

THE BEHAVIOUR OF HEAT TRANSFER MEDIA IN SOLAR ACTIVE THERMAL SYSTEMS IN VIEW OF THE STAGNATION CONDITIONS

Frank Hillerns, Ph.D, TYFOROP GmbH, Hamburg

This paper was presented at the *IEA-SHC Task 26 Industry Workshop* in Borlänge, Sweden, April 3, 2001. It is based on a presentation given at *9th Symposium Thermal Solar Energy* in Staffelstein, Germany, May 5-7, 1999.

Abstract

On-going technical development of solar collectors significantly raise the demands to the heat transfer medium regarding its ability to take thermal stress.

However, stagnation temperatures of up to 200 °C in flat plate collector systems still can be mastered by *conventionally inhibited* solar fluids. In contrast to this, absorber temperatures of up to 300 °C as reached in evacuated tubular collectors require the application of a more advanced medium containing *reversibly evaporizable* corrosion inhibitors. Practical application experiences concerning such a recently developed fluid are in the meantime available.

Introduction

Water is predestined to function as a heat transfer medium in solar active thermal systems. This is on the one hand due to its outstanding thermophysical properties, e.g. highest specific heat and thermal conductivity, and lowest viscosity of all the fluids considered for heat carriers. On the other hand, water is non-toxic, non-flammable, cheap, and easily available. However, parameters that reduce its general suitability are: corrosivity to metals and alloys, precipitation of hardness constituents at higher temperatures, and a relatively small temperature range of operation determined by its freezing and boiling point, respectively.

It is well known that this application range can be extended when aqueous solutions of inorganic salts, monohydric alcohols, or dihydric alcohols (glycols) are used. In spite of very effective freezing-point depression and good thermal transport properties, salt solutions are not applicable for solar systems due to uncontrollable corrosivity at temperatures > 0 °C. On account of better material compatibility, favorable viscosity, and low costs, methyl and ethyl alcohol solutions have been widely used since 1920 till the early seventies in automotive cooling as well as in many other applications.

Unfortunately, methanol and ethanol are toxic and readily volatile due to low boiling points (meth: 64 °C, eth: 78 °C) [1], hence depressing the boiling points of its aqueous solutions.

In comparison with monoalcohols, ethylene and propylene glycol (b.p. 197 °C, 188 °C) [2], cause similar freezing-point depressions, but simultaneously raise the boiling points of its mixtures with water. Regardless higher costs and inferior thermophysical properties, nowadays non-toxic propylene glycol is exclusively used as the basic compound for solar heat transfer media instead of „injurious-to-health“ classified ethylene glycol.

Solar Fluids - Demands and Composition

Heat transfer media have to meet a variety of challenging requirements to ensure trouble-free operation of the solar system over a long period of time:

- Frost resistance down to -50 °C maximum
- Thermophysical properties equivalent to water
- Non-inflammability
- Corrosion protection for metals and alloys
- Compatibility with sealing materials
- Endurance under thermal stress conditions
- Prevention of deposits and foaming
- Low ecotoxic potential, bio-degradability
- Long-term stability
- Reasonable price

As already stated above, water is in general corrosive to metals. Factors that strongly govern the grade of corrosivity are the content of oxygen, the pH value, the temperature, and the presence and concentration of dissolved chemical substances. The latter point is of great importance regarding the practical use of „pure“ propylene glycol / water solutions: compared to neat water as well as to neat propylene glycol, the corrosivity of those mixtures is significantly enhanced - in inverse proportion to the glycol concentration. Hence this effect must be compensated by addition of inhibitors, which predomi-

nantly prevent corrosive attack by forming thin protective layers on the metal surfaces.

Solar systems typically consist of different materials like copper, brass, solder, steel, grey cast iron, and (rarely nowadays) aluminium. Unfortunately there is no universal inhibitor available hitherto. Thus several organic and inorganic compounds possessing metal-specific protective potentials have to be combined to an efficient, low-toxic and environmentally friendly *inhibitor package*.

