Stray Gassing of different refinery streams and impact of metal deatctivators

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Stray Gassing Of Refinery Streams And Transformer Oil Produced From Them

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Abstract— Refinery processing determines the chemistry of the base oils used in transformer oils. Increasing the severity of the processing leads to a more stable base oil. Performance additives can modify the chemistry of the system and potentially lead to unintended consequences. This study examines how processing differences and additives affect the generation of stray gasses at low temperatures.

Keywords—stray gassing; refinery streams; severe hydroprocessing; passivators

I. Introduction

Since the early 1990's the phenomenon of new transformer oil releasing high concentrations of gases at low temperatures (90°C to 200°C) has been reported [1]. This process of generating gases, primarily hydrogen, at low temperatures was termed "Stray Gassing" by CIGRE. Many of the instances of stray gassing have been noticed during transformer factory acceptance tests before they are ever put into service. After 2000 this phenomenon increased to the point that both Doble [2] and CIGRE started investigations to find the cause. They studied oil types, transformers, building materials and transformer operating conditions.

This project was performed to see if refining processes could be the cause of stray gassing. In some prior presentations and reports it has been suggested that more severe refining technology could be responsible for stray gassing [3-5]. Hopefully, this project will shed more light on this possibility. Refiners have access to streams before and after additives are added or blending performed to make the finished transformer oil. The data should show whether stray gassing is the result of different refining processes used on oils or other actions taken to produce a final product. This project is limited to refining differences and chemical additives. It does not investigate other potential parameters such as oxygen content, water content, paper insulation, metals, varnish/paint, acid generation, variable temperatures, or inhibitor content.

II. Project Basis

Mineral oils used as transformer oils are processed using two basic techniques (1) solvent extraction and (2) severe hydroprocessing which is the predominate process used today. Refinery streams were selected and testing was set up to analyze them neat and after they were blended with other streams or additized with property enhancing substances. Three naphthenic base stocks used to make Ergon's transformer oils and the finished transformer oil products were selected. The naphthenic base stocks were treated to two different levels of saturation. One base stock was treated to high saturation and the second to very high saturation. An Isoparaffin 60 was selected because of the very severe hydro-cracking process used to produce it. The Isoparaffin 60 was obtained from a distributor and it is not known if it was stored under conditions appropriate for transformer oil. Chemical additives, e.g., 2,6-di-tert-butyl-p-cresol (BHT or DBPC), Irgamet® 30, Irgamet® 39, see Fig. 1, and refinery blend components, e.g., Aromatic Naphtha and a Solvent Neutral, were selected.

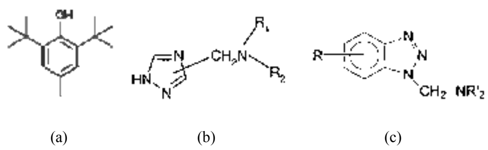

Fig. 1. (a) BHT or DBPC; (b) Irgamet 30; and (c) Irgamet 39

Each sample was tested for stray gas generation using the procedure from CIGRE document 296. They were tested first with no heat incubation, degassed under vacuum, saturated with air then heated in a 30 cm^3 syringe for 16 hours at 120°C. Samples were tested for hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, acetylene and total combustible gases (TCG).

Ergon's finished products are formulated to meet ASTM Type II (Hyvolt II), IEC 60296 Standard Grade (Hyvolt I) and IEC 60296 Special Application (Hyvolt III). Hyvolt II and Hyvolt III are made using the straight base stocks from the refinery with only BHT added as an oxidation inhibitor. Hyvolt I is a specialized blend of the refinery base stock and a secondary base stock to supply natural inhibitors for oxidation stability.

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The Hyvolt I and Hyvolt II base stocks are hydrotreated to the same level and are equivalent in their chemistry. The Hyvolt III base stock is more highly hydrotreated and will have lower aromatics and different chemistry. The Isoparaffin 60 is a hydro-cracked stock and has the highest saturation level of these base stocks. The solvent neutral is an extracted base stock and is used for its specialized chemistry. Aromatic naphtha is another refinery stream added to products to obtain specialized characteristics. The additives BHT, Irgamet 30 and Irgamet 39 are used to enhance oxidation stability or as passivators. BHT is an approved additive by both ASTM and IEC for enhancing oxidation stability. Irgamet 30 and Irgamet 39 have been used to passivate oil for corrosive sulfur but are also thought to enhance oxidation stability. Additives were added to the neat base stocks and finished formulated products to look for differences in stray gas generation.

