



TECHNICAL BULLETIN

Susterra® Propanediol: Heat Transfer Fluid is Advantaged for High Temperature Applications

Introduction

This experiment was conducted to evaluate relative stability of three 50% glycol-based heat transfer fluids, which were inhibited with 2.2% Penray 2792 inhibitor. The heat transfer solutions that contained either 50% ethylene glycol (EG), 50% 1,3-propanediol (PDO), or 50% propylene glycol (PG) were chosen for the study. The results showed that the PDO-containing fluid was most stable to thermal degradation, when compared to EG or PG-containing fluids, and generated lower levels of organic acids, and related thermal degradation products. The PDO fluid showed a significantly lower conductivity than the EG or PG fluids following exposure to elevated temperatures. Higher chemical stability of the PDO based heat transfer fluid resulted in a lower level of organic acid, and other corrosive compounds. Lower levels of thermal degradation products improves overall stability of the fluid, resulting in a lower corrosion potential for components in the heat transfer system, and a longer lifetime of the fluid.

Background

This experiment was conducted to evaluate relative stability of three glycols using the same Penray inhibitor package (2.2% of Penray 2792). The test consisted of incubating three aqueous glycol-based heat transfer fluids in a reflux system for 16 hours at $192^{\circ}\text{C}\pm 10$. The glycols included, 50% ethylene glycol (EG) in deionized water, 50% 1,3 propanediol (PDO) in deionized water, and 50% propylene glycol (PG) in deionized water. The study showed that the PDO fluid was chemically more stable than EG or PG fluids. In all samples, the nitrite species decreased, which was followed by a corresponding increase in nitrate. Formate and glycolate, which are the thermal decomposition products of glycols, were found to be 5-10 times higher in concentration when compared to the PDO fluid.

Experimental Design

Three aqueous 50% glycol solutions were used in the experiment; ethylene glycol (Sigma Chemical, 99% purity), 1, 3-propanediol (DuPont Tate & Lyle Bio Products, 99.9% purity), and propylene glycol (Sigma Chemical, 99% purity). Water used for dilution of the glycols to a final concentration of 50% based on volume, was deionized to 18 megOhms. The diluted glycols, inhibited with a 2.2% Penray 2792 were boiled in a reflux system for 16 hours at $192 \pm 10^{\circ}\text{C}$. This period of reflux was intended to simulate a stagnant high thermal event for a semi-closed loop heat transfer system. The following analytical measurements were performed on heat transfer fluids that were sampled during the trial:

- Visual appearance
- GC-MS: Agilent Technologies 7820A/5975 MSD Innowax 19091N-133 (30m x 0.25mm x 0.25 μ m) 50° to 250°C at 1.5 mL/min (He)
- Agilent 8453 UV-Visible Spectrophotometer
- Conductivity & pH Denver Instrument 250
- ICP-AES Optima 2100 DV
- Water content by volumetric Karl Fischer Mettler Toledo V20
- Antek 9000HN

Results

The visual appearance of samples shown in Figure 1 indicated that significant chemical changes had occurred in EG-containing fluids, and to a lesser extent in the PG and PDO fluids. The EG and PG fluids exhibited a darker color than the PDO fluid, which was corroborated by the ultraviolet (UV) absorbance data at 220 nm and 270 nm, as well as the wavelength scans completed from 225 to 450 nm wavelength range on equivalent (1:6) dilutions of the fluids.

Conductivity for the three glycol-containing fluids differed significantly. Higher conductivity of the EG and PG fluids correlated well with the elevated concentrations of glycolate and formate. Total inorganic ions (Table 2) were found to be similar for the three fluids, confirming that charged organic species are likely responsible for the differences in conductivity.

