Synthetic Lubricants of Monoester Type

LIVIU E. MIRCI*, LIDIA ISMANA
University Politehnica Timisoara, Industrial Chemistry and Environmental Engineering Faculty, 4 Piata Rusel, 300056, Timisoara, Romania

The paper presents results concerning the synthesis and characterization as polymer processing aids (lubricants) and/or as tribological lubricants of some monoesters of different monocarboxylic acids with variable length, along with some special aliphatic-aromatic alcohols with a complex structure and/or with superior (larger) alcohols (exclusively aliphatic). The monocarboxylic acids considered were n-butyric, n-octanoic and oleic, respectively, while the alcohols taken into consideration were isodecyl (iso-C_{10}), isotridecyl (iso-C_{13}), as for the aliphatic group, 2-phenoxy-ethanol, 2-[(o-sec-butyl)phenoxy]ethanol, and 2-[(p-nonyl)phenoxy]ethanol, respectively, as for the complex aliphatic-aromatic group. Under these circumstances it became possible to investigate the influence of the structure on the main physico-chemical properties of these synthetic oils as well as on their lubricating characteristics. The results recorded fully certified the validity of the research program.

Keywords: complex monoesters, synthetic oils, lubricants, phenoxy-ethanols

Nowadays reducing energy consumption represents a major challenge for every industrial technology .Polymer processing constitutes a significant share of this aspect, and every act that promotes a decreasing power input contributes to solve this desideratum.

The use of lubricants in order to fulfil this request either in calendering, extrusion, injection, vacuum forming or in other processing ways, has acquired unanimous recognition. But, concurrently, in the last time some other impediments emerged as regards the use of lubricants, that is referring to their impact on the environment. Thus, beside the obvious technical characteristics assigned to promote a new lubricant, a supplementary quality started to be taken into account, that is its biodegradability potential.

The review of the last years literature reveals a considerable research effort in order to accomplish the more restrictive requirements regarding the capacity of a presumptive lubricating oil to be ingested and destroyed by the environment, and also the high demand for superior levels of properties of the new formulated synthetic lubricants.

One obvious and/or at hand solution, was to use vegetable oils as base for the construction of such new lubricants. As it is well known, the vegetable oils are derived from a renewable source, biodegradable, nontoxic, possess high flash points and have low volatility. However, their inadequate oxidative stability, poor low temperature properties and, last but not least, their preferential or restrictive compatibility with different polymers, limit their versatility.

In order to confer adequate features and to diminish their deficiencies, some chemical modifications have to be performed on the chemical structure of vegetable oils.

Several examples selected from the literature can support the direction of investigation stated above.

Thus, the synthesis of esterified epoxidized unsaturated vegetable oils for manufacture of synthetic oxidation-resistant lubricating oils has been reported [1] .The vegetable oils are typically epoxidized at their sites of unsaturation and the epoxides are converted to the alcohols or vicinal diols (e.g., by hydroxylation with $HClO_4$) which, in turn, can be reacted with the corresponding acid anhydride to yield the vicinal diesters. Suitable vegetable oils include cottonseed oil, castor, canola, linseed, oiticica, safflower, soybean, sunflower, corn, tung oil. The resulting derivatives are characterized by thermal and oxidative stability, have low temperature performance properties, are environmentally friendly, and have multiple directions of uses [1].

The same authors also show that the use of vegetable oils-based lubricants have a favorable environmental impact. The authors report the development of chemical modifications methods to improve the functional properties, and the resultant vegetable oils derivatives having diester substitution at the sites of unsaturation show comparable properties with non-destructible by the environment traditional lubricants [2].

Preparation and properties of a lubricant basestock from epoxidized soybean oil and 2-ethyl-hexanol represents the subject of a paper reported by the same team of authors [3].Thus, synthetic lubricants basestocks were prepared from epoxidized soybean oil and 2-ethyl-hexanol to be used alone or with polyalphaolefin. Sulfuric acid-catalyzed reaction of epoxidized soybean oil with 2-ethyl-hexanol involves a ring opening reaction at the epoxy group followed by transesterification at the ester group. Reaction with other catalysts including *p*-toluenesulfonic acid, Dowex 50 W-X8, BF_3, and CH_3ONa was also examined. Pour points of the products were observed as low as -21°C and -30°C without and with 1% pour point depressant, respectively. When the hydroxyl groups in the products were esterified with an acid anhydride, lower pour points were observed [3].

