

Understanding Dissolved Gas Analysis of Ester Fluids - Part 1: “Stray” Gas Production under Normal Operating Conditions

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Introduction

Dissolved Gas Analysis (DGA) of electrical insulating fluids was developed over fifty years ago and has been in widespread use for more than thirty years. Over this time, most practitioners’ experience has been with the DGA of mineral oils. Under normal operating conditions the mineral oil in oil-filled transformers is not expected to produce gases. Nonetheless, it not uncommon to see small amounts of gas produced over the lifetime of a normally operating transformer.

The refining practices used to manufacture mineral insulating fluid have changed considerably over the 120 year history of their use. Notably, beginning in the late 1980’s significant changes in the refining practices resulted in the observance of various fault gases being produced from slight temperature excursions. Because these gases are not the result of fault processes, they have come to be identified as ‘stray gasses’.

Increased awareness of stray gas production has led to industry studies and the development of standardized tests such as ASTM D7150-05 to characterize various oils.

Synthetic ester fluids have been in use for more than thirty years. In the last ten years natural ester fluids have come into much wider use. As with mineral oil, under normal operating conditions the ester fluid in transformers is not expected to produce gases.

In the course of testing in-service ester fluids over the last decade, ethane has frequently been observed without apparent fault activity (Table 1). Subsequently, similar ethane production has been reported as a ‘stray gas’ under the conditions of ASTM D7150.

Gas	ppm
H ₂	27
CH ₄	0
C ₂ H ₆	179
C ₂ H ₄	5
C ₂ H ₂	0
CO	69
CO ₂	673

Table 1. An example of “Stray Ethane”

The concern to practitioners is to know when those gases associated with both faults and stray gassing are, in fact, being produced by faults. Revelation of the unidentified non-fault related mechanisms of gas production should assist the practitioner in making this determination.

Production of Alkanes from Ester Fluids

A review of ester fluid literature reveals well documented chemical pathways that yield alkanes from fatty acids. These processes have been studied in biological and biochemical systems to such a degree that the alkanes, octane, pentane and ethane, have reliably been used as both markers for and quantifiable indicators of certain fatty acid presence within these systems. These chemical pathways are part of a larger system of reactions thoroughly documented by the food and flavorings industry.

Production of alkanes via these pathways begins with the oxidation of unsaturated fatty acids. An examination of the fatty acid composition of several natural ester fluids (Table 2) shows their composition to be nearly 100% of the mixture of palmitic, stearic, oleic, linoelic, and linolenic acids. Considering these predominant components, we can limit our discussion of unsaturated fatty acids to oleic acid, linoleic acid, and linolenic acid (Figure 1).

	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Sum %
Grape Seed	8	4	15	73	<1	100
Peanut	11	2	48	32	<1	93
HO Sunflower	5	4	82	9	<1	100
Walnut	11	5	28	51	5	100
Soybean	11	4	24	54	7	100
Canola	4	2	62	22	10	100
Flax Seed	3	7	21	16	53	100

Table 2. Fatty Acid Composition (%) of Some Natural Ester Fluids

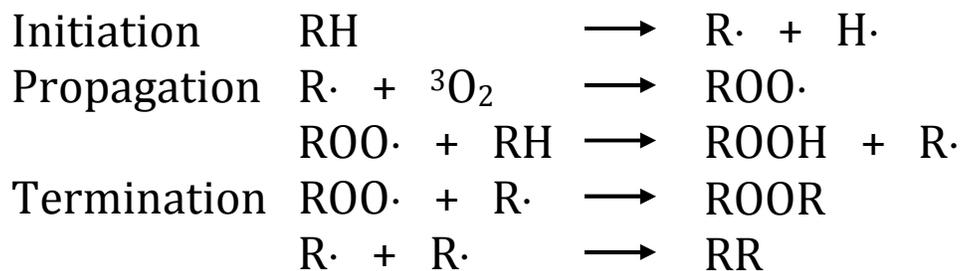


Figure 1. Common Fatty Acids in Natural Ester Fluids

The oxidation of these unsaturated fatty acids proceeds by two mechanisms, formation of hydroperoxides by autoxidation and formation of hydroperoxides by singlet oxygen reactions.

In this discussion we can think of autoxidation (Figure 2) as the common mechanism for oxidation. Autoxidation requires the formation of a lipid free radical to begin. The propagation is supported by triplet oxygen. Autoxidation occurs more rapidly at elevated temperatures and in the presence of polyunsaturated fats, which are more susceptible to initiation than saturated and monounsaturated fatty acids.