III. Project

First, the neat refinery base stocks were tested for stray gassing without any additives. Then the individual base stocks were additized with specific additives and retested. BHT was added at 0.27 wt% for ASTM Type II or 0.37 wt% for IEC Special Application grades. The Irgamets were added at 100 mg/kg, the aromatic naphtha at 0.4 wt% and the solvent neutral at 3 wt%.

All samples were tested at zero hours at 20°C. There was no stray gas generated except for two samples that had 2 µL/L of methane.

A. Neat Base Stocks

Table I, Section 1 shows the data for the four neat base stocks. The base stocks differed by the type of processing (severe hydroprocessing, hydro-cracking, solvent extraction) and the severity of the processing. The solvent neutral had the highest amount of gassing, 99 µL/L of hydrogen, 178 µL/L of CO, 247 µL/L of CO_2, 2 µL/L of methane and 2 µL/L ethylene. The oxygen level was severely reduced indicating the onset of oxidation. The two severely hydrotreated naphthenic base stocks had no detectable amounts of gassing. The oxygen levels were maintained indicating no oxidation. The two base stocks differed only by the severity of the hydroprocessing. The Isoparaffin 60 showed gassing and oxidation, however, it was concluded that contamination could be the issue.

B. Formulated Commercial Samples

The second samples testing involved the formulated transformer oils made from the base stocks. Samples were taken from actual customer shipments. Data from this testing are shown in Table I, Section 2.

Hyvolt I and Hyvolt II are produced from the same base stock. Hyvolt I is enhanced with a secondary base stock while Hyvolt II is additized with 0.27 wt% BHT. Hyvolt III is produced from a more severely processed base stock and it is additized with 0.37 wt% BHT.

Hyvolt I, uninhibited, generated a level of gassing with a significant reduction in the oxygen level. The inhibited oils, Hyvolt II and III, showed no gassing and no reduction in the oxygen level. This suggests that the secondary, non-severely hydrotreated base stock in Hyvolt I, which provides natural inhibitors, generates the stray gassing. Natural inhibitors and other reactive molecules remaining in the secondary base stock can participate in the free radical process that generates the stray gassing. These types of reactive molecules are not seen in the severely hydrotreated base stocks.

C. Additized Samples

The Ergon commercial samples and the Isoparaffin 60 were tested with the various additives. The data are given in Table I, Sections 3 - 6. Fig. 2 shows the effect of passivators on the formulated transformer oils.

The uninhibited Hyvolt I was additized with BHT, Irgamet 30, Irgamet 39 and Aromatic Naphtha. The results are given in Table I, Section 3. The addition of BHT altered the mix of gases generated but the total amount was about the same. The addition of the Aromatic Naphtha did not significantly affect the gassing, the results were very similar to the Hyvolt I. The addition of either Irgamet 30 or 39 greatly increased the gas generation. The hydrogen content increased from 214 µL/L for the Hyvolt I to 2249 µL/L with the addition of Irgamet 30 and to 1079 µL/L with the addition of Irgamet 39. There were also increases in CO, CO_2, methane, ethane and ethylene.

The inhibited Hyvolt II and III differ by the severity of the processing and the amount of BHT. The Hyvolt III base stock was processed at a higher severity leading to a base stock with a higher degree of saturation. The Hyvolt III also contains slightly more BHT, 0.37 wt% versus 0.27 wt%. The response to the additives was nearly identical. The data are given in Table I, Sections 4 and 5. The Irgamets led to an increase in hydrogen to 350 – 555 µL/L. The CO increased to about 50 µL/L and CO_2 increased to about 100 – 400 µL/L. The Aromatic Naphtha led to a slight increase of hydrogen, about 10 µL/L and slight increases in CO and CO_2, 56 – 84 µL/L. There was only a slight reduction in oxygen levels. The BHT inhibitor reduced the degree of oxidation which reduced the gas generation due to the additives.

The Isoparaffin 60 was tested with 0.37 wt% BHT, 100 mg/kg Irgamet 39 and 3 wt% solvent neutral. The data are given in Table I, Section 6. The Isoparaffin 60 with the BHT was comparable to the Hyvolt III containing the same amount of BHT. Hydrogen was below the detection limit and there was slightly more CO and CO_2. The addition of Irgamet 39 gave results very similar to the Hyvolt III with Irgamet 39.