The capacity of vegetable base oil, described as "green lubricant", to be ingested and degraded by the micro-organisms of the environment, represents a concern all over the world and numerous papers review and study their biodegradability potential and suggest different methods of improving their oxidation stability [4].

Some researches report the use of modern techniques in order to settle the lubricant environment pollution, such as HFRR (High Frequency Reciprocating Ring) test ring [5].

An American patent reports the use of unsaturated fatty acid-based triglyceride vegetable oils for use in lubricating oils. The lubricating oil consists of ≥ 50 wt % of C_{16}-C_{26} fatty

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* *email: liviu.mirci @chim.upt.ro*

acid-containing triglyceride-based vegetable oil consisting of: (1) ≤ 9 wt % fatty acid content and (2) ≥ 65 wt % of polyunsaturated fatty acid content; the saturated fatty acids are palmitic and stearic, while the polyunsaturated fatty acids are linoleic and linolenic acids, and the monounsaturated fatty acid is oleic acid [6].

Glycerol monooleate is reported as being the base oil of a lubricant formulation with different directions of use [7].

The literature also records some studies which report attempts in order to realize biodegradable dimmer acid esters and analyze their tribological characteristics. Thus, a series of dimer acid esters were synthesized by using dimer acid and different chain length alcohols, and the molecular structures of synthetic dimer acid esters were identified. Results showed that viscosity temperature property of these products has good performance. Viscosity increases and pour point decreases with alkyl chain, and pour point of branching dimeric esters is much lower. Integrated characteristics of di-*iso*-octanol dimer acid ester are the best among the synthetic dimer esters [8].

Another research that seems to be very close to our direction of investigation, has in view the synthesis of some pentaerythritol esters by taking in consideration monoacids and consequently realizing pentaerythritol tetra-2-ethylhexanoate (PEB 8), and pentaerythritol tetra-nonanoate (PEC 9), respectively. The highest viscosity index (VI) value has been obtained for PEC 9 [9].

One can also record the fact that many studies underline a very significant situation that the pressure for increased use of vegetable oils in lubrication, due to both environmental and health & safety considerations, is likely to continue [10]. It is also emphasized that economic trends are likely to make vegetable oils increasingly more attractive than in the past in many areas of the globe, and all these factors will probably result in an increased use of vegetable oils as lubricants. By using the epoxidation process, significant improvements of the anti-oxidation characteristics have been assessed and reported [10].

The idea of using monocarboxylic aliphatic acids in conjunction with some polyhydroxylic alcohols was used in order to realize lubricating oil esters [11]. Thus, under microwave irradiation the esters of lubricating were synthesized by the reaction of 1,1,1-tris(hydroxymethyl) propane or pentaerythritol with C_5 to C_9 carboxylic acids. The authors report that the reaction time under microwave irradiation is largely shortened and the reaction velocity increases ten to fifteen times, and they also stated that the method worked out under such circumstances is very simple and the structures of the products have been and ascertained by ^{1}H NMR and ^{13}C NMR and IR spectra [11].

A paper, which verges on our interests in the field, reports the realization of ester oils or lubricant base oils particularly as fatty monoesters and/or fatty polyol esters [12].Thus, palm fatty acids are obtained from the fat splitting process and they are esterified with a monohydric alcohol or a polyhydric alcohol, in the presence of an acid catalyst at elevated temperature, wherein an azeotropic agent, particularly toluene, is used to facilitate continuous removal by distillation of water formed as a byproduct during the esterification reaction. The esterification reaction is completed within 5 h and these new conceived esters exhibit comparable lubricity and biodegradability [12].

Finally, one can also mention a patent (Japan) which describes the manufacture of lubricant esters which are prepared by reacting an aliphatic polyhydric alcohol with an aliphatic monocarboxylic acid, removing the unreacted acid from the reaction mixture, decolorizing the reaction product and further removing the unreacted acid [13].

