Thin-Film Test to Investigate Liquid Oxypolymerization of Nonvolatile Analytes: Assessment of Vegetable Oils and Biodegradable Lubricants

Svajus Asadauskas and Sevim Z. Erhan*
Oil Chemical Research, USDA, ARS, NCAUR, Peoria, Illinois 61604

ABSTRACT: A thin-film oxidation test was developed to investigate liquid oxypolymerization of nonvolatile analytes. Gel permeation chromatography (GPC) showed that the test delivered the required degree of oxidation with better than ±5% accuracy. The following oils were ranked according to their decreasing resistance to oxypolymer formation at 150°C: 90% oleic sunflower oil, triolein, meadowfoam oil, castor oil, canola oil, lesquerella oil, and soybean oil. Higher degrees of oxidation demonstrated the occurrence of oxidative gelation. Oxypolymerization tendencies of hydraulic fluids based on canola and rapeseed oils were comparable to those of canola oil without additives. The relative amount of C–C polyunsaturation present in the fatty acid chain was a major differentiating factor. However, oxidation inhibitors also reduced the rates of oxypolymerization, as demonstrated by sunflower oil-based hydraulic fluid. Canola and rapeseed lubricants needed better oxypolymerization control.

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A better understanding of oxidative polymerization (oxypolymerization) of vegetable oils is important in such applications as drying oils, vegetable oil-based lubricants, and frying oils. Oxypolymerization is one of the consequences of oxidative degradation. Free radical addition and sometimes cycloaddition reactions can be seen as the main causes of the production of oxidative polymers (oxypolymers) in triacylglycerols, especially if the content of methylene-interrupted polyunsaturated fatty acids is high (1,2). Scission reactions contribute the most to the formation of volatile oxidation products (3,4). Other reactions, hydroperoxide decomposition in particular, can also create hydroxy, epoxy, keto, and a series of other functionalities within the oxidized triacylglycerols (5), which are referred to as polar materials.

The oxypolymerization kinetics of vegetable oils have been studied somewhat less than the formation of volatiles or polar matter and still remain unclear. Some investigators have focused on oxypolymerization mechanisms in drying oils (6,7), suggesting that the occurrence of biperoxy radicals in highly polyunsaturated triacylglycerols favors subsequent free radical addition and oxypolymerization. However, their findings have yet to be confirmed. The complexity of oxypolymerization increases with higher temperatures, exposure to metals, and the presence of additives with free radical-scavenging or peroxide-decomposing abilities. Therefore, chemical pathways of triacylglycerol oxypolymerization in field systems, such as with biodegradable lubricants in hydraulic equipment, remain uncertain, and experimental investigations are necessary to predict their susceptibility to oxypolymer formation.

The lubricant industry routinely tests the resistance of lubricants to increased viscosity with oxidation, which can be related to investigations of oxypolymerization. However, tests such as the universal oxidation test (UOT; 8), or thermal and oxidative stability test (TOST; 9) usually are not applied for purposes other than simple qualitative comparisons among the series of formulated lubricants. A more academic approach has been chosen in micro-oxidation, which covers a family of tests used in the lubricant industry. These tests require small amounts of oil (up to 20 μL) to be incorporated in the form of a thin film on a metal sheet. The degree of oxidation is usually controlled simply by selecting test temperature and/or test duration. Selection of surface metals, inlet gas, and sample film thickness also affects the degree of oxidation. In most cases the micro-oxidation is carried out to determine the time required for the oil to solidify or to demonstrate a sudden increase in high molecular weight (MW) product formation. Gel permeation chromatography (GPC) coupled with the refractive index (RI) detector (10,11) has been shown to determine the distribution of oxidation products relative to their molecular weight (MW). Most micro-oxidation studies have been carried out on petroleum-based lubricants and other unsaturation-free fluids with oxidation temperatures ranging from 200 to 350°C (12–16).

In this investigation a thin-film test was designed to quantify oxypolymerization tendencies more accurately. Because micro-oxidation represents a simple and extensively described method to obtain the amount of thermal evaporation and insoluble deposit formation, its principles were used in this study to investigate oxypolymerization kinetics in triacylglycerols, vegetable oil-based lubricants, and other fluids.