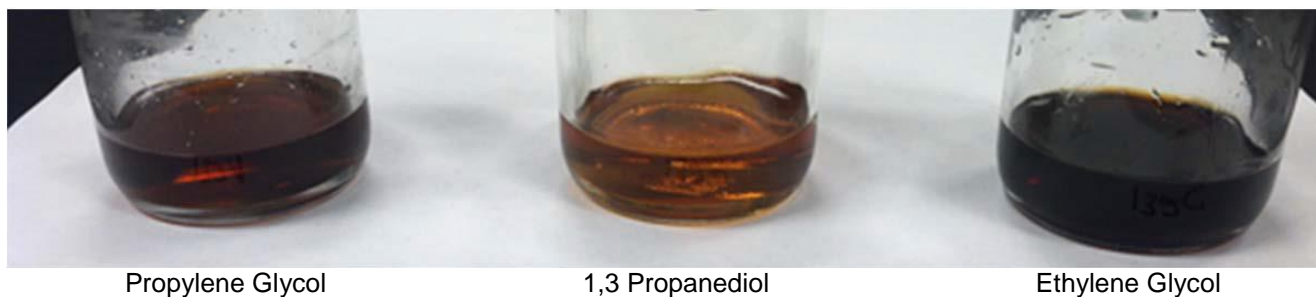


Image 1. Visual appearance of fluids after reflux

Conversion of nitrite (NO₂⁻), made available through the inhibitor package, to nitrate (NO₃⁻) via a 2 electron oxidation provides indication that a significantly higher level of oxidation products are present in the EG and PG fluids.

Samples	pH	Conductivity (μs/cm)	UV 220nm	UV 270nm	Nitrogen Concentration (ppm)
712-132A	11.15	228	103.07	20.78	1377.1
712-132B	9.1	168	83.1	13.45	1279.6
712-132C	10.97	676	75.24	20.8	1291.1

Table 1. Analysis of glycol samples

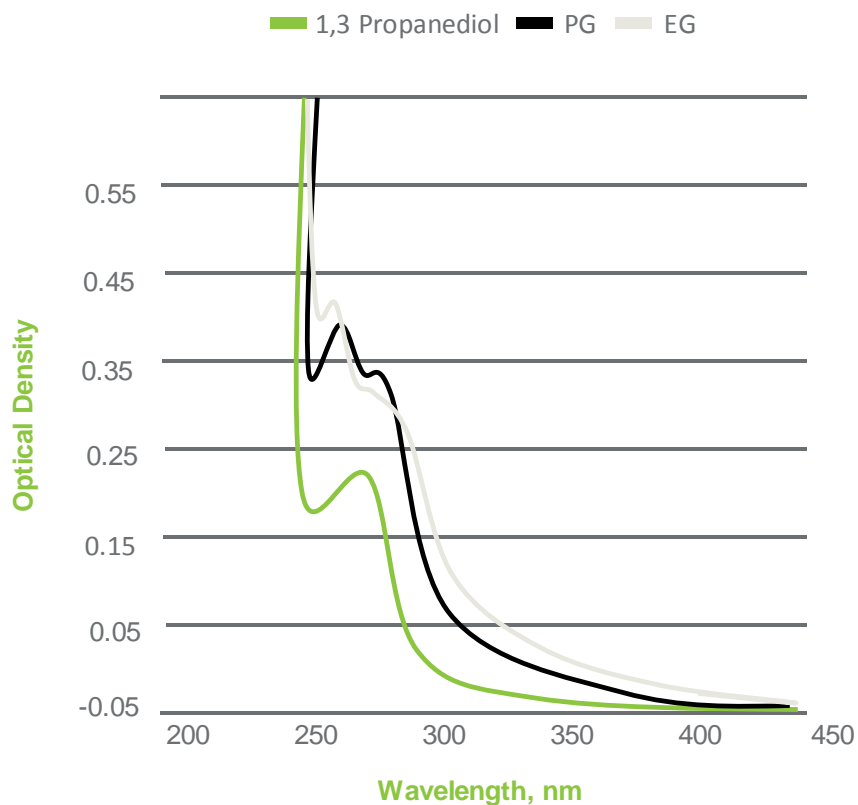


Figure 1. UV/Vis 220nm-450nm

Samples	Ca	Mg	Na	K	Fe	Cu	Si	Mn	Zn	P	S	Co
712-132A	2.71	0.63	4454	13.01	0.83	0.23	437.3	0.06	2.39	19.56	232.3	0
712-132B	5.19	0.78	4637	12.88	1.51	0.46	571.9	0.06	2.89	26.61	269.5	0
712-132C	4.11	0.34	4502	10.35	0.39	0.18	470.1	0.04	2.38	20.2	253.3	0

Table 2. ICP-AES analysis results in PPM

Sample ID	Coolant (2.2%v 2792)	Cook Temp. (°F)	Yield	pH	Boron (µg/g B)	Nitrates (mg/l NO2)	Nitrates (mg/l NO3)	MBT (mg/l MBT)	Formate (mg/l)	Glycolate (mg/l)	Sulfate (µg/g SO4)
712-132D	PG uncooked	NA	NA	10.58	450	3183	931	540	ND	ND	7
712-132A	PG cooked	385	144 of 250	11.93	858	2218	1873	ND	62	2399	44
	PG boiling pt.	387	Adjusted		494	1278	1079	ND	36	1382	25
712-132E	PDO uncooked	NA	NA	11.23	418	3061	892	383	ND	ND	8
712-132B	PDO cooked	362	248 of 250	9.41	438	2452	1141	101	342	219	8
	PDO boiling pt.	417	Adjusted		434	2432	1132	100	339	217	8
712-132F	EG uncooked	NA	NA	11.12	478	3356	985	542	ND	ND	10
712-132C	EG cooked	393	142 of 250	11.5	844	731	2056	ND	220	3443	127
	EG boiling pt.	371	Adjusted		479	415	1168	ND	125	1956	72