As for our research program, we have chosen a specific way of approach stated many years ago in order to realize complex esters with valuable lubricity properties. In fact we have grounded our investigations on two main concepts such as the (chemical) polyfunctionality and the (molecular) asymmetry principles, and on this basis we have realized complex esters by using aliphatic-aromatic alcohols along with aliphatic alcohols with variable length (usually from C_3 up to C_{13}) and by taking into account different acid skeletons like trimellitic, pyromellitic, citric, phosphoric, *o*-phthalic, adipic and sebacic, respectively. The results of these researches were patented, presented within the frame of international and/or national congresses and were also published [14-24].

By analyzing the latest reports offered by the literature, one can observe the interest afforded to the lubricating vegetable oils on account of a lot of reasons, which were essentially underlined above.

But it become obvious the fact that the part of the molecular structure of the vegetable oils which brings about their valuable properties is represented by the acid moiety, which is constituted by a long unsaturated (less or more) aliphatic chain, usually of eighteen carbon atoms.

There are some studies which have reported the use of this part (exclusively) of vegetable oils in order to built some synthetic esters, like trimethylol-propane trioleate (TMP trioleate) [25,26].

But one can easily notice that this alternative seems to give products which are not very distinct from typical vegetable oils, by observing that glycerol was substituted by another triol, which is not very different in structure, that is TMP.

Under these circumstances we have taken into consideration these presumed qualities of the acid moiety of a vegetable oil, and we grounded a program with the aim to perform lubricants of monoester type. For fulfilling this purpose we have chosen oleic acid while for alcohols we have used, on the one hand, some special aliphatic-aromatic complex alcohols and, on the other hand, superior (larger) aliphatic alcohols.

In order to ensure the possibility to have a fair overview of this new class of monoesters with presumable beneficial lubricating properties, we considered as necessary to extend the program by taking into account two other monoacids with shorter chain length.

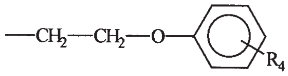
Thus, it would be possible to have a sort of reference and, under this situation, it emerged the means to better record/reveal/understand the molecule structure influence.

The structures of these synthetic monoesters are represented below within the general formulae (I) and (II):

$$R_1\text{–COOR}_2 \text{ (I)} \qquad R_1\text{–COOR}_3 \text{ (II)}$$

where:

R_1 = oleic, *n*-octanoic and/or *n*-butyric acid radical
R_2 = isodecyl (iso-C_{10}), and/or isotridecyl (iso-C_{13}) radical
R_3 = an alkyl-aryl radical with the following structure:



R_4 = H, *o*-sec-butyl, and/or *p*-nonyl radical

On the basis of these models it becomes possible to quantify the influence of different chemical functions that are present in the considered molecule on the overall properties, the presence or the absence of the aromatic ring brought in by the complex aliphatic-aromatic alcohol involved in the syntheses, and also the length and position of the alkyl pendant group attached to the aryl ring.

First results of this attempting approach were presented within an international congress (Germany, January 2008) [27], on the occasion of the XXX Romanian National Chemistry Conference (October 2008) [28], and were also patented [29].

Experimental part

Materials

The aliphatic-aromatic complex alcohols used in this work were the following: 2-phenoxyethanol, 2-[(*o*-sec-butyl)phenoxy]ethanol, and 2-[(*p*-nonyl)phenoxy]ethanol, respectively. These alcohols were synthesized by ethoxylation of the corresponding phenols with 1,3-dioxolane-2-one (ethylene carbonate), according to our previous stated procedures [30].

The main physico-chemical characteristics of these special alcohols are:

A.2-phenoxyethanol, molecular formula $C_8H_{10}O_2$; molecular mass, M = 138; density (20°C), d = 1.109 g/cm^3; refractive index, n_D^{20} = 1.5370;

B.2-[(*o*-sec-butyl)phenoxy]ethanol, molecular formula $C_{12}H_{18}O_2$; molecular mass, M = 194; density (20°C), d = 1.0164 g/cm^3; refractive index, n_D^{20} = 1.5175 ;

C.2-[(*p*-nonyl)phenoxy]ethanol, molecular formula $C_{17}H_{28}O_2$; molecular mass, M = 264; density (20°C), d = 0.978 g/cm^3; refractive index, n_D^{20} = 1.5113 .

The superior (larger, aliphatic) alcohols used, that is isodecanol (iso-C_{10}) and isotridecanol (iso-C_{13}), were supplied by BASF (Germany).