The singlet oxygen mechanism is dependent on the presence of photosensitive species and exposure to light (Figure 3). Photosensitive species that might be found in natural ester fluids include chlorophyll, pheophytins, and pheophorbides.



(R : lipid alkyl)

Figure 2. Free radical initiation, propagation and termination steps of the autoxidation mechanism.

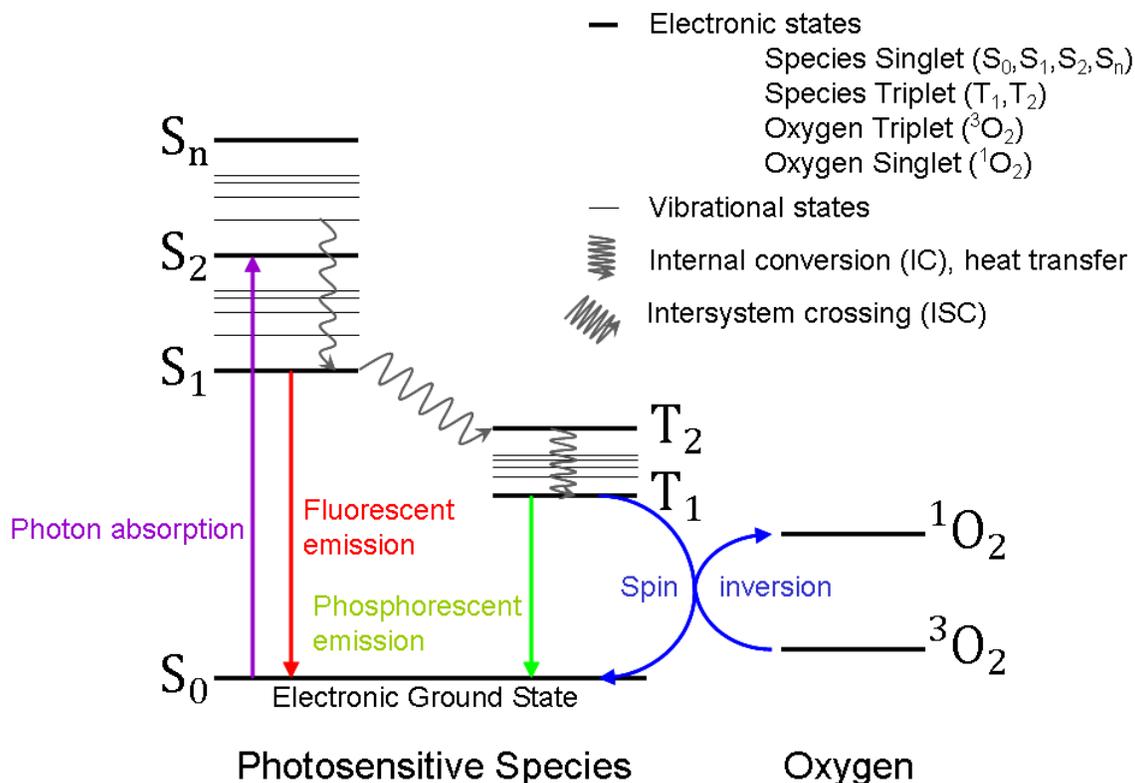


Figure 3. Formation of singlet oxygen via photosensitive species. The process starts with the absorption of a photon causing an electronic transition to an excited singlet state. A radiationless internal conversion (IC) can occur followed by heat transfer to the medium that transitions the electron to a lower excited singlet state. In this state one of two transitions will occur: 1. The electron will return to the ground state with the emission of a photon (Fluorescence) or 2. The species will make a radiationless transition from an excited singlet state to an excited triplet state (ISC). If path 1 is followed we observe fluorescent light. If path 2 is followed, the excited triplet state can further transition via an internal conversion and heat transfer to a lower excited triplet state. Finally, a photon is emitted (Phosphorescence) returning the photosensitive species to the ground state or oxygen interacts and is promoted from a triplet state to the excited singlet state as the photosensitive species returns to the ground state.

The two mechanisms work differently but produce some of the same products. Figures 4 and 5 illustrate this with the unsaturated fatty acid linoleic acid. Linoleic acid has unsaturated carbons at carbon positions 9, 10, 12, and 13. Autoxidation produces hydroperoxides at carbon positions 9 and 13 whereas the singlet oxygen mechanism produces hydroperoxides at carbon positions 9, 10, 12, and 13.