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*To whom correspondence should be addressed at Oil Chemical Research, USDA, ARS, NCAUR, 1815 N. University Street, Peoria, IL, 61604.
E-mail: erhansz@mail.ncaur.usda.gov

Micro-oxidation has already been used to investigate conventional vegetable oils (17,18). However, the test requires a rigorous setup and does not account for the increased reactivity of unsaturated materials. Major modifications were introduced in this work to take advantage of the relatively low volatility and lower oxidative stability of vegetable oils as compared to conventional lubricants. Therefore, a new test was designed utilizing the concepts of thin-film oxidation and GPC analysis that originated from micro-oxidation tests. Experimental evaluation of oxidative polymerization of several conventional vegetable oils confirmed the applicability of such a test to study oxypolymerization, and it revealed tendencies of oxypolymer formation in the oils.

EXPERIMENTAL PROCEDURES

Materials. Alkali-refined canola (NutraClear™ oil) and soybean oil (refined, bleached, deodorized) were commercial products of the Bunge Edible Oil Corporation (Kankakee, IL). Refined meadowfoam and castor oils were provided by the Fanning Corporation (Chicago, IL). Ninety percent oleic sunflower and lesquerella oils were supplied by International Flora Technologies, Ltd. (Gilbert, AZ). Extra purity triolein (99+% oleic) was provided by Nu-Chek-Prep (Elysian, MN). All oils were stored below −5°C under a nitrogen atmosphere. Their fatty acid contents are listed in Table 1. Antioxidants employed in the hydraulic fluids were based on hindered phenols and aromatic amines. A dry hydrocarbon-free air supply was used; the nitrogen used contained less than 0.4 wt% oxygen. Chromatographic-grade solvents, tetrahydrofuran (THF), acetone, and acetonitrile (all supplied by Aldrich, Milwaukee, WI), were used for GPC and high-performance liquid chromatography (HPLC) without additional pretreatment.

Determination of fatty acid contents. Triacylglycerols were converted to their fatty acid methyl esters by treatment of the oils (~10 mg) with 0.5 mL of 0.5 M KOH/MeOH for an hour in a sealed vial at 100°C. The vial was cooled to room temperature and 1 mL of 1.0 M H_2SO_4/MeOH was added. The vial was resealed and placed at 100°C for 10 min. After cooling to room temperature, the contents were extracted into hexane (2 mL). The hexane was washed with saturated brine and then dried over Na_2SO_4. The resultant ester mixture was analyzed by HPLC and identified using standards supplied by Alltech Associates (Deerfield, IL). The HPLC analyses were performed on a Thermo Separation Products instrument with a P2000 binary pump and AS2000 autosampler/injector (Fremont, CA), which is coupled to a UV2000 detector set at 295 nm. It utilized a 25-cm nonpolar C8 column Onift Tube 5. Gradient elution at 1 mL/min with acetonitrile/acetone (50:50) was programmed at 0 min with linear propagation to 100% acetone at 12 min and reversed to 50:50 at 17 min. Here HPLC was used for fatty acid analysis and GPC was used for MW determinations.

Test for investigation of liquid oxypolymerization of nonvolatile analytes (ILONA test) with GPC analyses. The ILONA test utilizes less than 50 µL of analyte placed on a nearly flat steel pan in the form of a thin film and subjected to specified durations of oxidation under controlled temperature and inlet air flow. As heating medium, a Mirak^{TM} hot plate with built-in thermocouple controller (Thermolyne, Inc., Dubuque, IA) was used, which was able to maintain temperatures of up to 200°C with ±1°C accuracy without considerable temperature gradients across the heating surface. A rectangular Al slab (25 × 125 × 125 mm) was placed on top of the hot plate to ensure a uniform heat transfer to the sample pans. The slab had a hole drilled on the side to insert a thermocouple (Teflon-coated Ni-Al and Ni-Cd, supplied with the hot plate) for the temperature control. Four sample pans loaded with analytes were placed on the slab and covered with the bottomless impingers. Either flat sample pans were used (verifying that the surface tension forces prevented the fluid from spillage), or the edge of the pan was slightly raised to reduce the risk of spills. Analytes were applied in the form of a homogeneous film on the sample pans before placing the pans on the heated block. The pans with the samples were weighed, placed on the slab, and covered with the glass impingers. Controlled air flow ensured the absence of oxygen concentration gradients in the gas phase. The size of the glass