The acids, oleic, *n*-octanoic and *n*-butyric, were pure samples, source ALDRICH.

Esters synthesis

The synthesis of the monoesters was performed in a solution esterification process, solvent toluene, using *p*-toluenesulfonic acid as catalyst, the water being extracted azeotropically according, in general, to our standard procedures described elsewhere [31], and to a particularized method for this case [29].

Measurements and characterization

The purified products were characterized by general chemical and physical indices usually recorded for this class of organic compounds, while their specific lubricating features were determined by using standardized techniques.

Thus, dynamic viscosity was measured at 20°C, by means of a rotation viscometer, i.e. Rheotest Type RV, VEB Prufgerate–Werk, Medingen/Dresden, Germany, measuring device S 1, shear rate within the interval 1.6-1310 /s. Kinematic viscosity was determined in a classical way, using an Ubbelohde viscometer, according to ASTM D 445, while the viscosity index (VI) was calculated from the data. The pour (flow) point was measured according to ASTM D 97 and the flash point according to ASTM D 92. The four ball test was accomplished on a SETA machine according to ASTM D 4172.

The polymer lubricity features were determined on a Brabender Plastograph, type PL/3S, on the basis of a standard receipt, that is: PVC (suspension) Kw = 67, 100 p, tribasic lead sulphate (special stabilizer without any lubricating effect) 2 p, lubricant 1 p. The amount of the receipt was reduced at the level of PVC 30 p, using the 30 cm^3 vat, domain 5, rotation 30 rot/min, and at a temperature of 160°C.

The lubrication number was calculated on the basis of the Botner-Rosenthal relationship, [32]:

$$C_L = 1000 \frac{E}{T \cdot m_D}$$

where:

C_L = lubrication number

E = total quantity of ingredients, expressed as percentage of the PVC quantity

T = the vat temperature, °C

m_D = minimal couple, Kg·m , depicted from the Brabender plastogram

Note. In order to facilitate the reading of tables and make easier the identification of the synthesized monoesters, a coding system was used involving an abbreviation principle. Thus, 2-phenoxyethanol is identifiable as FE (phenol ethoxylated); 2-[(*o*-sec-butyl)phenoxy]ethanol as OSECBUT ; 2-[(*p*-nonyl)phenoxy]ethanol, as p-N. Similarly, oleic acid was defined as OL, *n*-octanoic acid as OCT, and *n*-butyric acid as BUT. Accordingly, the monoesters could be ranged in the following order: OL-IZOTRI, OL-IZODEC, OL-p-N, OL-OSECBUT, and OL-FE, for the oleic series; OCT-IZOTRI, OCT-IZODEC, OCT-p-N, OCT-OSECBUT, and OCT-FE, for the *n*-octanoic series; BUT-IZOTRI, BUT-IZODEC, BUT- p-N, BUT-OSECBUT and BUT-FE, for the *n*-butyric series.

Results and discussion

The main chemical and physical indices of these three series of monoesters are listed within table 1. From the data recorded in this table one can observe the following:

Table 1

VALUES OF THE MAIN PHYSICAL AND CHEMICAL PARAMETERS

No.	Parameter Code	Molecular formula	Molecular mass	Density g/cm^3 20°C	Refractive index, n_D^{20}	Dynamic viscosity, mPa·s 20°C	Flash point, °C	Pour (Flow) point, °C
1	OL-IZOTRI	$C_{31}H_{60}O_2$	464	0.8662	1.4618	20.32	186	-30
2	OL-IZODEC	$C_{28}H_{54}O_2$	422	0.8688	1.4602	14.20	182	-27
3	OL-p-N	$C_{35}H_{60}O_3$	528	0.9257	1.4895	61.47	220	-33
4	OL-OSECBUT	$C_{30}H_{50}O_3$	458	0.9338	1.4888	29.53	189	-30
5	OL-FE	$C_{26}H_{42}O_3$	402	0.9416	1.4864	21.03	195	-18
6	OCT-IZOTRI	$C_{21}H_{42}O_2$	326	0.8649	1.4485	10.00	160	-36
7	OCT-IZODEC	$C_{18}H_{36}O_2$	284	0.8679	1.4432	7.29	158	<-42
8	OCT-p-N	$C_{25}H_{42}O_3$	390	0.9579	1.4935	84.67	188	-39
9	OCT-OSECBUT	$C_{20}H_{32}O_3$	320	0.9701	1.4895	15.66	160	<-42
10	OCT-FE	$C_{16}H_{24}O_3$	264	0.9986	1.4890	10.50	162	-10
11	BUT-IZOTRI	$C_{17}H_{34}O_2$	270	0.8653	1.4422	5.78	148	-42
12	BUT-IZODEC	$C_{14}H_{28}O_2$	228	0.8674	1.4347	4.35	128	-42
13	BUT-p-N	$C_{21}H_{34}O_3$	334	0.9728	1.4957	57.82	176	-39
14	BUT-OSECBUT	$C_{16}H_{24}O_3$	264	1.0024	1.4870	9.28	152	-40
15	BUT-FE	$C_{12}H_{16}O_3$	208	1.0656	1.4980	7.01	134	<-42

