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BETAINE BASED HEAT TRANSFER FLUID AS A SOLUTION FOR TOXICITY AND CORROSION PROBLEMS IN HEATING AND COOLING SYSTEMS

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ABSTRACT

A betaine-water solution was tested and developed for heat transfer use. Betaine is a by-product of the sugar industry and is acquired from sugar beet. Betaine is by nature non-toxic and non-harmful to the environment. Adequate freezing protection is achieved with betaine concentrations of 20-55 % by weight. This solution was found to have other good qualities as well; it has good heat transfer capabilities, is not harmful to materials regularly used in equipment and is less corrosive than pure water.

Development work consisted of freeze protection and pipe burst protection measurements with different betaine concentrations, measuring physical properties and developing the additive package for enhanced corrosion protection. Laboratory and field-tests showed that a betaine-water solution performs well as a heat transfer fluid in the HVAC industry. The concrete result was a patented new product for the industry for the temperature range of -45 to +110 °C (-49 to +230 F).

INTRODUCTION

The transfer of heat is commonly required in industry, buildings and municipal engineering systems. While the advances made in heat transfer technology and equipment have been great, the potential and benefits provided by a careful choice of the heat transfer medium are often overlooked. The selection of the right fluid offers savings in materials and running costs and can therefore significantly affect the life cycle cost.

The most important technical characteristics of a heat-transfer fluid are freezing protection, thermal and microbiological stability, physical properties which ensure good heat transfer properties, and low induced corrosion.

The increasingly stringent environmental legislation and public attitude call for improved environmental performance and non-toxicity. Consequently, development efforts focus on new types of heat transfer fluids that are environmentally friendly and less toxic than current solutions but possess excellent cold flow characteristics and heat transfer properties.

The main environmental characteristics of a heat transfer fluid are that it has a low environmental impact, that it is non-toxic, safe to use, and easy to dispose of or recycle, and that the total costs over the product's life cycle are competitive.

The starting point for this R&D effort was the toxicity problem of many conventional heat transfer fluids. Fluid toxicity in building systems and industrial use is becoming increasingly less acceptable. Alternative fluids have been sought from among salt solutions and vegetable oils. Technical difficulties have not made extensive use of these alternatives very attractive. Main technical problems have been high viscosity and corrosion.

The research work focused on Betaine (Trimethyl glycine or Glycinebetaine or TMG, see Figure 1) and its possibilities for avoiding existing problems in conventional glycol and salt solution use. Chemically betaine is a quaternary ammonium compound with three methyl groups attached to the nitrogen atom of a glycine molecule.

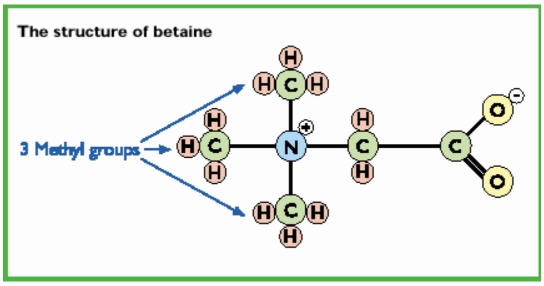

Figure 1: The structure of Betaine (Trimethyl glycine)

The Betaine used in this research and development work is fully natural and is acquired from sugar beet, the most common source for betaine (1). Conventional uses of Betaine include animal feeds, human food supplements, pharmaceuticals (2) and cosmetic products.

1 BETAINE TECHNICAL PERFORMANCE RESEARCH

The quality of a heat transfer fluid is defined by its technical performance, environmental aspects and economical impact. Technical performance was evaluated by measuring several different physical properties of betaine-water solutions and by conducting field tests in actual HVAC systems (heating, ventilation, air conditioning and refrigeration). Most measurements were done in or for the Fortum Technology Center, Porvoo, Finland.

