POLYALKYLENE GLYCOL ESTERS OF ETHYLENE-
DIAMINETETRAACETIC ACID AS LUBRICANT
DISPERSANTS
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ABSTRACT OF THE DISCLOSURE
A new class of compounds and a series of novel lubri-
cant compositions are disclosed. Polyalkylene glycol-ethyl-
enediaminetetraacetic acid addition compounds which are
useful as dispersants in polyalkylene glycol lubricant fluids
as sludge dispersants and lubricant fluid compositions
including such compounds are described.

BACKGROUND OF THE INVENTION
Field of the invention
This invention relates to chemical compositions and,
more particularly to chemical compositions useful as lub-
ricating fluid additives and to lubricating fluid composi-
tions. Still more particularly, this invention relates to poly-
alkylene glycol-ethylenediaminetetraacetic acid lubricant
additives and lubricant compounds.

Description of the prior art
Motor fuel lubricants, such as conventional automobile
motor oil or oils designed for special applications, e.g.,
marine, aircraft and stationary engines, conventionally
include oxidation inhibitors and dispersant additives. Vi-
cosity improvers, etc. are also conventionally added to the
basic lubricant fluid to provide particular characteristics
desired in the end lubricating compositions.

Many hydrocarbon-based or hydrocarbon-containing
additives are commercially available for use in conven-
tional hydrocarbon lubricating fluids. It is, of course,
esential that any successful additive be soluble in the lub-
ricating fluid at all potential operating or handling con-
titions. Long chain aliphatic hydrocarbon substituted suc-
cinic acid-amine derivatives have been proposed as dis-
persant additives for hydrocarbon-based lubricant fluids,
see U.S. Pat. No. 3,172,892, LeSuer and Norman, for ex-
ample.

A new class of potentially commercially valuable lubri-
cating fluids has been developed, however, in which most
known dispersant additives are insoluble or of limited
solubility. It is, accordingly, an object of this invention to
provide improved dispersant additives for non-hydro-
carbon lubricant fluids.

SUMMARY OF THE INVENTION
A new class of synthetic crankcase oils for use in
automobile engines, aircraft engines, marine engines, sta-
tionary engines and the like, are described. The basic fluid,
in the preferred embodiment, is a doubly end-blocked poly-
propylene glycol diether polymer identified hereinafter as
Ucon fluid DBL—200E. It has been found that while many
oxidation inhibitors useful in petroleum derived hydro-
carbon lubricant fluids may be used with the synthetic
 crankcase oils of this invention, none of the dispersant
additives previously known are sufficiently soluble and
non-toxic are otherwise successful as dispersants in the syn-
thetic crankcase oil compositions of this invention. It is,
accordingly, a principal object of this invention to provide
a new and improved dispersant additive for use in propyl-
ene glycol diether polymer synthetic lubricating fluids.

Similarly, a principal object of the invention is to pro-
vide improved synthetic lubricant fluids for use as crank-
case oils and as lubricants generally, which comprise poly-
propylene glycol diethers, as base fluids and an improved
sludge dispersant additive.

A more specific object of the invention is to provide an
improved dispersant additive comprising polyalkylene gly-
col-ethylenediaminetetraacetic acid compounds.

An additional and more specific object of the invention
is to provide a lubricating composition including a poly-
alkylene glycol diether lubricant base fluid in combina-
tion with a sludge dispersant additive comprising polyal-
kylene glycol-ethylenediaminetetraacetic acid compounds.

A further and more specific object of the invention is
to provide a class of polyalkylene glycol-ethylenediamine-
tetraacetic acids for use as lubricant additives.

A process for preparing lubricant additives and lubric-
iant fluids constitutes an additional and still more specific
object of the invention.

The provision of the specific compounds described here-
inafter and the specific processes for producing these com-
 pounds and the described lubricant fluids constitutes an
additional and highly specific, but non-limiting, object of
the invention.