Table 2
REPRESENTATIVE LUBRIFYING PAMETERS

No.	Parameter Code	Wear scar diameter, mm, 40 daN, 60 min			Kinematic viscosity, mm^2/s		Viscosity index, VI
		Base oil	Additivated oil		40°C	100°C	
			1.5% Zn dithiophosphate	Special additive			
1	OL-IZOTRI	0.92	0.78	0.52	13.43	3.59	161
2	OL-IZODEC	1.05	1.08	0.87	11.18	3.36	184
3	OL-p-N	0.63	0.72	0.52	33.52	5.63	107
4	OL-OSECBUT	0.82	0.82	0.50	16.85	3.87	132
5	OL-FE	0.62	0.62	0.37	13.31	3.41	140
6	OCT-IZOTRI	0.82	0.82	0.33	6.12	2.00	117
7	OCT-IZODEC	0.87	0.85	0.38	4.20	1.66	-
8	OCT-p-N	0.78	0.78	0.51	31.93	4.70	34
9	OCT-OSECBUT	0.84	0.80	0.49	8.45	2.24	58
10	OCT-FE	0.75	0.74	0.53	5.80	1.76	-
11	BUT-IZOTRI	0.88	0.80	0.54	3.62	1.46	-
12	BUT-IZODEC	0.93	0.89	0.70	2.43	1.27	-
13	BUT-p-N	0.85	0.85	0.62	23.81	3.61	-56
14	BUT-OSECBUT	0.90	0.87	0.55	5.45	1.81	-
15	BUT-FE	0.81	0.78	0.59	3.94	1.35	-

As for the special additives the formulations were the following:
Samples 1 and 2 were additivated with 1.5% Infineum G 361
Samples 3 and 4 were additivated with 1.2% CIBA ML 605 A IRGALUBE
Samples 5 -15 were additivated with 1.5% Lubrizol 1046

-the molecular mass presents values between 208 and 528 mass units, which is a suitable interval that falls in the usual domain of synthetic oils;

-the density shows a gradual variation within each series and also in the frame of the groups admitted by taking in consideration the variation promoted by the alcohols; the smooth variation recorded confirms the validity of the theoretical structures suggested and, in the same time, emphasizes the high purity level of the products;

-refractive index also presents a gradual variation, remarkable being the fact that this parameter is able to discern and record the very fine modifications of the molecular structure;

-the dynamic viscosity shows reduced values for all terms of these series; as expected, the higher values are recorded for the monoesters built by taking in consideration the complex aliphatic-aromatic alcohols, the highest value being attributed to the complex alcohol with the highest molecular mass, i.e. 2-[(*p*-nonyl)phenoxy]ethanol, (p-N);

-the flash points are ranged between 134°C and 220°C; one can easily remark that with the decrease of the molecular mass the flash point values also decrease, due to the fact that, obviously, the volatility of the products increase, an aspect which can fully explain the overall behavior;

-as regards the pour (flow) points, the values registered present very negative (good) levels, and are set out from -10°C up to even -42°C (which was the maximum level of refrigeration of the device used), and this feature constitutes a remarkable quality; as far as this parameter is considered, it wholly illustrates the validity of the two main concepts stated within the preamble of the paper, that is the (chemical) polyfunctionality and (molecular) asymmetry principles.