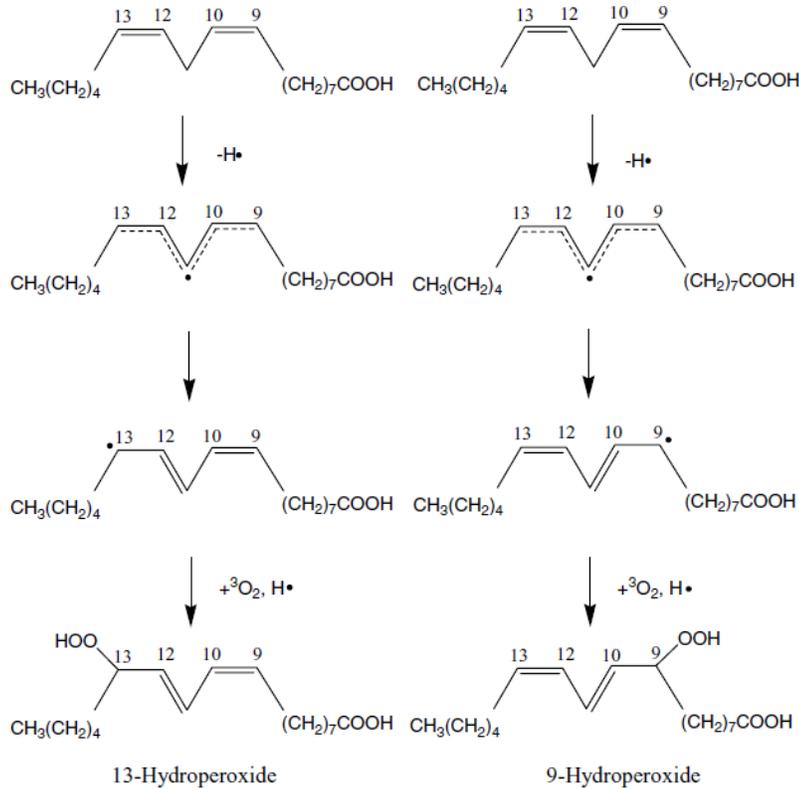


Figure 4. Hydroperoxide formation in linoleic acid by autoxidation

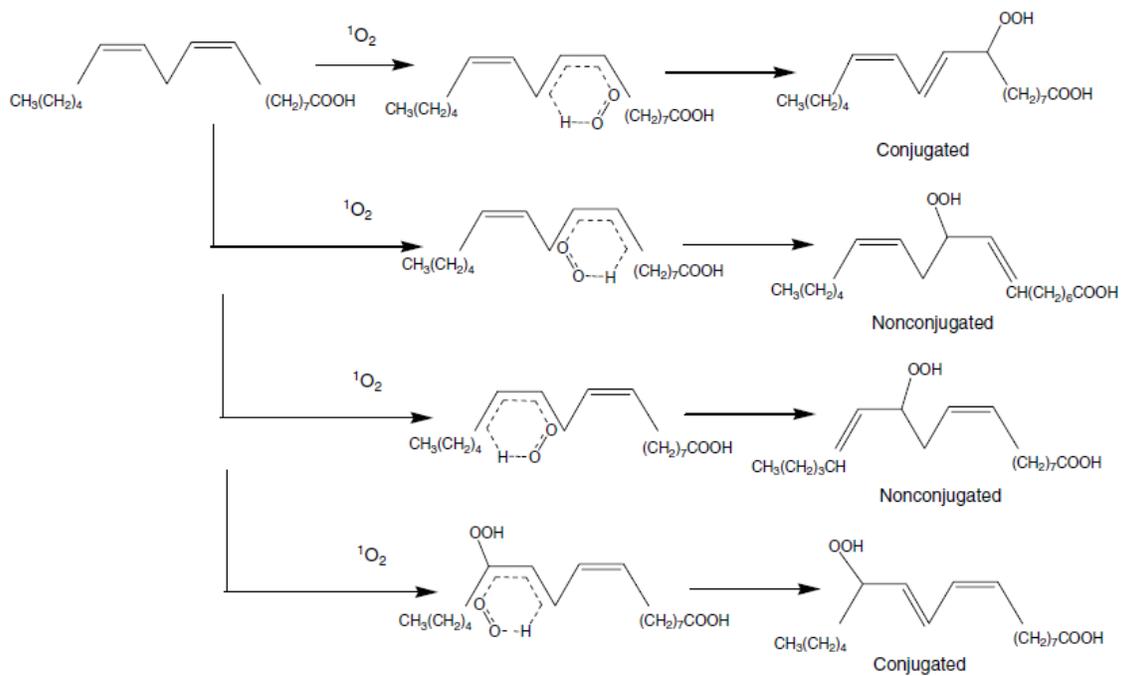


Figure 5. Hydroperoxide formation in linoleic acid oxidation by singlet oxygen

The hydroperoxide at carbon position 13, which is closest to the ω end of linoleic acid, is produced by both oxidation mechanisms.