DESCRIPTION OF THE PREFERRED
EMBODIMENT
The foregoing and additional objects are accomplished
in general by preparing the desired polyalkylene glycol-
ethylenediaminetetraacetic acid (EDTA) compounds and
blending the resultant product with a propylene glycol di-
ether polymer lubricating fluid generally of the type iden-
tified as Ucon fluid DBL—200E or equivalent.

The dispersant additives of this invention are prepared,
in general, by refluxing ethylenediaminetetraacetic acid
(EDTA) with a polyalkylene glycol at a temperature suffi-
ciently high to initiate the reaction and remove water. A
solvent, such as toluene, xylene, etc., may be used during
the refluxing operations, if desired.
The reaction, the formation of the polyalkylene glycol
ester of EDTA is carried out under atmospheric pressure,
with or without the addition of solvent, at temperature of
from about 75° C. to about 300° C., and preferably in the
range of about 120° C. to 180° C. for from about 1
300 500 600
0.1 mole of EDTA and 0.1 mole of a polypropylene
glycol ether identified as Ucon fluid LB—385, produced
by Union Carbide Plastics and Chemicals Department,
New York, along with 100 mls. of toluene and 0.005
mole of sulfosalicylic acid as a catalyst were introduced
into a 500 ml. reaction flask. Ucon LB—385 has an ap-
parent specific gravity of 0.995 at 20° C., a viscosity
index (ASTM D—567) of 144, a viscosity, Saybolt sec-
onds, at 210° F. of 75, at 100° F. of 385, and at 0° F.
of 15,000, a viscosity in centistokes at 210° F. of 14.3,
at 100° F. of 83.3, and at 0° F. of 4,700, with a pour point
(ASTM D—97) of —35° F. and a fire point (ASTM
D—92) of 500° F. The molecular weight of the poly-
propylene glycol is about 1200—1500.
The reaction mixture was refluxed for one hour. At
the end of this time there had been no color change and
no H₂O removal. The temperature was gradually in-
creased, with distillation of toluene, to 180° C. At this
point, 1.2 ml. water and 70 ml. toluene were removed.
The material was dark brown with a significant amount
of coagulated solids. The solids were filtered off the so-
solution through a flint glass filter with Celite and rinsed
with 50 mls. of toluene. The sample was heated to distill
off the excess toluene and was then submerged in an oil
bath, under vacuum, and heated to 150°C. The vacuum was gradually increased to 7 mm. Hg pressure. After 3 hours, the experiment was stopped.

102 grams of the product of the foregoing reaction, the EDTA-polypolypropylene glycol addition product, was obtained. Infrared analysis indicated, however, that only a comparatively minor portion of the compound was esterified. The preceding experiment was substantially duplicated except that the maximum temperature achieved was 200°C. Similar results were obtained.

The product of the above reaction was blended with an end-blocked polypropylene glycol ether identified as Ucon fluid DLB-200E. The composition was clear with no observable cloudiness or separation. An oxidation inhibitor Oranite 254 was added at a 3 percent level.

Dispersant effectiveness was tested by blending the additive to used Ucon DLB-200E obtained from engines used in dynamometer tests. The dispersant additive product of the aforementioned process was mixed with the material to be tested in a Waring Blender for 5 minutes. The sample was observed for sludge separation, and paper chromatographic spot tests were made to determine dispersant effectiveness. Data showing the relative effectiveness of the composition of this invention are given in Table I along with comparative data using other known and experimental dispersant additives.