TABLE 1
Fatty Acid Contents in Tested Vegetable Oils and Vegetable-Based Hydraulic Fluids (HF) Determined by High-Performance Liquid Chromatography

		% Fatty acid contents					
Vegetable oil-based fluid	Processing/ manufacturing	Palmitic 16:0 and stearic 18:0	Oleic 18:1-Δ9	Linoleic 18:2-Δ9,12	Linolenic 18:3-Δ5,12,15	Specialty	Antioxidants
Canola	Alkali refined	3	60	30	7	0	Natural
Castor	Alkali refined	3	4	4	0	89 of 19:1-12OH	Natural
Meadowfoam	Refined	1	80 of 20:1-Δ5	1	0	18 of 22:2- Δ5,13	Natural
Soybean	Alkali refined, winterized	16	23	53	8	0	Natural
Sunflower	Alkali refined	4	88	5	1	0	Natural
Lesquerella	Crude	2	15	7	18	58 of 20:1-14OH	Natural
Triolein	Synthetic	0	>99	0	0	0	None
Canola HF	Formulated	9	61	21	7	0	1% Phenol
HOSO HF[a]	Formulated	5	88	5	1	1	1% Phenol/amine
Rapeseed HF	Formulated	8	60	23	9	1	1% Phenol/amine

[a] HOSO, high oleic sunflower oil.

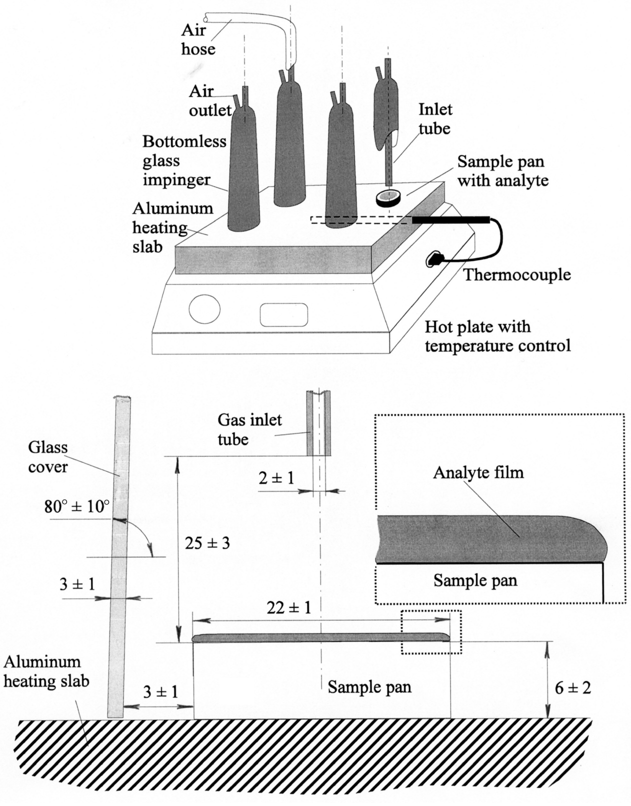

FIG. 1. Apparatus of a test for the Investigation of Liquid Oxypolymerization of Nonvolatile Analytes (ILONA test). General view and cross sections of sample pan placement and analyte film. Units of measurement: mm.

impinger guaranteed effective elimination of volatile oxidation products by condensation on the impinger walls, while keeping the sample heat losses minimal. The ILONA test apparatus is shown in Figure 1.

The procedure for the ILONA test, analogous to that of heated-block micro-oxidation described in Reference 19, involved polishing the pan and heating block, weighing the empty pan, applying 40 μL (~36 mg) of sample in the form of a homogeneous film, placing it on the thermally equilibrated aluminum slab, covering it with the bottomless impinger, and supplying 0.1 MPa dry air flow at 20 cm^3/min. After a given duration, the sample pan was removed and placed on a clean, cold metal surface for shock cooling. Then the pan was weighed and the oxidized sample washed off with THF. The weighing before washing with THF allowed volatile losses (or gains due to oxidation) to be determined, whereas the weighing after the washing determined the possible formation of solids or corrosives dissolving the surface metal. GPC was employed to investigate oxypolymerization kinetics.