1.1 Freeze Protection and Burst Protection

The most basic function of a heat transfer fluid is freeze protection. Due to low ambient temperatures or low operational temperatures of systems it is quite common for HVAC systems and industrial processes to require heat transfer in sub-zero conditions. In the operational temperature range fluids must remain in liquid form and not damage equipment by freeze-expansion (burst protection). The phase change chemistry of heat transfer fluids can be very problematic. With water it is easy to determine the freezing point. Phase change is immediate and self-evident. When antifreeze agents are used the phase change becomes less evident, a non-stable area can be observed. For technical reasons two interesting temperature points are measured: the freezing point and the congealing point.

The freezing point is the temperature below which solid crystals may build up in a solution. The method used for freeze point determination in this study is the ASTM D 2386-97. To determine the freezing point, a solution is cooled down while stirring, until crystals appear. After the first crystals have built up, the solution is left to warm up slowly while stirring. The temperature in which all the crystals have disappeared is the freezing point of the solution. At the freezing point, and at least 4 degrees Centigrade below this point, the fluid is still functional, but the viscosity starts to climb rapidly. This is the non-stable area, where crystallization can appear suddenly. It is most common that the freezing point value is given for heat transfer fluids according to this method.

The congealing point is the other interesting point. The method used for congealing point determination in this study is the ASTM D 1177-65. The congealing point is determined in the same way as the freezing point, but cooling is continued as long as the sample has undergone so-called thickening, i.e. the viscosity has increased so much that the solution cannot be pumped around in a system any more. Therefore the congealing point is the temperature below which the fluid cannot perform as a heat transfer fluid any longer. For low-concentration betaine-water solutions, the congealing point is about 4 degrees Centigrade lower than the freezing point, for high-concentration solutions it is about 10 degrees lower.

With betaine-water solutions the equipment burst protection reaches well beyond the freezing and congealing points of the fluid. No permanent physical changes could be induced in piping or other heat transfer equipment. Typically burst protection was tested 20-30 degrees Centigrade below freezing point.

The water solubility of betaine is 160g / 100g water. This gives the maximum betaine concentration of 61.5 % by weight in room temperature. Because the solubility decreases slightly in lower temperatures a concentration of 50 to 55 % by weight is considered the practical limit for actual heat transfer system use.

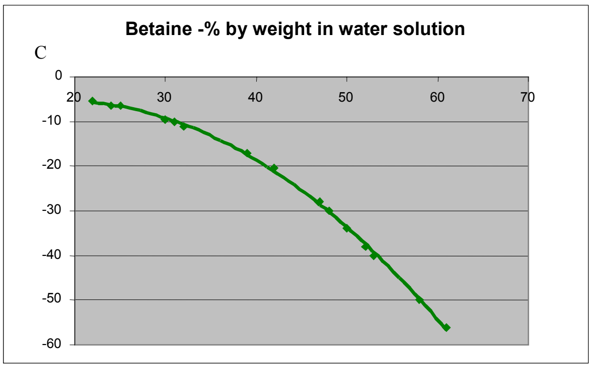

Figure 2: The freezing point in Centigrade of a betaine-water solution by betaine concentration.

1.2 Specific Heat Capacity

The specific heat capacity of a heat transfer fluid is one property affecting performance. Usually heat capacity values of fluids are compared to the value of pure water (app. 4.19 kJ/kgK). Most heat transfer fluids have a lower heat capacity than water.

The heat capacity of betaine-water solutions was found to be in the same range as that of traditional fluids, although slightly lower than glycols'. In Figure 3, the comparison is illustrated with heat transfer fluids having the same freezing point of -15 degrees Centigrade. The fluids used for comparison are the most commonly used traditional fluids ethylene glycol and propylene glycol based water mixtures.

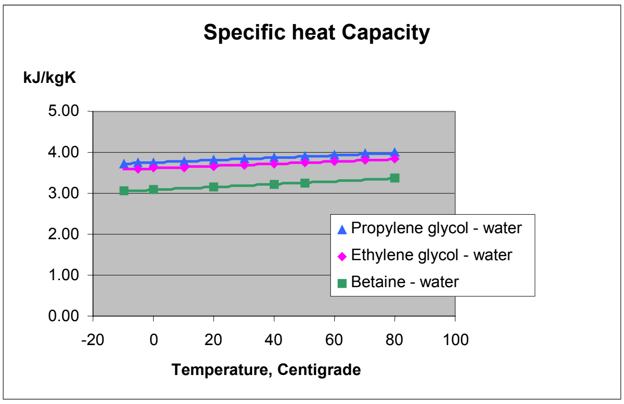

Figure 3: The specific heat capacity of a betaine-water solution compared to traditional fluids.