Table 3. Before and after testing

Conclusions

A PDO-containing heat transfer fluid, inhibited with 2.2% Penray 2792 was shown to have improved stability to thermal decomposition when compared to EG or PG-containing heat transfer fluids. In all three heat transfer fluids, nitrite levels decreased over time, and the nitrate levels increased, indicating that changes in redox occurred in the samples during the test. The highest levels of nitrate were observed for the EG-containing fluid, and the lowest level were observed for the PDO-containing fluid.

Formate and glycolate are thermal decomposition products of glycols. No glycolate or formate was detected in any of the samples prior to the thermal exposure period; however, both the EG and PG were found to generate higher levels of glycolate after thermal exposure when compared to the PDO-containing fluid.

Sulphate is an oxidation product of mercaptobenzothiazole (MBT), which is a corrosion inhibiting chemical in the inhibitor package. Levels of sulfate in the EG and PG fluids were 4 to 16-fold higher than the PDO fluid, indicating that thermal degradation of MBT was significantly lower in the PDO-containing fluid.

PDO showed significantly lower conductivity than the EG and PG fluids following exposure to elevated temperatures. Higher chemical stability of PDO-containing heat transfer fluids results in a lower level of organic acids and other corrosive compounds that are generated through thermal decomposition of the heat transfer fluid. A lower concentration of these compounds may lead to reduced corrosion potential of metal components in the heat transfer system, and a longer lifetime of the heat transfer fluid.

References

Monticelli C, Brunoro G, Grignani A, Zucchi F. Corrosion behavior of the aluminium alloy AA 6351 in glycol/water solutions degraded at elevated temperature *Werkstoffe und Korrosion* 1988. 39, 379-384

Ye L, Zhang F, Zhang L, Qi F, Theoretical Studies on the Unimolecular Decomposition of Propanediols and Glycerol. *J. Phys. Chem. A* 2012, 116, 4475-4465

Madera M, Höflinger W, Kadnar R, Ion chromatographic identification and quantification of glycol degradation products. *Journal of Chromatography A*, 997 2003 279-284

Evangelista J W, Thomas Avedisian C, Wing Tsang, Thermal and catalytic decomposition of aqueous ethylene glycol mixtures by film boiling *International Journal of Heat and Mass Transfer* 55 2012 6425-6434

Veltman S, Schoenberg T, Switzenbaum M S, Alcohol and acid formation during the anaerobic decomposition of propylene glycol under methanogenic conditions. *Biodegradation* 9: 1998, 113-118

Díaz E, Sad M E, Iglesia E. Homogeneous oxidation reaction of propanediols at low temperatures. *ChemSusChem* 2010, 3, 1063-1070

For additional information or samples:

DuPont Tate & Lyle Bio Products Customer Service

198 Blair Bend Drive
Loudon, TN 3777

Tel: +1-866-404-7933
www.duponttateandlyle.com



Copyright © 2016 DuPont Tate & Lyle Bio Products Company, LLC. Susterra® is a registered trademark of DuPont Tate & Lyle Bio Products Company, LLC, for its brand of bio-based propanediol. All rights reserved.

This technical product information is presented in good faith and is believed to be accurate and reliable as of the date of publication. DuPont Tate & Lyle Bio Products makes no guarantee or warranty of any kind, expressed or implied, regarding the product or information contained herein. Purchaser assumes all risk and liability in acting on the information provided herein. It is the sole responsibility of the Purchaser to determine whether Susterra® propanediol is appropriate and suitable for the Purchaser's specific end use and, as required, to obtain approval by appropriate regulatory authorities for such use. Statements made concerning the use of Susterra® propanediol are not to be construed as recommendations, suggestions or inducements to use it in the infringement of any patent or in violation of any applicable laws or regulations. DuPont Tate & Lyle Bio Products disclaims any liability for infringement of any patent by reason of customer's use of any products or information contained herein in combination with other materials or in any process. (3/2016)