Hydroperoxides formed in the initial oxidation are reported by some researchers to be labile, but certainly, with modest thermal stress they will decompose or react further to form a variety of products (Table 3). The comparable list produced via singlet oxygen is even greater.

Class	Oleic acid	Linoleic acid	Linolenic acid
Aldehydes	Octanal	Pentanal	Propanal
	Nonanal	Hexanal	Butanal
	2-Decenal	2-Octenal	2-Butenal
	Decanal	2-Nonenal	2-Pentenal
		2,4-Decadienal	2-Hexenal 3,6-Nonadienal Decatrienal
Carboxylic acid	Methyl heptanoate	Methyl heptanoate	Methyl heptanoate
	Methyl octanoate	Methyl octanoate	Methyl octanoate
	Methyl 8-oxooctanoate	Methyl 8-oxooctanoate	Methyl nonanoate
	Methyl 9-oxononanoate	Methyl 9-oxononanoate	Methyl 9-oxononanoate
	Methyl 10-oxodecanoate	Methyl 10-oxodecanoate	Methyl 10-oxodecanoate
	Methyl 10-oxo-8-decenoate		
	Methyl 11-oxo-9-undecenoate		
Alcohol	1-Heptanol	1-Pentanol	
		1-Octene-3-ol	
Hydrocarbons	Heptane	Pentane	Ethane
	Octane		Pentane

Table 3. Secondary oxidation products of the hydroperoxides of the fatty acid methyl ester formed by autoxidation.

Those hydroperoxides that form closest to the omega end of the unsaturated fatty acids yield alkane fragments from their decomposition. The products for oleic acid, linoleic acid and linolenic acid are shown below. Oleic acid oxidizes to become 10-hydroperoxy-8-octadecenoic acid, linoleic acid oxidizes to become 13-hydroperoxy-9,11E-octadecadienoic acid, and α - linolenic acid oxidizes to become 16-hydroperoxy-9Z,12,14E-octadecatrienoic acid.