Table 1 displays the composition of a conventional solar fluid concentrate based on propylene glycol, suitable for common solar installations (equipped with flat plate collectors, stagnation temperature 200 °C max.).

Compound	% w/w	Function
Propylene Glycol	92 – 94	Frost Resistance
Salts of Organic Acids	3 – 4	Ferrous Metal protection
Silicates	< 1	Aluminium protection
Triazoles	≤ 0.2	Yellow Metal protection
Borax	1 –1.5	Reserve Alkalinity
Potassium Hydroxide	< 1	Reserve Alkalinity
Water	3 – 4	Solvent for Inhibitors
Stabilizer, Dispersant, Defoamer, Dye	0.1 – 0.3	Stabilization of water hardness, Anti-foam, Coloration

Conception and Design of Solar Systems

The life-span of thermal solar systems strongly depends on the grade of corrosion stress the several components are subjected to. To minimize corrosion problems and hence reach the aim of long-term and trouble-free operation, both installation and fluid must be optimally adapted to each other. Assuming correct application and performance of the heat transfer medium, important plant technology parameters in this respect are the operation temperature, the heat flux, the flow conditions, and furthermore electrochemical effects caused by mixed installations or external voltages.

Special attention is to be paid to keep the internal metal surfaces free of encrustation or scaling. Inhomogeneously covered surfaces implicate lower heat transfer efficiency, giving rise to locally increased temperatures, which cause thermal stress to the medium and accelerate corrosion in those areas. Explicitly to be mentioned in this context is black cupric oxide - as shown by Figure 1 - which forms at high temperatures in the course of component production or system assembly (hard-soldering) due to local overheating of copper surfaces in presence of oxygen. Such insoluble scale can be mechanically detached by the hot solar fluid, but this occurs slowly and incompletely in most cases. Sub-

sequently, those dispersed particles often sedimentate in low flow areas and may lead to blocking of collector tubes and filter elements as well as to pump malfunction



Figure 1: Copper Scale collected from a Solar Plant

Increased Collector Efficiency - Increased Thermal Stress to Solar Fluids

Systems equipped with Flat Plate Collectors

Dynamic development of solar technology over the last decade has led to improved corrosion resistance of components like pumps, membrane expansion vessels, and of course collectors. Consequently, corrosion damages in flat plate collector systems are nowadays rarely to be observed. Simultaneously achieved enhancement of collector efficiency on the other hand causes remarkably increased thermal stress to the heat transfer medium due to now possible stagnation temperatures of up to 200 °C.

Propylene glycol / water based solar fluids are subject to premature aging at such temperatures, indicated by darkening of the fluid and a slowly decreasing pH value.



Figure 2: Un-used Solar Fluid (left, pH 8.2), compared to overheated Fluid (pH 6.8)

Chemically speaking, propylene glycol then undergoes decomposition in the course of oxidation reactions. Acidifying organic compounds, e.g. lactic, oxalic, acetic,

or formic acid [3] are formed, which initially can be neutralized by the reserve alkalinity (ref. table 1) to a certain extent. But due to limited concentration of buffering substances, repeated overheating finally brings the pH of the fluid down to values < 7 , hence the system is not protected against corrosion anymore. It can be said in general that the velocity of propylene glycol degradation is proportional to temperature stress and oxygen concentration. Further acceleration effects caused by the presence of unprotected copper surfaces and heavy metal ions have been reported [3].

Taking the above mentioned facts into consideration, it becomes essential to prevent the medium from exposure to excessive temperatures over longer periods of time, especially during stagnation state of the system. A precautionary measure proven to be worthwhile in practice is to install expansion vessels of suitable size to ensure that all of the medium can drain out of the collector when stagnation temperature is reached.