**TABLE I—DISPERSENT TESTS**

<table>
<thead>
<tr>
<th>Code Number</th>
<th>Percent concentration</th>
<th>Structure</th>
<th>Percent separation, slurry settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>649-97-1</td>
<td>5</td>
<td>(C₆H₅OOH)₂₅(C₆H₅OCH₃)₂₅(C₆H₅OCH₂)₂₅(C₆H₅OCH₃)₂₅</td>
<td>3 128</td>
</tr>
<tr>
<td>649-9-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>48 175</td>
</tr>
<tr>
<td>649-6-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>50 170</td>
</tr>
<tr>
<td>649-8-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>6 118</td>
</tr>
<tr>
<td>649-5-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>2 18</td>
</tr>
<tr>
<td>649-10-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>(5)</td>
</tr>
<tr>
<td>649-14-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>(9)</td>
</tr>
<tr>
<td>649-19-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>3 158</td>
</tr>
<tr>
<td>649-20-1</td>
<td>2</td>
<td>C₆H₅-CH₃</td>
<td>(9)</td>
</tr>
<tr>
<td>649-23-1</td>
<td>5</td>
<td>Malic acid plus triethylentetramine</td>
<td>2 (9)</td>
</tr>
<tr>
<td>649-23-1</td>
<td>5</td>
<td>Ethylenediaminetetraacetic acid plus Pluronic L-62</td>
<td>30 (9)</td>
</tr>
<tr>
<td>649-31-6</td>
<td>5</td>
<td>CH₃</td>
<td>4 43</td>
</tr>
</tbody>
</table>
TABLE I.—Continued

<table>
<thead>
<tr>
<th>Code Number</th>
<th>Percent conc. Structure</th>
<th>Percent separation, lurs, settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>649-43B</td>
<td>2, N,N,N',N' tetraethyl sebamide</td>
<td>4, 39</td>
</tr>
<tr>
<td>649-31-7</td>
<td>CH₃</td>
<td>5, 18</td>
</tr>
<tr>
<td></td>
<td>CH₃H₂· CH₃CO· CH₃H₂· CH₃HH₂· OR</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CO· (N· CH₃CH₃)· NH₃</td>
<td></td>
</tr>
<tr>
<td>649-35-1</td>
<td>Reaction product of tetraglycosylocic anhydride plus Ucon LD-385</td>
<td>2, 19</td>
</tr>
<tr>
<td>649-35-1</td>
<td>Reaction product tetrahydrodiethylene</td>
<td>2, 14</td>
</tr>
</tbody>
</table>

The advantages of the ester addition compounds of EDTA and polyalkylene glycol are immediately apparent from the foregoing table. The significant advantage of these compounds as dispersant additives, as compared with structurally related and similar compounds, is quite unexpected. As an examination of the table will show, it is quite impossible to predict with any degree of certainty the potential effectiveness of a compound as a dispersant additive.

While we do not wish to be bound by the following reaction mechanism, it is believed, on the basis of infra-red data, molecular weight, etc., that the following equation properly describes the reaction of the inventive process. Side reactions of an undetermined nature are also believed to occur, however.

Reaction scheme

\[
\begin{align*}
\text{HOOCCH₃} & \quad \text{CH₃COOH} + R_{1} \left(\text{OCH₃CH₂O}\right)_{n} \text{OH} \\
\text{HOOCCH₁} & \quad \text{CH₃COOH} \\
R_{1} \left(\text{OCH₃CH₂O}\right)_{n} & \quad \text{OOCCCH₃} \\
R_{2} \left(\text{OCH₃CH₂O}\right)_{n} & \quad \text{NCH₁CH₂N} \\
\end{align*}
\]

wherein \( R_{1} \) and \( R_{2} \) are hydrogen or lower alkyl and \( n \) is a positive integer from 1 to 100, e.g., 25 in the specific examples hereinbefore described.

Obviously, depending upon the reaction conditions, a mixture of mono, di, tri and tetrapolyalkylene glycol esters of ethylenediaminetetraacetic acid may be formed. The product of the aforementioned reactions comprises essentially an equilibrium mixture of these mono, di, tri and tetrapolyalkylene glycol-EDTA esters.

The lubricating compositions of this invention are preferably formed by blending the compounds heretofore described with end-blocked polyalkylene glycol ether lubricating fluids, for example, the end-blocked polypropylene glycol ether identified as Ucon fluid DLB-200E available from Union Carbide Plastics and Chemicals Department, New York. The dispersant additive concentration level is from 0.1 to 30 percent generally, preferably from about 1 percent to about 25 percent, by weight. Oxidation inhibitors are also added in the 0.1 percent to 5 percent range, preferably in the range of from 0.5 percent to 3 percent. Many conventional oxidation inhibitors were tested and found to be successful, for example, 3 percent Oronite 254 is the preferred additive but 1 percent concentration of 4,4-methylene, bis-2,6-ditertiary butyl phenol (Ethyl 702), an alkylated phenol (Lubrizol 814), phenyl alpha-naphthylamine, and an alkylated diphenylamine (VanLube SL) were found to be successful oxidation inhibiting additives.