GPC analyses were carried out on a Thermo Separations Products instrument with a P 4000 pump and AS 3000 autosampler/injector. A THF flow rate of 3 mL/min used partial recirculation through a Peak Cutter™ by Waters-Millipore (Milford, MA). Four columns of PLgel 5 μm, 300 × 7.5 mm and an adequate guard column by Polymer Laboratories Ltd. (Church Stretton, Shropshire, United Kingdom) were maintained in the air bath at 40 ± 1°C. Each injection consumed ~0.3 mL of the sample solution in THF at ~1 wt%. Refractive index detector data from a Waters M411 Differential refractometer (Milford, MA) vs. retention time was stored on file at 0.6-s intervals and then transferred to spreadsheet files for further analysis.

RESULTS AND DISCUSSION

Three key elements were identified as most influential when comparing traditional micro-oxidation to the ILONA test: (i) the possibility of more pronounced temperature gradients on the heated block surface as compared to a liquid metal bath; (ii) the effect of the surface roughness of both the sample pan and heating block on heat transfer to the sample in the ILONA test as compared to heat transfer from a liquid metal bath to the sample pan *via* the impinger glass wall in micro-oxidation; and (iii) the influence of the sample film distribution on oxidation rates of unsaturated materials as compared to those of usually unsaturation-free lubricating fluids. All three factors were investigated experimentally to evaluate their effect on the delivered degree of oxidation. It was found that factors (i) and (ii) did not affect the delivered degree of oxidation by more than ±5%, whereas the sample film thickness and its homogeneity needed to be controlled more accurately than for petroleum liquids. Unsaturated materials are more susceptible to oxidation; therefore, oxygen concentration gradients are sharper within the film. With the assumption that minor fluctuations of the film thickness (owing to surface profile inconsistencies or oxidative evaporation) did not have an appreciable effect (15), the amount of sample was held constant at 40 μL ± 5%.

In general, the above analyses and additional investigations (19) showed that such tests produced lower than ±5% error in delivering a required degree of oxidation. Optimal conditions for the ILONA test require that the oxidation temperatures be below 175°C, that durations be beyond 30 min, and that the film thickness be held constant by controlling the sample size (40 ± 1 μL) on a sample pan with a nearly flat surface. After accounting for these factors, selected vegetable oils without additives were oxypolymerized at 150°C for durations of 30, 45, and 60 min. The ILONA test and GPC permitted quantification of triacylglycerol oxydimers and oxytrimers as well as unpolymerized monomers. An example of soybean oil is shown in Figure 2.

In order to simplify the data interpretation, partially decomposed triacylglycerols (e.g., owing to scission reactions) were attributed to the unpolymerized triacylglycerols, or monomers. As described in the Experimental Procedures section, volatile losses were determined gravimetrically, as were the THF-insoluble and THF-soluble fractions. ILONA test and GPC results are listed in Table 2. In agreement with hydroperoxide theory, during early stages of oxidation the oxygen abstraction results in negative volatile loss, as is evident

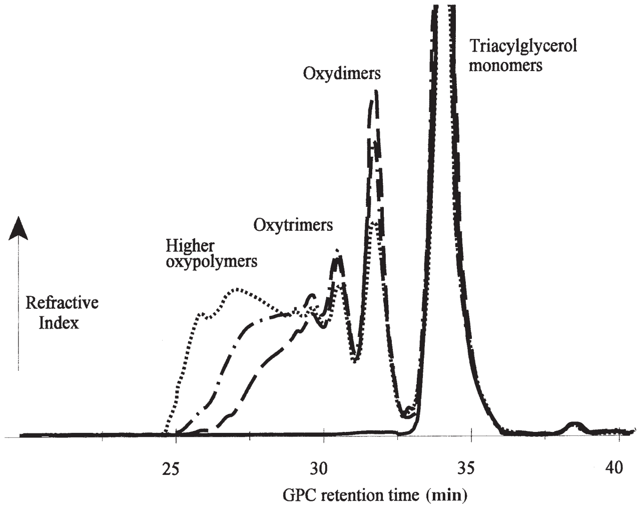

FIG. 2. Superposition of gel permeation chromatography (GPC) spectra of original and three oxypolymerized soybean oils using the ILONA test at 150°C. Oil before oxidation (solid line), after 30 min (dashed line), 45 min (dot-interrupted line), and 60 min (dotted line) oxypolymerization. Peaks of triacylglycerol monomers truncated. Solvent region beyond 40 min. See Figure 1 for abbreviation.