IV. Conclusions

Several variables were investigated to determine the effects on the generation of stray gassing. Severe hydroprocessing did not have a negative impact on stray gassing. Different levels of hydroprocessing produced base stocks without any

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stray gassing. The hydrocracked Isoparaffin 60 showed low levels of gassing, but since the oil may not have been maintained at transformer oil quality, those low levels may be an artifact. When the additized Isoparaffin 60 samples were compared to the other oils, the responses were similar which would indicate that the stability was similar. It is believed that some slight contamination led to the oxidation and subsequent gassing. Solvent extraction produced a base stock with some stray gassing.

Severe hydroprocessing, including hydrocracking, produces oxidatively stable base stocks. Unstable and reactive molecules are effectively converted or removed during severe hydroprocessing. This is evidenced by the lack of stray gassing, including CO_2, and the maintaining of the oxygen levels for the neat base stocks. Oils produced under different process conditions, such as the solvent neutral, are less stable and consume oxygen. The Aromatic Naphtha which is used for negative gassing tendency does not significantly impact stray gassing. There is a slight increase in oxidation and gas generation. The addition of solvent neutrals, which are less oxidatively stable than severely hydrotreated oils, increases the oxidation and stray gassing.

Passivators such as Irgamet 30 or 39 are designed to be reactive and are known to chemically bond to metal surfaces. Irgamet 30 and 39 are thought to chemically degrade either due to free radicals such as peroxides [6] or during binding to the copper surface [7]. The chemistry of the passivators is independent of the oxidation of the mineral oil since the highly refined oils exhibited no oxidation and no gas formation in the absence of passivators but exhibited oxidation and gas formation in the presence of passivators.

Oxidation is a complex free radical process. Once the process starts, other reactive components such as the Irgamet additives can participate in the reactions and produce by-products. These by-products can be hydrogen and the lower hydrocarbons.

Since Hyvolt I is an uninhibited oil, it is the most prone to oxidation. When reactive additives are present, they can participate in the free radical reactions. Since there is more oxidation occurring, there are more free radicals generated, and hence more stray gassing. Hyvolt II, Hyvolt III and the Isoparaffin 60 are more oxidatively stable and stray gassing does not occur. When the additives are present, some stray gassing is generated but to a lesser extent since there is less oxidation occurring, less free radicals being generated.

Scatiggio, et al. described "classical stray gassing" as hydrogen and hydrocarbon gasses formation and "passivator induced stray gassing" as entirely due to H_2, CO, and CO_2, without the formation of hydrocarbon gasses [8]. Our observations are in agreement. The severely hydroprocessed base stocks and formulated oils without passivators did not generate gasses. When passivators were added to these oils, only H_2, CO, and CO_2 were observed, leading to "passivator induced stray gassing". The other, less severely processed solvent neutral oil without passivators exhibited "classical stray gassing" and generated H_2, CO, and CO_2 as well as hydrocarbons.

Stray gassing, the low temperature generation of gasses, is a consequence of free radical reactions occurring during the oxidation of the transformer fluid. Severe hydroprocessing produces stable base stocks that resist oxidation and limits the amount of stray gassing. The presence of reactive additives enhances the generation of stray gassing.

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Table I. Stray Gassing Results (120°C after 16 hours, µL/L)