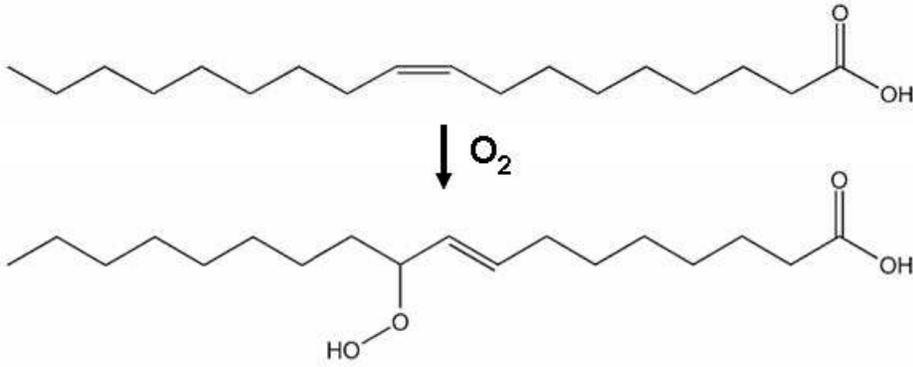


Figure 4a. Oxidation of Oleic Acid to 10-hydroperoxy-8-octadecenoic acid

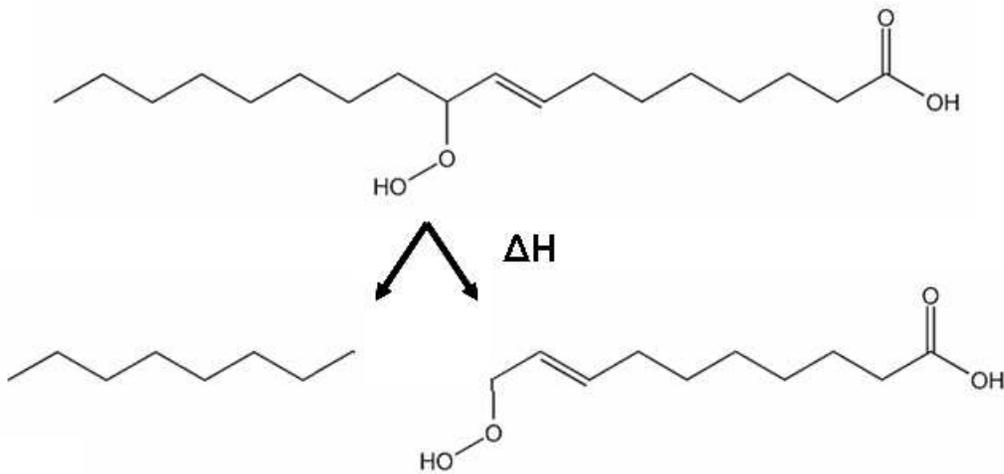


Figure 4b. Formation of octane from 10-hydroperoxy-8-octadecenoic acid

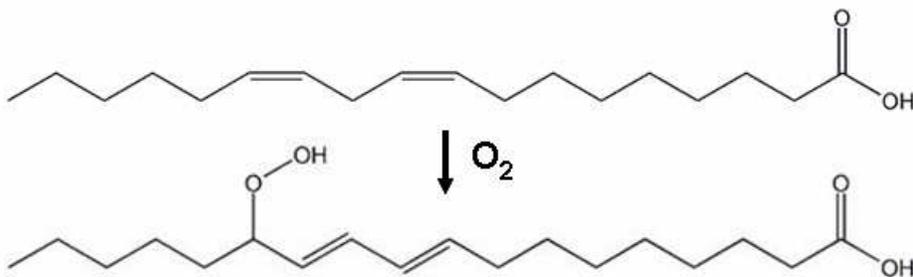


Figure 5a. Oxidation of linoleic acid to 13-hydroperoxy-9,11E-octadecadienoic acid.

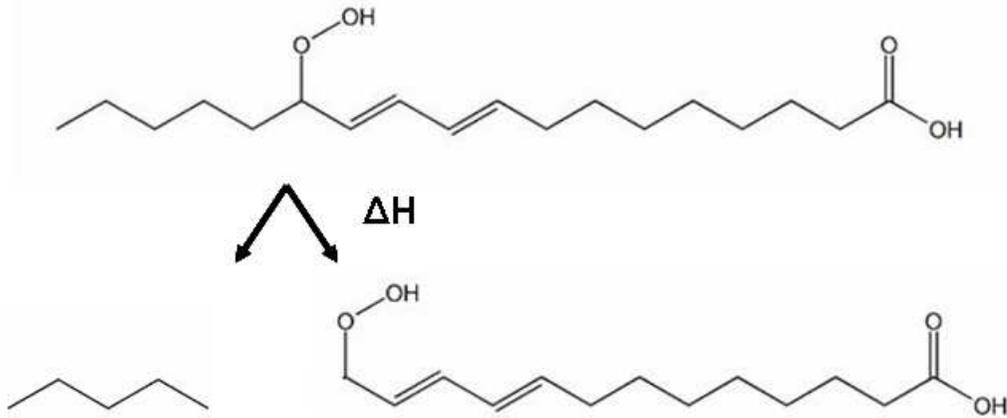


Figure 5b. Formation of pentane from 13-hydroperoxy-9,11E-octadecadienoic acid

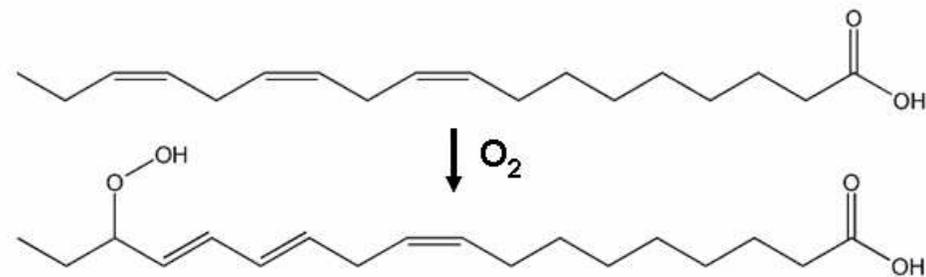


Figure 6a. Oxidation of linolenic acid to 16-hydroperoxy-9Z,12,14E-octadecatrienoic acid.