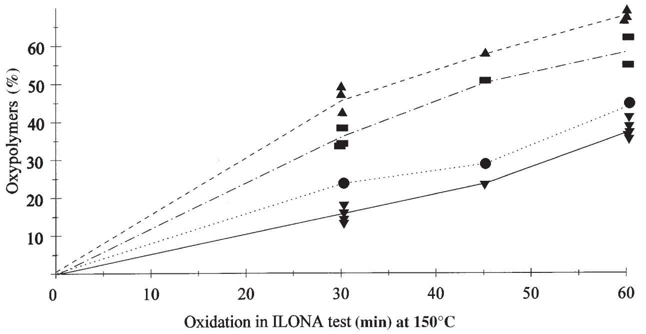

FIG. 3. Oxypolymerization tendencies of soybean (triangles and dashed line), canola (squares and dot-interrupted line) and sunflower (inverted triangles and solid line) oils, and triolein (circles and dotted line). GPC data from Table 2. See Figures 1 and 2 for abbreviations.

in the case of 90% oleic sunflower oil at 30 and 45 min. Later scission reactions reduce the total amount of a sample. Oxidation may also result in dissolving some surface metals, causing the weight of the metal pan to appear lower after oxidation than before oxidation. This minor fluctuation appears as a negative amount of THF-insoluble products. A positive amount of THF-insoluble products indicates the formation of detectable levels of materials not soluble in THF. At these conditions both volatile products and insoluble precipitants are insignificant when compared to THF-soluble oxypolymers. Therefore, oxypolymer formation can be represented by the amounts of high-MW products in the liquid fraction of the oxidized analyte, as determined by GPC.

The assumption that the total amount of oxypolymers is always 100% may falsely suggest that oxypolymerization is the only process occurring under the ILONA test conditions. This occurs in the case of triacylglycerols because the volatile losses, being of relatively low MW, contribute very little compared to those of oxypolymerized triacylglycerols, which have a much higher MW. Therefore, the assumption that the total amount of oxypolymers could be determined by subtracting the amount of monomers from 100% does not introduce a significant deviation. This is necessary because the oxypolymers higher than oxytrimers could not be quantified with GPC, as shown in Figure 2. The data in Table 2 still demonstrate that fluctuations in determined oxypolymer amounts are generally below ±5% in the ILONA test.

It can be expected that the oxypolymerization rates of vegetable oils are related to their oxidative stabilities. Those rates are usually dictated by the contents of methylene-interrupted polyunsaturated fatty acids and antioxidants. As shown in Table 1, from the standpoint of oxidative stability, the major difference among triolein, sunflower, soybean, and canola oils is the distribution of oleic, linoleic, and linolenic acids, if differences in amounts of natural antioxidants are disregarded. Rates of oxidative polymerization of those oils are compared in Figure 3.

Ninety percent oleic sunflower oil containing only 5% linoleic acid shows higher resistance to oxypolymerization than antioxidant-free triolein. Conventional soybean oil is notably more susceptible to oxypolymerization than canola oil, which has lower levels of linoleic and linolenic acids. Both oils oxypolymerize much more rapidly than nearly polyunsaturation-free triolein and sunflower oil. Oxypolymerization of vegetable oils containing specialty fatty acids, meadowfoam oil, castor oil, and lesquerella oil are compared in Figure 4. Meadowfoam and castor oils contain relatively low amounts of methylene-interrupted polyunsaturated fatty acids and appear to oxypolymerize slower than lesquerella oil. Although castor oil has less unsaturation than meadowfoam, its oxypolymerization is more rapid, suggesting that the hydroxy functionality in ricinoleic acid favors oxypolymerization. Further oxidation results not only in higher levels of oxypolymers, but also in solid (or THF-insoluble) precipitates and