Ucon DLB-200 fluid is amber in color, has a viscosity at 210°C F. of 9.3 (SUS), at 100°C F. of 201 (SUS) and at 0°C F. of 5660 (SUS). The viscosity, in centistokes, is 9.70 at 210°C F., 43.2 at 100°C F., 1230 at 0°C F., 4140 at −20°C F. and 23,800 at −40°C F. The viscosity index is 161, the pour point is −50°C F., the flash point is 520°C F. and the fire point is 565°C F. This product is described in Union Carbide Chemicals Company Advance Technical Information publication F-40400, June 1959. Double end-blocked lubricants of this class generally may be used in the compositions of this invention, the primary consideration being the desired viscosity and viscosity index. The manufacture and properties of these compounds is discussed by Gunderson et al., Synthetic Lubricants, Reinhold, New York, 1962, chapter 3 on Polyglycols. Reference is made to this work and the publications and patents cited therein for a complete discussion of the lubricant base stocks used in the inventive composition.

It is difficult to overestimate the importance of providing the proper blend of lubricating fluid, dispersant additive, and oxidation inhibitor. To illustrate, using the fluids of the present invention, e.g., an end-blocked polyalkylene glycol ether lubricating base fluid, a dispersant additive of the type described, and an oxidation inhibitor, e.g., Oronite 254, there is provided a potential lifetime motor lubricant. The lubricating properties of the base fluid are not diminished under normal operating conditions; however, over long periods of time the base fluid may be oxidized to form volatile components which are discharged from the crankcase. An effective oxidation inhibitor is, therefore, necessary to prevent too rapid decomposition of the base lubricating fluid resulting in the necessity for continual addition of lubricant. Sludge is formed in every internal combustion engine from combustion products, wear products, etc. It is essential that this sludge be maintained in the lubricant and carried to an effective filter. Therefore, an effective dispersant additive is required to provide an essentially homogeneous circulating lubricant fluid in which the sludge forming materials are maintained in dispersion. As the homogeneous fluid is circulated through the oil filter, the sludge components are removed and the clean lubricating fluid is returned to the crankcase. Except for occasional addition of lubricating fluid, no additional attention need be given to a vehicle's engine lubrication system. The convenience and economy of this type of fluid are immediately apparent.

The lubricating compositions of this invention, the dispersant additives, and the process for preparing these products have been set forth in rather specific terms to
aid those skilled in the art to understand and to practice the invention. Departures from the specific disclosure will be made by those skilled in the art based upon the principles and teachings herein and such variations may be made without departing from the spirit and scope of the invention, as defined in the following claims.

We claim:

1. A composition comprising a mixture of mono-, di-, tri-, and tetrapolyalkylene glycol esters of ethylenediaminetetraacetic acid.

2. A lubricant composition comprising a major portion of an end-blocked polypropylene glycol diether and a minor portion of polyalkylene glycol esters of ethylenediaminetetraacetic acid.

3. A mixed ester product prepared by reacting ethylenediaminetetraacetic acid with polyalkylene glycol monoether at temperatures in the range of 75° C. to 300° C.

4. The product of the process of claim 3 wherein the polyalkylene glycol monoether is polypropylene glycol monoether of the formula

\[ R_1(CH_{2})_{n}OH \]

wherein \( R_1 \) is lower alkyl and \( n \) is from 1 to 100.

References Cited

UNITED STATES PATENTS

3,021,281 2/1962 Matson 252—51.5A
3,426,029 2/1969 Beavers et al. 260—482P

M. WYMAN, Primary Examiner
W. J. SHINE, Assistant Examiner

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