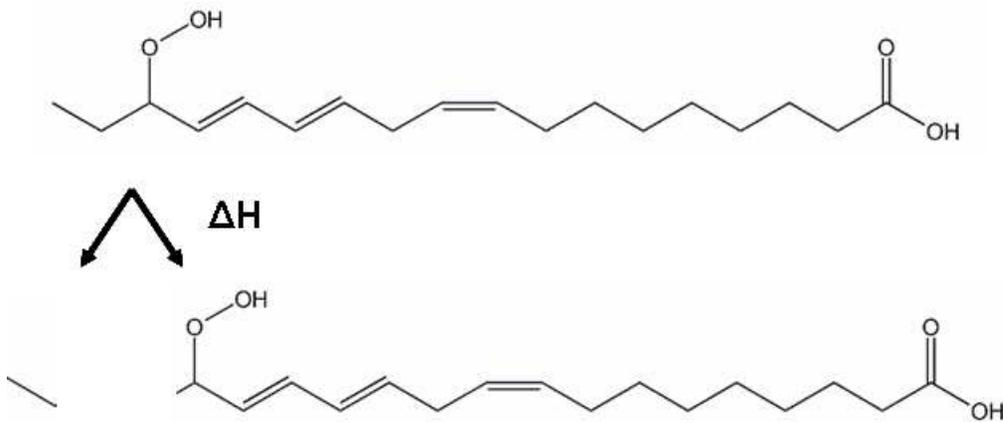


Figure 6b. Formation of ethane from 16-hydroperoxy-9Z,12,14E-octadecatrienoic acid.

In turn 10-hydroperoxy-8-octadecenoic acid yields octane, 13-hydroperoxy-9,11E-octadecadienoic acid yields pentane and 16-hydroperoxy-9Z,12,14E-octadecatrienoic acid yields ethane. Other unsaturated fatty acids will yield alkanes in the same way. The hydroperoxides that yield these alkanes can be formed by either the autoxidation or singlet oxygen mechanism.

Experimental Production of Ethane

Fortunately, the literature has suggested a compelling hypothesis that can easily be tested. A series of experimental trials were prepared to evaluate these oxidation mechanisms as the source of “stray gas” production in natural ester fluids. In these trials the gas under study was ethane. With this in mind, four key features were chosen to test these mechanisms:

1. The relationship of ethane to oxidation
2. The relationship of ethane to linolenic acid content
3. The relationship of ethane to temperature
4. The relationship of ethane to light exposure.

The coincidence of all four of these relationships to the hypothesis should be convincingly persuasive if not rigorously sufficient to confirm it.

The relationship of ethane to oxidation

Natural ester fluids have a particular susceptibility to oxidation that is managed with oxidation inhibitors. These fluids contain some natural oxidation inhibitors specific to autoxidation and some that are specific to singlet oxygen activity. Additional oxidation inhibitors are added to provide for specified levels of performance.

An easy test of the relationship between ethane production and oxidation is an examination of ethane content in the same fluid with and without the additional oxidation inhibitor (Table 4). In preparation of these samples, oxygen and heat were provided to promote oxidation prior to testing as per ASTM D7150. The data in table 4 indicate a direct relationship between ethane and the progress of oxidation.

	With Inhibitor	Without Inhibitor
H ₂	403	1049
CH ₄	17	16
C ₂ H ₆	448	2104
C ₂ H ₄	3	6
C ₂ H ₂	0	0
CO	188	195
CO ₂	954	952

Table 4. Comparison of ethane production to oxidation. Gas concentrations in ppm from soybean oils tested using ASTM D7150 (Air sparge, 1 day 120°C)

The relationship of ethane to linolenic acid content

	Sunflower ¹	Peanut	Soybean	Flaxseed
α-linolenic acid	≈ 0.2%	≈ 0.2%	≈ 7%	≈ 53%
H ₂	357	282	316	708
CH ₄	21	10	10	17
C ₂ H ₆	4	26	563	2371
C ₂ H ₄	8	16	7	16
C ₂ H ₂	0	0	0	0
CO	203	389	408	977
CO ₂	876	2232	1330	3212

1. High Oleic Sunflower seed oil

Table 5. Comparison of ethane production to linolenic acid content. Gas concentrations in ppm from selected fluids prepared using modified ASTM D7150 test data (Air sparge, 1 day, 120°C)

The relationship between ethane production and linolenic acid content was examined by comparing ester fluids with different fatty acid contents (Table 5). In preparation, oxygen and heat were provided to promote oxidation prior to testing as per ASTM D7150. The preparative method was modified to shorten the period of heating from seven days to one

day. This modification yielded approximately ninety percent of the ‘stray’ gas concentrations of the unmodified method while dramatically improving experimental throughput. The test data demonstrate a direct but not exactly proportional relationship between ethane and the linolenic acid content. It is suspected that the lack of an exact relationship arises from the different types and amounts of inhibitors added to each fluid.