Section 1. Neat Refinery Base Stocks without Additives									
	H_2	O_2	CO	CO_2	CH_4	C_2H_2	C_2H_4	C_2H_6	TCG
Hyvolt I & II base stock	<5	31171	<25	<25	<1	<1	<1	<1	0
Hyvolt III base stock	<5	30908	<25	<25	<1	<1	<1	<1	0
Isoparaffin 60	34	138	101	154	29	<1	5	53	222
Solvent Neutral	99	9282	178	247	2	<1	2	<1	281
Section 2. Formulated Commercial Products									
Hyvolt I	188	1667	157	428	54	<1	65	65	529
Hyvolt II	<5	28200	<25	<25	<1	<1	<1	<1	0
Hyvolt III	<5	30334	<25	<25	<1	<1	<1	<1	0
Section 3. Hyvolt I with Additives									
Neat Hyvolt I	214	234	136	201	68	<1	41	82	541
0.27 wt% BHT	213	7801	296	475	8	<1	55	<1	572
100 mg/kg Irgamet 30	2249	203	161	433	132	<1	30	134	2706
100 mg/kg Irgamet 39	1079	314	200	277	190	<1	32	190	1691
0.4 wt% Aromatic Naphtha	222	177	168	252	82	<1	54	96	622
Section 4. Hyvolt II with Additives									
Neat Hyvolt II	<5	28200	<25	<25	<1	<1	<1	<1	0
100 mg/kg Irgamet 30	545	21403	47	101	<1	<1	<1	<1	592
100 mg/kg Irgamet 39	420	23812	56	415	<1	<1	<1	<1	476
0.4 wt% Aromatic Naphtha	10	21722	60	84	<1	<1	<1	<1	70
Section 5. Hyvolt III with Additives									
Neat Hyvolt III	<5	30334	<25	<25	<1	<1	<1	<1	0
100 mg/kg Irgamet 30	555	22664	58	113	<1	<1	<1	<1	613
100 mg/kg Irgamet 39	350	22433	49	107	<1	<1	<1	<1	399
0.4 wt% Aromatic Naphtha	9	22218	56	63	<1	<1	<1	<1	65
Section 6. Isoparaffin 60 with Additives									
Neat Isoparaffin 60	34	138	101	154	29	<1	5	53	222
0.37 wt% BHT	<5	29256	54	83	2	<1	<1	<1	56
100 mg/kg Irgamet 39	236	28486	35	109	2	<1	<1	<1	273
3 wt% Solvent Neutral	150	28685	<25	148	2	<1	<1	<1	152

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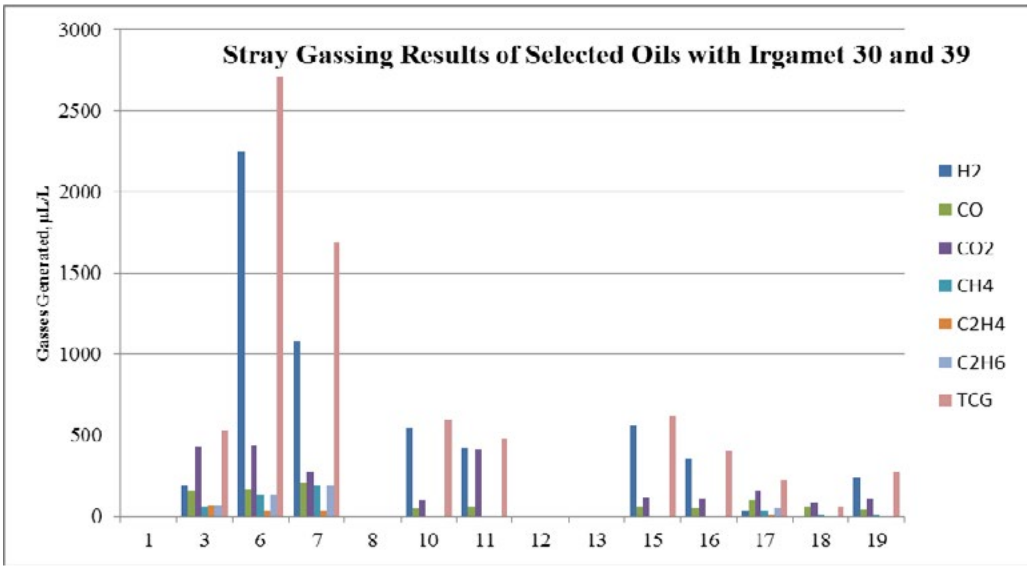

Fig. 2. Stray gassing results for selected neat base stocks, formulated transfomer oils, and samples with Irgamet 30 or Irgamet 39. (1) HyVolt I and II base stock, (3) HyVolt I, (6) HyVolt I with Irgamet 30, (7) HyVolt I with Irgamet 39, (8) HyVolt II, (10) HyVolt II with Irgamet 30, (11) HyVolt II with Irgamet 39, (12) HyVolt III base stock, (13) HyVolt III, (15) HyVolt III with Irgamet 30, (16) HyVolt III with Irgamet 39, (17) Isoparaffin 60 base stock, (18) Isoparaffin 60 with BHT, (19) Isoparaffin with Irgamet 39.