Table 2 records data of the representative lubrifying parameters. Thus, the viscosity index values are, for the oleic series, all above the level of 100 units with a maximum value of 184. This fact fully validates the a priori assumption of the benefic influence of the oleic radical on the lubricity potential of these monoesters. As regards the other two series, built on the basis of *n*-octanoic and *n*-butyric acid, respectively, only few of the realized products meet a satisfactory level of performance, from this point of view. The four-ball test confirms, to some extent, these considerations, by observing a quasi-overall good behavior for all these series, regardless of the length of the acid involved.

In order to define the polymer lubricity capability, which is expressed in this field by the well known "lubricant number", this parameter was calculated by using the couple values drawn out from the Brabender plastograms, recorded under previously stipulated conditions.

Figure 1 shows a representative Brabender plastograph diagram for this test, while the values of the lubricant number were calculated in accordance with the mentioned relationship. From the values registered from these diagrams it is difficult to withdraw a relevant conclusion, or to establish an univocal dependence, regarding the correlation of the structure with this parameter.That is why we preferred to realize a suggestive graphic relationship given in figures 2-6, in which the dependence of lubricant number with the length of the acid and with the nature of the alcohol involved, respectively, is represented.

From these diagrams one can ascertain a rise of the lubricant number value as the length of the considered acid increases. That is, a decrease of the molecular polarity or, reversely, an increase in the non-polar function content, promotes this behavior, which is in fully agreement with the theoretical anticipations. Under these circumstances one can observe that the monoesters with longer aliphatic chain show properties which characterize "external" lubricants, while those monoesters with shorter aliphatic chain are to be included within the "internal" lubricant class.

Conclusions

On the basis of (chemical) polyfunctionality and (molecular) asymmetry principles, some monoesters of oleic, *n*-octanoic and *n*-butyric acids, along with special alcohols of a complex alkyl-aryl structure, namely 2-phenoxyethanol, 2-[(*o*-sec-butyl)phenoxy]ethanol, and 2-[(*p*-nonyl)phenoxy]ethanol, respectively, and also with superior (larger) aliphatic alcohols, such as isodecanol (iso-C_{10}), and isotridecanol (iso-C_{13}), were synthesized and evaluated as synthetic lubricating oils.