The relationship of ethane to temperature

The relationship between ethane and temperature was repeatedly demonstrated in the various trials of this study. The three samples in Table 6 provide one demonstration. Oxygen was provided to all three samples and heat was provided to two samples to promote oxidation prior to testing. One of the samples was heated to 90°C and the other sample was heated to 120°C as per ASTM D7150. All samples were subjected to the same ambient light conditions. Examination of these data shows a direct relationship between oxidation and temperature. This direct relationship is consistent with what would be expected for the autoxidation mechanism.

	Ambient	90°C	120°C
H ₂	0	1060	403
CH ₄	0	9	17
C ₂ H ₆	0	314	448
C ₂ H ₄	0	2	3
C ₂ H ₂	0	0	0
CO	7	161	188
CO ₂	784	814	954

Table 6. Comparison of Ethane production to Temperature. Gas concentrations in ppm from soybean oil tested.

The relationship of ethane to light exposure

The relationship between ethane and light exposure is shown in Table 7. The material control was prepared and tested as per ASTM D7150 modified (as noted above). The fluorescent light control specimen was air sparged, covered to block light, but otherwise exposed to the conditions of the light exposure chamber and then heated prior to testing as per ASTM D7150 modified. The two control samples should be effectively identical and the test results confirmed this. The sample was air sparged, exposed to light for seven days, then heated and tested as per ASTM D7150 modified. The data shows a direct relationship to light exposure.

	Material Control	Fluorescent Light Control	Fluorescent Light Sample
H ₂	149	257	762
CH ₄	35	23	73
C ₂ H ₆	615	642	2192
C ₂ H ₄	7	6	20
C ₂ H ₂	0	0	0
CO	220	197	474
CO ₂	942	996	1998

Table 7. Comparison of ethane production to light exposure. Fluorescent light preparation followed by modified ASTM D7150 test method (Air sparge prior to fluorescent light preparation, 1 day, 120°C). Gas concentrations in ppm from soybean oil tested.

The fluorescent lights used for the light exposure produced visible light and a small amount of ultraviolet light. This raised the question of the effect of visible light versus ultraviolet light. To better understand the light relationship, the study was repeated using ultraviolet lights. During the exposure to ultraviolet light, a fluorescent effect was observed in natural ester samples (Figure 7). After several days the ultraviolet light exposure ceased to produce this effect. The fluorescence is a clear indication of a photosensitive species in the fluid (Figure 3). The fluorescence does not appear to be in the region of the spectrum commonly associated with chlorophyll, pheophytins or phoephorbides. At this time the specific photosensitive species remains unknown.

A first comparison of the effect of fluorescent light exposure to the effect of ultraviolet light exposure was made without further preparation immediately following the exposure. These data are shown in Table 8. One implication of this data is that ultraviolet light production of singlet oxygen is more efficient for hydroperoxide production. While the effect of the visible light component is not specifically measured, it is at least demonstrated to be less efficient.



Figure 7. Natural ester fluid showing fluorescence from photo activity (left) and after this activity had subsided (right).

Table 9 shows the comparative data for samples prepared by each light exposure method followed by the application of heat per ASTM D7150 modified. An interesting effect is observed. The combined effect of light exposure followed by heat treatment is greater than light exposure alone, heat treatment alone, or the sum of these individual preparations. Further, for the combined light exposure and heat treatment, the type of light exposure (visible versus ultraviolet) does not appear to have a different effect.

	Fluorescent Light Control	Fluorescent Light Sample	Ultraviolet Light Control	Ultraviolet Light Sample
H ₂	0	96	0	120
CH ₄	0	10	2	14
C ₂ H ₆	0	57	0	347
C ₂ H ₄	0	6	0	25
C ₂ H ₂	0	0	0	0
CO	17	170	3	1029
CO ₂	459	719	493	1211

Table 8. Comparison of the effect of fluorescent light preparation to the effect of ultraviolet light preparation. Gas concentrations in ppm from soybean oil tested.

	Fluorescent Light Sample	Ultraviolet Light Sample
H ₂	762	440
CH ₄	73	69
C ₂ H ₆	2192	1983
C ₂ H ₄	20	44
C ₂ H ₂	0	0
CO	474	559
CO ₂	1988	2783

Table 9. Comparison of the effect of fluorescent light preparation to the effect of ultraviolet light preparation followed by modified ASTM D7150 test method (Air sparge prior to fluorescent light or ultraviolet light preparation, 1 day, 120°C). Gas concentrations in ppm from soybean oil tested.