The „stagnation scenario“ can be described in a simplified way as follows: locally formed vapour bubbles - in fact a small quantity of vaporized propylene glycol / water - are pushing the main quantity of still liquid medium out of the collector when evaporation starts. Recalling that conventional heat transfer fluids consist of water, propylene glycol *and* dissolved solid inhibitors, it is evident that small amounts of those non-evaporizable components will remain on the hot tube walls. Hence another important quality feature of conventional heat transfer fluids is the *reversible dissolvability* of such inhibitors/residues when stagnation has terminated and cooled fluid streams through the collectors again. Figure 3 shows the appearance of a slightly overheated conventional fluid equipped with a suitable inhibitor system.

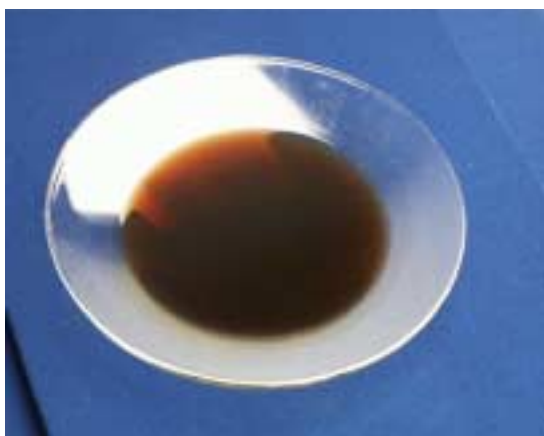


Figure 3: Slightly overheated conventional fluid with redissolvable inhibitors

Insufficient or lacking re-dissolvability may incur deteriorated performance up to blocking of the collector. Obviously, corrosion risk will be significantly enhanced due to depletion of inhibitor concentration in the fluid.

Systems equipped with Evacuated Tube Collectors

Stagnation conditions in flat plate collectors still can be mastered by using conventional solar fluids with suitably

formulated inhibitor packages to meet the above described requirements. Anyway, conventional media reach its limits when it comes to evacuated tube collectors. Absorber temperatures of up to $300\text{ }^{\circ}\text{C}$ lead to strongly accelerated propylene glycol degradation, indicated by darkening and pH drop already after several hours. Under permanent stagnation conditions, irreversible fluid damage takes place within 2-3 weeks, meanwhile considerable amounts of dark insoluble residues are formed, as displayed by Figure 4.



F4: Seriously damaged fluid, residues non-redissolvable

It became evident that further improvement of the inhibitor package was necessary to avoid formation of deposits as well as to offer enhanced buffer capacity to control the glycol decomposition even under such extraordinary thermal stress. A theoretically simple, but in view of its development nevertheless sophisticated remedy is the use of a *liquid* inhibitor package. In case of stagnation those components evaporize together with propylene glycol and water, thus the collector remains completely empty, and no damaging insoluble residues may lead to any flow obstruction or blocking.

In practice, recent experiences obtained from properly designed solar systems equipped with evacuated tubular collectors show that even standstill temperatures of up to $300\text{ }^{\circ}\text{C}$ can be mastered with this new medium (Brand name: TYFOCOR[®] LS). Nevertheless it must be emphasized again that under those conditions the fluid lifetime will be generally reduced. Annual lab check of e.g. density, concentration, inhibitors, and pH value is therefore highly recommended. Supposing that one of the mentioned parameters is found to deviate from the required values during analysis, the solar fluid must be replaced immediately.

References

- [1] Ullmanns Enzyklopädie der techn. Chemie, 3. Aufl. Bd. 8, München, Berlin, Wien: Urban; Schwarzenberg 1957, S.1
- [2] Ullmanns Encyclopedia of Industrial Chemistry, 5th ed. Weinheim, Vol A 10 (1987) 101, Vol A 22 (1993) 163
- [3] W.J. Rossiter Jr, P. W. Brown, McClure Godette, The determination of acidic degradation products in aqueous ethylene glycol and propylene glycol solutions using ion chromatography. Solar Energy Materials 9, 1983