Cracked Glycols – an underestimated problem

Why classical solar heat transfer fluids hit the limits

Summary

Due to the improving efficiency of solar collectors, solar heat transfer fluids are being exposed to a constantly increasing temperature stress. In vacuum collectors, temperatures of 270°C and above have been measured during periods of stagnation. It is also important to note that systems operating with an average fluid temperature of 200°C can have isolated pockets of solar fluid with temperatures surpassing 270°C. These isolated areas occur where the solar fluid has direct contact with a metal surface. At such high temperatures the so-called "cracking" of glycol can occur. Cracking refers to the thermal decomposition of the glycol material, leading to the formation of higher and lower molecular weight compounds or even carbon. In extreme cases, cracking can cause total blockage of the collector and require expensive cleaning or replacement of the collectors. In less extreme cases, cracking can lead to irreversible degradation to the corrosion protection properties of the heat transfer fluid. Without proper corrosion protection heat transfer fluids can shorten the life of the solar system due to increased corrosion.

Based on market research and customer feedback the following goals were specified for a new solar heat transfer fluid:

- constant use temperature stability between -25 °C and +200 °C
- excellent corrosion protection
- low viscosity
- optimized thermal properties

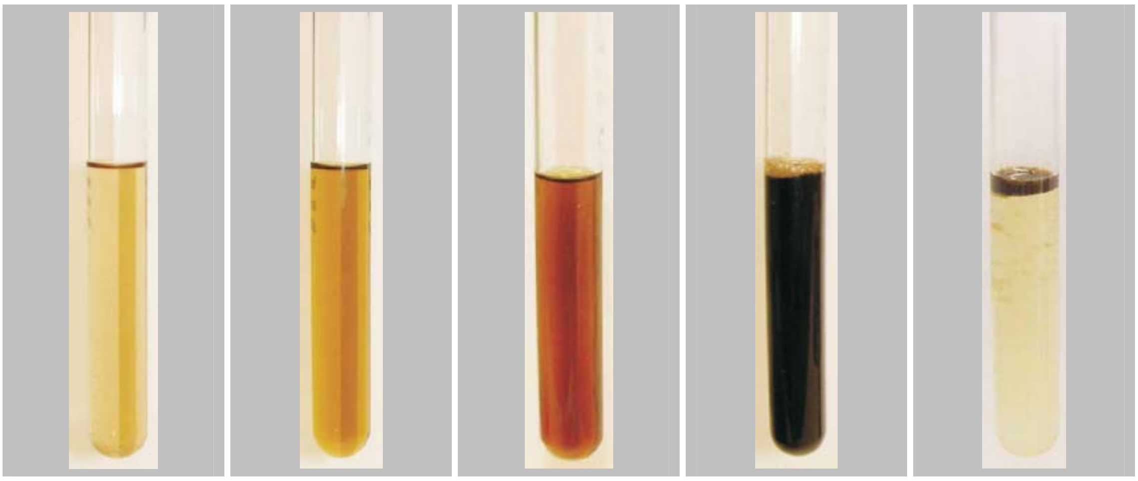
Antifrogen® SOL HT

Improvement of the thermal stability of the heat transfer fluid

Due to the increasing efficiency of solar collectors, solar heat transfer fluids are being exposed to more extreme thermal environments. Increasing temperatures loads require that all materials and heat transfer fluids perform without cracking or thermal decomposition.

Cracking or thermal decomposition begins with the darkening of the heat transfer fluid. In this phase, the darkening will not cause a negative impact on the collector or the physical properties of the fluid. Continued thermal decomposition will lead to a further darkening of the fluid accompanied by a burned smell. Finally, the formation of water-insoluble, tar-like decomposition products are observed. Once the tar-like residue is formed, it tends to build up quickly and constrict the flow of fluid. Replacement of the collector is the most common method of correcting this issue. However, this process entails significant expense and service interruption, ultimately impacting the system owner.