This enhanced ethane response in Table 9 appears to be due to lipid free radicals initiated by singlet oxygen during that phase of oxidation reacting with triplet oxygen during the heating phase of the preparation. The net effect is a normal singlet oxygen oxidation followed by an enhanced autoxidation.

The demonstration of photo activity has implications for the storage and handling of natural ester fluids and natural ester fluid samples. The data in Table 10 shows the effect of three years exposure to headspace oxygen and indirect sunlight while stored in a polyethylene tote.

	New	Stored
H ₂	0	34
CH ₄	0	1
C ₂ H ₆	0	10
C ₂ H ₄	0	5
C ₂ H ₂	0	0
CO	7	27
CO ₂	786	809

Table 10. Comparison of new soybean oil to stored soybean oil. Gas concentrations in ppm from soybean oil tested.

	New	Stored	New	New	Stored	New
			FL	D7150	D7150	FL+D7150
H ₂	0	34	77	149	431	762
CH ₄	0	1	4	35	58	73
C ₂ H ₆	0	10	70	615	1122	2192
C ₂ H ₄	0	5	7	7	14	20
C ₂ H ₂	0	0	0	0	0	0
CO	7	27	191	220	306	474
CO ₂	786	809	767	942	1529	1998

Table 11. Comparison of new and stored soybean oils to the same oils after light exposure and stray gassing tests. Gas concentrations in ppm from soybean oil tested.

The data in Table 11 shows the relative progress of oxidation and ethane production for this stored fluid. The three year period of storage in light and air has advanced the oxidation and ethane production but not by as much as one week of exposure to intense fluorescent light.

To better understand the relative impact of environmental light exposure and to examine concerns about sample storage, a series of light exposures were conducted on natural ester fluids in glass syringes. Table 12 shows the comparison of a sample exposed to ambient fluorescent light at counter top height, a sample exposed to ambient fluorescent light on the top tray of a mobile laboratory storage rack (three feet above the counter top), and a sample exposed to direct sunlight. The samples were exposed for one week.

	Counter Top	Top Tray	Sunlight
H ₂	76	78	824
CH ₄	0	0	30
C ₂ H ₆	2	3	785
C ₂ H ₄	0	0	59
C ₂ H ₂	0	0	0
CO	23	22	6420
CO ₂	362	440	1566

Table 12. Comparison of test samples stored in various locations for 1 week prior to testing. Gas concentrations in ppm from soybean oil tested.

The samples in Table 12 were processed at ambient temperature using ASTM D3612a. Data for identical samples tested using ASTM D3612c at 70°C are shown in Table 13.

	Counter Top	Top Tray	Sunlight
H ₂	165	155	1380
CH ₄	4	4	131
C ₂ H ₆	2	2	2418
C ₂ H ₄	0	0	114
C ₂ H ₂	0	0	0
CO	37	39	5922
CO ₂	463	554	1883

Table 13 Comparison of test samples stored in various locations for 1 week prior to testing. Samples were tested using the headspace method (ASTM D3612c) at 70°C. Gas concentrations in ppm from soybean oil tested.

Proper storage of samples prior to processing is important. Both ambient temperature and light exposure can produce a measurable change in test results. The effect under normal laboratory conditions appears to be small. On the other hand, samples stored in direct light during collection and transport could demonstrate dramatic shifts in results.

Discussion

A correlation between the oxidation mechanisms detailed in the literature and ethane evidence seen in electrical insulating ester fluids has been demonstrated. The correlation includes several points of coincidence: the relationships to oxidation in general, to linolenic acid content, to free radical oxidation or autoxidation, and singlet oxygen oxidation including the presence of photosensitive species.

The range of ethane levels that might be found from these processes is suggested by these studies. From our experience to date, the non-fault related ethane levels remain within the bounds suggested by these studies. Using a data pool of 2800 in-service, soybean oil samples, the highest non-fault related ethane level was 1230 ppm. The 90th percentile for non-fault related ethane from these samples was 72 ppm.

By using other markers produced by these same oxidation processes, it should ultimately be possible to determine the fault related ethane contributions for more complete diagnostic assessments.

Clearly, there are other gases observed in these studies to detail in similar fashion to ethane. That work is ongoing and the results of those studies will be presented as they are completed.

The opportunity for photoactivity presents some concerns for fluid storage and sample handling that do not seem to be realized in the limited cases examined in this paper. Further examination is suggested to better clarify the likelihood of these concerns having a material consequence.

Finally, it is the express wish of the authors, that this examination will have initiated a useful clarification of this 'stray gas' production for diagnosticians evaluating ester filled electrical equipment.

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