1.3 Kinematic Viscosity

Viscosity is also one of the key elements in determining the technical performance of a heat transfer fluid. Typically viscosity values rise when temperature drops and therefore forced circulation of the fluid becomes more energy consuming and heat transfer less efficient.

In Figure 4, the comparison is illustrated with heat transfer fluids having the same freezing point of -15 degrees Centigrade. Properties of ethylene glycol and betaine based fluids can be seen as very similar. Propylene glycol based fluids differ from the group with much higher viscosity.

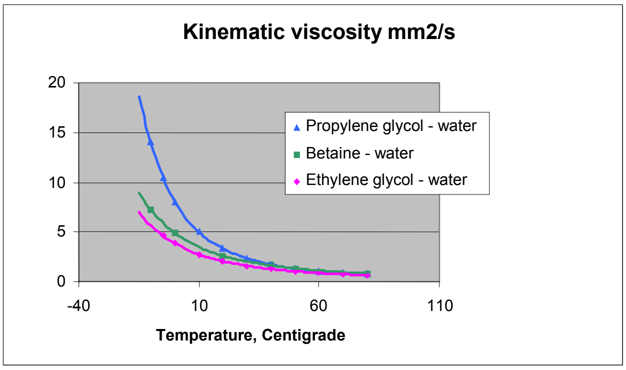

Figure 4: The viscosity of a betaine-water solution compared to traditional fluids.

1.4 Heat Conductivity

Heat conductivity is an important property, but very hard to measure in liquids. The results given in figure 5 are measured with fluids having the same freezing point of -15 degrees Centigrade.

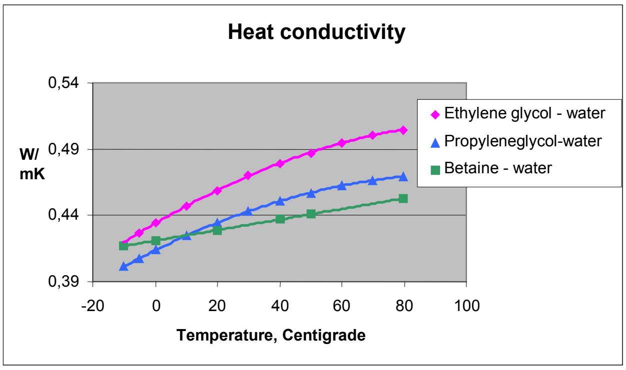

Figure 5: The heat conductivity of a betaine-water solution compared to traditional fluids.

1.5 Conclusions from Physical Properties Measurements

All the measured properties above offer some insight into the fluids actual performance in heat transfer systems. However, it is important to notice that the importance of each property can vary from application to application and can sometimes be even misleading. The operating temperature range and flow characteristics in the particular system have to be taken into account. For example, distinction and evaluation between laminar flow and turbulent flow conditions is difficult. Generally flow dynamics are a factor often ignored by equipment dimensioning software.

Heat transfer efficiency of betaine based fluids has in field-tests been observed to even top that of most commonly used ethylene glycol based fluids. Below is presented a typical test result from an existing office building heat recovery system (Table 1). Thermal efficiency given in the table was measured by the following procedure:

1. Existing fluid was examined and found to be ethylene glycol with freezing point of -30 Centigrade
2. System thermal efficiency data was gathered by measuring inlet and outlet temperatures of air and fluid for a long period

3. System was drained and a betaine-water fluid with freezing point of -30 Centigrade was filled in. No operating parameters were changed (same flow etc)
4. System thermal efficiency data was again gathered by measuring inlet and outlet temperatures of air and fluid for a long period
5. From the gathered data a period with similar outdoor climatic conditions was selected and thermal efficiency of heat transfer from outlet air into inlet air was calculated. Results in table 1.

