aqueous solution of 85% by weight phosphoric acid and 15% by weight water; and the Surfynol 475, is an ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7 - diol containing 75% by weight ethylene oxide and 25% by weight 2,4,7,9-tetramethyl-5-decyne-4, 7-diol.

As for the complex esters of this invention, the present invention is in no way limited by any theory concerning the structure of the complex esters thereof and the exact nature of the over-all reactions are not entirely known; in general, the structural aspects may be tentatively summarized as follows, by referring to one fundamental monomeric unit. As the esters polymerize, a plurality of these units are joined together with each other or with incompletely formed partial units. The fundamental unit is:



n^* being the number of monomeric groups in the polymer, in which:

X is a boric acid or phosphoric acid radical which may contain one or two unsubstituted hydrogens.

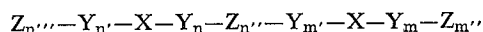
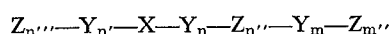
Y is a polyhydroxylic alcohol radical which may contain between zero and five unreacted hydroxyl function groups. Y may also be a triethanolamine or diethanolamine radical in which there are one or two unreacted hydroxyl groups.

Z is a saturated or unsaturated aliphatic dicarboxylic acid radical containing four to twenty-four carbon atoms. Z may also be the phthalate radical.

n and n' are the number of moles of Y radicals present. n or n' may be zero. In the present invention, the sum of n plus n' is preferably between 0.4 and 6.0.

n'' and n''' are the number of moles of Z radicals present. n'' or n''' may be zero. In the present invention, the sum of n'' plus n''' is preferably between 0.4 and 2.7.

A couple of examples of simple polymers may be represented as:



(The symbols m , m' , and m'' are used to indicate that the quantities may be different from n , n' , and n'' .)

With the above tentative summary in view, a general-

ized structural composition and mole ratios of examples as above are summarized in the following table:

Examples	$n+n'$	Number of equivalents of hydroxyl	$n''+n'''$	Number of equivalents of carboxylic acid
I	1.96	5.88	1.89	3.78
II	1.96	5.88	1.89	3.78
III	1.96	5.88	2.08	4.16
IV	2.05	6.15	1.10	2.20
V	3.09	6.18	1.48	2.96
VI	3.09	6.18	1.54	3.08
VII	2.00	8.00	1.00	2.00
VIII	1.62	9.72	2.64	5.28
IX	3.00	6.00	1.50	3.00
X	2.00	6.00	1.88	3.76
XI	2.01	-----	1.50	3.00
XII	0.68	-----	1.50	3.00
XIII	2.35	7.05	1.88	3.76
XIV	1.37	2.74	2.14	4.28

These concepts encompass the complete family of dicarboxylic acids and the concepts are not limited to these examples specifically cited.

In addition to the acids named in the above examples, I have experimented with other related acids such as: oxalic, malonic, succinic, glutaric, adipic, pimelic and suberic.

A number of tests were run in connection with the rust-inhibiting characteristics of the lubricants of this invention. These included outdoor exposure of 1½ x 2 inch cold rolled 18-gauge mild steel panels coated with a solution of 0.05% ester of this invention in isopropyl alcohol. Exposure to air and rain disclosed only slight rusting over a period of a month's exposure, while a like panel, similarly exposed, but uncoated, typically started rusting in one day and was badly rusted in about four days. As a further test, a lubricant of this invention was used as a wire-drawing lubricant to draw bright basic wire in two holes from 1½/32 inch rod down to 0.2437 inch. Exposed to the air, snow and rain, and compared with a like sample containing a lubricating film of approximately 20% potassium oleate, 5% lime and the balance water, the first-named wire had scattered areas of slight rusting at the end of a period from mid-November to mid-December, while the second-named wire had rust areas after three days and a uniform coating of light rust at the end of the same test period and under similar exposure conditions. In another test, cold-rolled carbon steel panels were highly polished, cleaned with distilled water, alcohol and Freon TF. They were then quickly dipped into a fluidized sample of selected lubricant and allowed to drain. The samples were then placed in a humidity cabinet maintained at 95° F. and 95% relative humidity. The samples were periodically observed and,

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when significant corrosion appeared, they were removed. The lubricants of this invention showed no rusting of significance until an elapse of 72 hours while the panels coated with a conventional lubricant showed rusting after 48 hours. With the humidity cabinet maintained at 140° F. and 95% relative humidity like panels were tested. The panels containing lubricants of this invention showed first rusting at 84 hours while those containing conventional lubricants, showed first corrosion at 34 hours. The tests employing the humidity cabinet were carried out essentially the same as that of the American Society for Testing Materials Methods (Method No. D-1748 "Rust Preventative Evaluation in the Humidity Cabinet").

What is claimed is:

1. Complex esters obtained by reacting at at least about 110° C. for about 150 to about 300 hours, an aliphatic dibasic carboxylic acid or its anhydride, a polyhydric alcohol, and boric acid, said dibasic acid being an acid or anhydride selected from the group consisting of sebacic, azelaic, phthalic, maleic, oxalic, malonic, succinic, glutaric, adipic, pimelic, and suberic, said polyhydric alcohol being selected from the group consisting of glycerin, ethylene glycol, hexylene glycol, pentaerythritol, sorbitol, polyethylene glycol, having a molecular weight of about 200, and ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol con-

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taining about 75% by weight ethylene oxide and 25% by weight 2,4,7,9-tetramethyl-5-decyne-4,7-diol, said mole ratio of acid and alcohol per mole of boric acid being from about 1.0 to 2.6 and 0.6 to 3.0, respectively.

2. The composition of claim 1 where the acid is sebacic and the alcohol is glycerin.

3. The composition of claim 1 where the acid is azelaic and the alcohol is glycerin.

4. The composition of claim 1 where the acid is a mixture of azelaic and phthalic and the alcohol is glycerin.

5. The composition of claim 1 where the acid is azelaic and the alcohol is ethylene glycol.

6. The composition of claim 1 where the acid is maleic and the alcohol is glycerin.

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