Picture 1 shows solar heat transfer fluids in various stages of thermal decomposition. Darkening of the fluid is pictured in 1.a – 1.d with the water insoluble residue pictured in 1.e.



1.a 1.b 1.c 1.d 1.e

Picture 1. Appearance of solar fluids after various stages of thermal decomposition

As basis for the selection of a more thermally stable heat transfer fluid, different glycols (propylene glycol, higher glycols, etc.) were exposed to temperatures which can be achieved in the latest generation of solar collectors. As an assessment criterion, a pressure increase was used as an indication for the formation of low boiling break down products. Each sample contained 200mL of fluid and the presence of copper with a surface of 21.0 cm², prepared according ASTM D 1384. The test fluids were exposed to 3 bar oxygen.

	Test temperature	Maximum pressure increase
Mono propylene glycol	230 °C	12 bar
	270 °C	23 bar
Higher boiling glycols	230 °C	5 bar
	270 °C	8 bar

Table 1. Results of temperature testing with corresponding pressure increase

The results in Table 1. above, supported by the results of physical-chemical investigations, show that with change from propylene glycol to higher boiling glycols the thermal resistance can be increased significantly.

Improvement of corrosion protection

ASTM D 1384 is used as the main quality test (picture 2.) for judging the corrosion performance of existing and developmental glycol based heat transfer fluids.

In this test, various metal coupons (copper, brass, soft solder, steel, cast iron and cast aluminium) are submerged in an aqueous dilution of the heat transfer fluid for 336 hours. Temperature is maintained at 88°C, with introduction of six liters of air per hour. After the test, the weight change is measured. The difference before and after is used as a quality criterion for the stability and the corrosion protection of the heat transfer fluid.

Picture 2. ASTM D 1384

Only virgin heat transfer fluids are currently exposed to ASTM D 1384. The influence of break down products formed at elevated temperatures and the thermal stability of the corrosion protection additives on the corrosion behaviour have not been considered. To test the efficacy of corrosion additives under more realistic conditions, the solar heat transfer fluid in the usage dilution were exposed to a higher temperature load (230°C, 3 days, presence of air) and then again tested according to ASTM D 1384.

Table 2. shows the test chains according ASTM D 1384 after thermal load for 3 days at 230°C of Antifrogen SOL HT and two commercially available solar heat transfer fluids. The difference in weight loss and appearance is easy to see. This can be regarded as a proof for the stability of the additive system. Antifrogen SOL HT is the result of a number of tests under the above described test conditions.

Solar heat transfer fluid (A)

Weight change in g/m²

	before tempature stress	**after tempature stress**
Copper	-0.9	-30.3
Soft solder	-5.0	-7.9
Brass	-1.8	-34.8
Steel	-0.6	-4.1
Cast iron	±0	-38.5
Cast alumimium	-1.7	-0.1

Solar heat transfer fluid (B)

Weight change in g/m²

	before tempature stress	**after tempature stress**
Copper	-0.7	-37.8
Soft solder	-1.7	-9.8
Brass	-1.2	-7.0
Steel	-0.2	-1.8
Cast iron	-0.1	-1.6
Cast alumimium	±0	+0.2

Antifrogen SOL HT

Weight change g/m²

	before tempature stress	**after tempature stress**
Copper	-1.1	-3.3
Soft solder	-2.2	+2.1
Brass	-0.6	-3.1
Steel	-0.1	-0.3
Cast iron	-0.2	-0.4
Cast alumimium	+0.1	+0.2

Table 2. Thermal stability results of various solar heat transfer fluids

Antifrogen SOL HT – the latest development in the field of heat transfer fluids for solar applications – meets the increased temperature requirements. Antifrogen SOL HT, based on higher boiling glycols, offers an outstanding frost and corrosion protection and an increased stability against oxygen and thermal load in comparison to propylene glycol based fluids. Increased performance of the heat transfer fluid allows for higher use temperatures, warranty protection and peace of mind for the system owner in times of system stagnation.

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