Table 1. System efficiency field-test. Existing office building heat recovery system.

Circulating fluid	Measured Thermal Efficiency
Ethylene glycol-water mixture, -30 °C freezing protection	28,8 %
Betaine water solution, -30 °C freezing protection	30,1 %

The importance of flow characteristics is evident from the results of table 1. Here, the results would be expected to be favorable for ethylene glycol rather than betaine based fluid if only the physical properties listed in 1.1 - 1.4 are taken into account. In this particular comparison the operating main temperature of the system is so low that the flow dynamics seem to take precedence over heat capacity properties. This is not a general physical fact, but something that follows from the difference in the physical properties of the compared fluids.

2 ENVIRONMENT AND SAFETY RESEARCH

Safety of use and operation, as well as environmental aspects are increasingly important in heat transfer fluid quality evaluation. Betaine as a natural substance has been found to have excellent qualities in this respect. Most important results will be discussed in the following chapter.

2.1 Toxicity

Here the main toxicity measurements and studies are summarized. Most are based on unpublished studies made during 1988-1992 for Cultor Ltd. Finnsugar Bioproducts, the betaine producer for this study.

- For betaine anhydrous, acute oral median lethal dosage, LD50 (oral) rats, is 11.179 $\pm$ 0.725 g/kg B.W. Therefore the product is not classified as toxic for acute health hazards (3).
- Bacterial reverse mutation assay (Ames test with Salmonella typhimurium) showed that betaine monohydrate is not mutagenic when assayed up to 5000 mg/plate (4).
- Metaphase analysis of human lymphocytes showed that betaine monohydrate is not a clastogen to human lymphocytes (5).
- Sensitization test in the guinea pig showed that there is no evidence to suggest that betaine monohydrate acts as a sensitizer. Betaine would be classified as a non-allergenic or as a weak, grade 1 sensitizer on the Magnusson and Kligman scale, having produced a sensitization rate of 0 % (6).
- Acute eye irritation study with 10 % by weight betaine monohydrate in distilled water did not result in any ocular irritation, and it can be considered non-irritant at this concentration (7).
- The primary skin irritation potential test showed that betaine monohydrate at levels over 3.5 % produced a highly significant reduction in the irritant potential of solutions containing 5.15 % to 10.3 % Sodium Lauryl Ether Sulphate (SLES). The extent of this effect was shown to be concentration dependent. In addition, 50 % (w/v) solution of betaine monohydrate appeared to give rise to even less irritation than the deionized water control sample (8).
- The Minimum Inhibitory Concentration (MIC) of betaine monohydrate against nine selected microorganisms was shown to be greater that 10 % w/v. Betaine monohydrate did not appear to affect the growth rate of any of the micro organisms at concentrations up to 10% w/v (9).
- Betaine has food approval in Japan and Korea and Dietary supplement status by FDA in the US.

2.2 Biodegradability and Oxygen Demand

The ability to decompose betaine is widespread among microorganisms and both anaerobic and aerobic are known to degrade betaine. Laboratory tests by Cultor Ltd. Finnsugar Bioproducts have shown that betaine degrades fully within two weeks in sandy clay soil due to the action of soil microbes. Mineralisation of betaine after 28 days was over 88 %, therefore betaine can be considered readily biodegradable (15).

Biological oxygen demand of technical grade betaine anhydrous crystals (purity over 97 % on dry matter basis) has been analyzed to be 1000 mg O/ 1g betaine.

Chemical oxygen demand (COD) values analyzed have been somewhat higher, up to 1300 mg O/ 1g betaine.

Chemical oxygen demand (CODCr) values analyzed have been around 70 - 100 mg O/ 1g betaine.

3 CORROSION AND ADDITIVES NEEDS

Corrosion rates for various materials with betaine based solutions were measured. The results show that corrosion rate even without any corrosion inhibitors added is well below levels accepted by equipment manufacturers in the HVAC industry (for copper for example, a corrosion rate up to 2.0 μm p.a is most commonly accepted). Corrosion speed for pure water was higher.