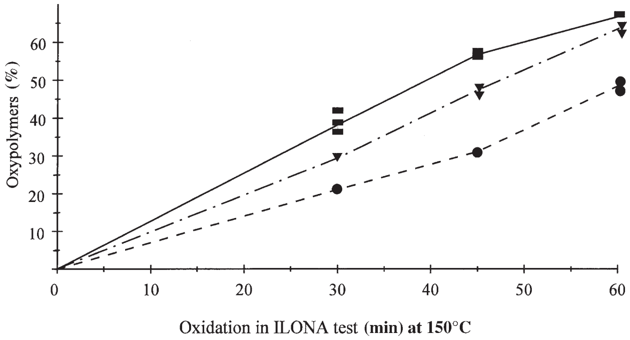

FIG. 4. Oxypolymerization tendencies of lesquerella (squares and solid line), castor (inverted triangles and dot-interrupted line), and meadowfoam (circles and dashed line) oils. GPC data from Table 2. See Figures 1 and 2 for abbreviations.

TABLE 2
Oxypolymerization Tendencies of Conventional Vegetable Oils Using the ILONA Test at 150°C[a]

Vegetable oil	Duration (min)	wt% THF-insoluble	wt% THF-soluble	wt% Volatile loss	% Triacylglycerols (from GPC) Monomer	Oxydimer	Oxytrimer
	0	0	100	0	100	0	0
Canola		–0.5	100.0	0.5	66.2	15.3	7
	30	–1.4	100.8	0.5	67.9	15.3	6.6
		–0.5	98.6	1.9	62.1	16.8	8.4
	45	–1.1	98.6	2.5	49.6	15.8	9.6
	60	0.0	96.7	3.3	38.6	13.7	8.7
		–0.8	94.8	6.1	45.5	15.7	9.7
Castor	30	–0.3	97.7	2.5	72	12.7	6
	45	–0.8	96.7	4.1	56.7	15.8	9
		–0.8	96.6	4.2	58.5	15.3	8.7
	60	–0.3	95.1	5.1	43.5	15	9.1
Lesquerella	30	–0.5	97.0	3.6	64.5	14.1	7.4
		–0.8	95.8	5.0	66.6	13	7.5
		–0.6	95.8	4.7	61.8	13.6	7.8
	45	0.0	93.5	6.5	49.7	14.1	8.2
		–0.6	93.9	6.6	48.4	13.4	8.1
	60	0.3	94.2	5.5	40.7	14.4	8.3
Meadowfoam	30	–0.3	100.0	0.3	78.8	12.5	2.9
		–0.5	99.7	0.8	79.9	11.9	3.6
	45	–0.6	100.0	0.6	71	16.1	ND
	60	–0.3	97.0	3.3	57.6	21.8	0
		–0.3	95.9	4.4	55	17.1	ND
Soybean	30	–0.5	99.7	0.8	51.7	17.9	10.2
		–0.3	80.3	20.0	58.9	18.2	8.8
		–1.1	99.7	1.4	52.9	17.8	9.4
	45	0.3	98.4	1.3	42.1	17	10.4
		0.6	95.6	3.9	33.2	13.2	8.7
	60	0.3	97.0	2.7	31.5	13.1	9.1
		1.9	95.2	3.0	32.4	13.1	8.9
90% oleic sunflower	30	1.1	99.4	–0.6	85.3	9.2	2
		–1.1	103.9	–2.8	80.9	9.2	0.1
		–1.8	102.6	–0.8	83.3	8.7	1.7
		0.8	101.6	–2.5	86.8	6.8	0.1
	45	–0.5	100.8	–0.3	76.8	14.9	4.9
	60	0.0	96.7	3.3	57.3	19.3	9.7
		0.5	97.1	2.4	64.5	17.9	7.8
		0.0	98.1	1.9	65.5	18.2	7.7
		0.3	95.9	3.9	61.9	18.1	8.5
		–1.1	96.7	4.4	63.3	18.3	9
		–0.8	97.6	3.3	62.6	17.3	8
		0.8	96.1	3.1	65.9	17.4	7.3
Triolein	30	0	99	1	76.9	14.1	4.8
	45	0	98	2	71.8	16.9	6.3
	60	0.5	96	2.5	56.9	19.9	10.2