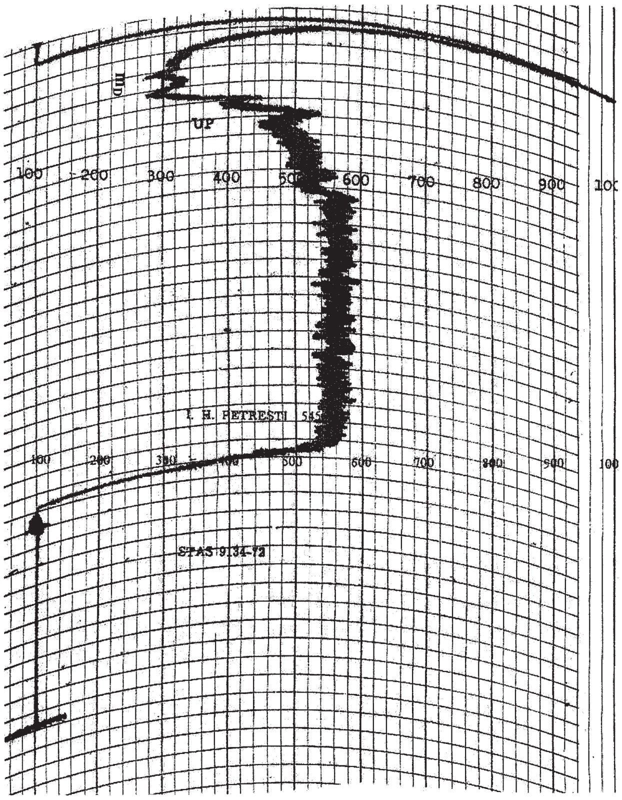


Fig. 1. Brabender plastograph diagram

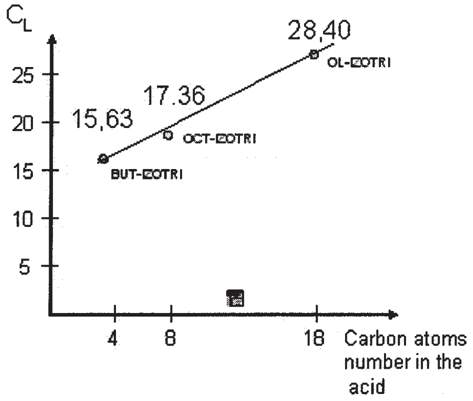


Fig. 2. Izotridecanol

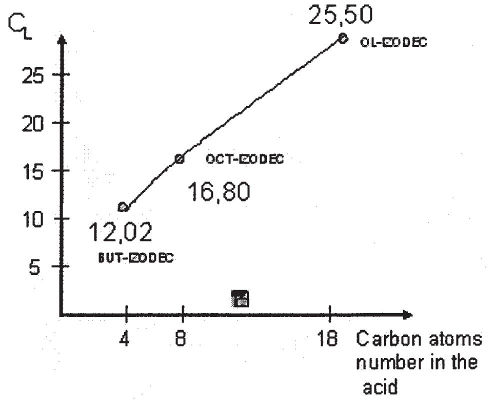


Fig. 3. Izodecanol

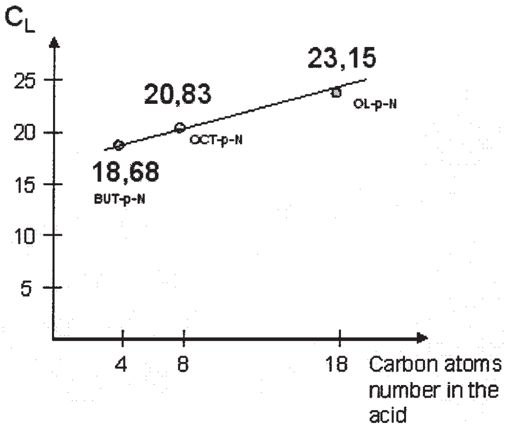


Fig. 4. 2-[(p-nonyl)phenoxy]ethanol

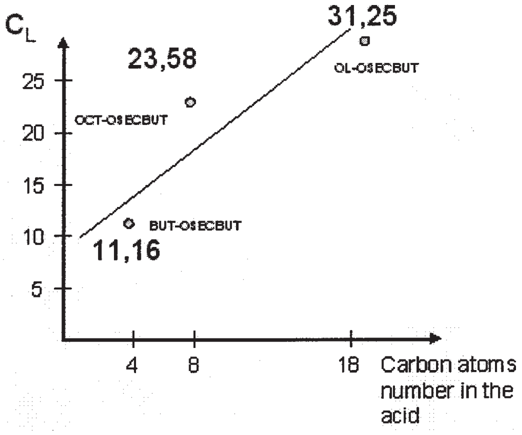


Fig. 5. 2-[(o-sec-butyl)phenoxy]ethanol

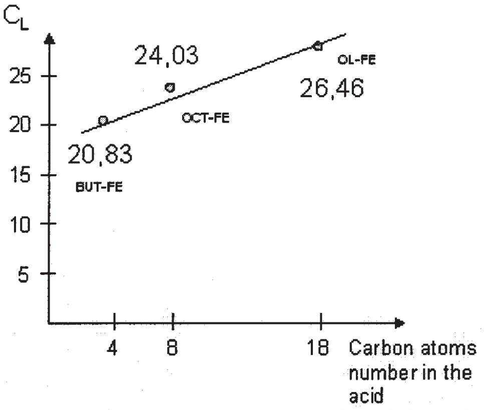


Fig. 6. Phenoxy-ethanol

These new compounds present very good pour (flow) points (negative temperature values), high flash points, and, some of them show very good viscosity characteristics. From the results of four-ball test, good lubricity qualities have been recorded.

When evaluated as specific polymer processing aids, the synthesized monoesters present doubtless adequate lubricant features. Depending on the relationship between the polar and non-polar chemical structures, either "external" or "internal" lubricant characteristics are emphasized.

This class of monoesters represents a priority, not being previously reported in the literature, the intrinsic structure, the synthesis conditions and the methods of purification being protected by a patent.

By taking in consideration the overall behavior of these new synthetic oils, it could be ascertained the validity of the theoretical concepts considered, which were fully proved and expressed by the consistent valuable lubricating features of these monoesters.

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