[a]ILONA, Investigation of Liquid Oxypolymerization of Nonvolatic Analytes; GPC, gel permeation chromatography; THF, tetrahydrofuran; ND, not detectable.

higher volatile losses. Increasing MW of oxypolymers eventually leads to oxidative gelation. Therefore, if higher degrees of oxidation are delivered, the ILONA test also permits investigation of the kinetics of oxidative gelation. Its occurrence in triolein and sunflower oil at 175°C is demonstrated in Table 3. Past the gel point, the oxidized sample does not appear soluble in THF, although a substantial part of the oxidation products that contribute to the sol fraction can still be dissolved. For both triolein and sunflower oil, oxidative gelation occurs between 30 and 60 min. Because differentiation between THF-soluble and THF-insoluble in the cases of gel formation is based essentially on the ability of the sol fraction

TABLE 3
Occurrence of Oxidative Gelation in Triolein and 90% Oleic Sunflower Oil Using the ILONA Test at 175°C[a]

Sample and duration	wt% THF-insoluble	wt% THF-soluble	wt% Volatile losses	% Oxypolymers in THF soluble
Sunflower, 30 min	2	90	6	59
	1	91	8	57
	2.5	92	5.5	61
Triolein, 30 min	2	90	6	59.1
	1.5	90	6.5	58.9
Sunflower, 60 min	60.7	25.9	13.4	62.2
	51.0	36.0	13.0	52.5
	45.3	42.0	12.7	64.0
Triolein, 60 min	51.1	30.8	18.1	54.1
	56.9	34.4	8.7	50.5
	50.0	29.9	20.5	52.2

[a]See Table 2 for abbreviations.

TABLE 4
Oxypolymerization of Vegetable Oil-Based Hydraulic Fluids Using the ILONA Test at 150°C

Sample	Duration (min)	wt% THF-insoluble	wt% THF-soluble	wt% Volatile loss	% Oxypolymers
Canola oil-based commercial HF	30	–1	100.5	0.5	30.9
		0	96.5	3.5	36.2
		–1.5	99.5	2.0	32.1
	60	1.5	94	4.5	56.5
		1.3	94	4.7	62.2
Rapeseed oil-based commercial HF	30	–0.5	97	3.5	27.2
		0	96	4	32.1
	60	0	100	0	41.6
		0.5	96	3.5	43.4
90% Oleic sunflower oil-based experimental HF	30	0.5	98	1.5	0.5
		0.3	97.5	2.2	0.5
	60	0.5	100	–0.5	1.0
		0	100.5	–0.5	0.5

[a]See Tables 1 and 2 for abbreviations.

to migrate from the gel fraction, rather than on the degree of oxidation, fluctuation in the amounts of THF-insoluble is large. The same is true for the amounts of high-MW products in THF solutions. Therefore, oxypolymerization can be reliably quantified only before the occurrence of the gel point.

Oxypolymerization tendencies in vegetable oil-based fluids containing proprietary additives are hard to predict theoretically. The ILONA test can be used not only to characterize the tendencies in such fluids as biodegradable hydraulic oils, but to some degree it can also be used to simulate qualitatively the environments to which the lubricants are exposed in actual lubricating systems: elevated temperatures, steel surfaces, and oxidative atmosphere. Oxypolymerization tendencies in three hydraulic fluids based on canola, rapeseed, and 90% oleic sunflower oils were compared using the ILONA test at 150°C, results are shown in Table 4.

It appears that the additives (which remained proprietary at the time of investigation) used to improve oxidative stability in canola- and rapeseed-based fluids did not affect oxypolymerization rates as much as did amounts of methylene-interrupted polyunsaturated fatty acids. The two commercial hydraulic fluids still demonstrated lower resistance to oxypolymer formation than even additive-free sunflower oil. ILONA test results clearly demonstrated superiority of the experimental hydraulic fluid based on 90% oleic sunflower oil compared with the two commercial products.

Thus, there is a pressing need to improve the oxypolymerization of vegetable-oil-based hydraulic fluid owing to its inherent tendency to viscosity increase and filterability problems upon use. Application of tests such as micro-oxidation or the ILONA test can help not only lubricant developers but also producers of frying oils or drying oils.

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