Table 2. Corrosion rates for a 50% betaine-water solution. The higher figure indicates the corrosion rate at the beginning of the tests and the lower figure the rate stabilised with time (~48h) (16).

Material	**Loss in material thickness, μm p.a**
Copper	1.5 to 0.5
Carbon steel Fe52	75 to 10
Brass	1.5 to 0.2
Red bronze	125 to 2
Cast iron	0.9 to 0.2

Further tests were done according to demands of other than the HVAC industry. In the automotive industry, for example, the demands are much higher and standardized test methods are used. Very common is the ASTM 1384 test. Betaine fluid was tested with a conventional film forming corrosion inhibitor according to this test. Concentrations of the inhibitor package's active ingredients were from 0,05% to 0,1%. Results are given in Table 3 as loss in material thickness and mass loss.

Table 3. ASTM 1384 corrosion test results for a 35% betaine-water solution containing conventional film forming corrosion inhibitor used in the HVAC industry.

Material	**Loss in material thickness, μm p.a**	**Mass loss, mg**
Copper	0.3	0.2
Fe37	0.3	0.2
Solder	0.3	0.2
Bronze	0.3	0.2
Cast iron	22	16.5
Aluminum	2.4	1.8
Zn	4.0	3.0

Further standardized test performed included the Double Chamber Cavitation Corrosion Test (CEC C-23-T-99), the Hot Plate Corrosion Test (ASTM D 4340) and the Simulated Service Corrosion Test (ASTM D2570-96). The betaine based fluid fulfilled requirements set by the AFNOR NFR 15-601 norm for automotive coolant use.

3.1 Conclusions from corrosion and additives testing

The requirements of different industries were closely examined. Heat transfer fluids are used in a variety of systems and conditions. Most important variable is the temperature range of operation. The fluid needs to be thermally stable and have acceptable corrosion properties.

It was found that generally the need for additives is very low for betaine based fluids. Additives are most commonly used in conventional fluids for corrosion protection, pH stability, anti-foaming, coloring and flavoring. Betaine based fluids performed so well in the testing that in many application areas no additives were found necessary to fulfil requirements (especially in the HVAC industry applications such as: air conditioning, heat recovery, heat pumps, phase change heat transfer systems). Only to fulfil the harshest test requirements of the automotive industry, corrosion inhibitors were required. However, the needed concentration of inhibitors was substantially lower than is common with conventional fluids.

CONCLUSIONS

The physical properties and technical performance of betaine based fluids were found to be very acceptable according to the industry standards found. In actual system design it is important to understand that a complex mix of different physical properties determines the total performance of a fluid. The software used should have all these data and not use traditional assumptions based on properties of conventional fluids. Technical performance of betaine based fluids was found to be higher in empirical tests than in simulations with conventional tools.

The environmental and health qualities of betaine are certainly superior to that of most often used conventional fluids. Even in the applications where a small package of corrosion inhibitors is required, a betaine-based fluid can still be held non-toxic and safe to the environment.

Betaine has a natural anti-corrosive nature. In closed systems with temperatures typical for the HVAC industry in most cases no corrosion inhibitors are required. In areas with stricter requirements, such as the automotive industry, corrosion is easy to handle with mild dosages of common inhibitors.

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RESUME

Une solution à base d'eau et de bétaïne a été testée et développée afin d'être utilisée comme fluide caloporteur. La bétaïne est un dérivé de l'industrie du sucre ; on l'obtient à partir de la betterave sucrière. C'est pourquoi la bétaïne ne présente aucune toxicité et n'est pas néfaste pour l'environnement. La bétaïne offre une protection idéale contre le froid lorsque sa concentration en poids est comprise entre 20 et 55 %. Il s'avère que cette solution présente également d'autres qualités : elle présente de bonnes propriétés caloporteuses, elle n'est pas néfaste pour les matériaux avec lesquels elle est mise en contact et est moins corrosive que l'eau pure.

Les travaux de développement avaient pour but de mesurer ses propriétés de protection contre le froid et contre l'éclatement des conduites et ce, à différents taux de concentration de bétaïne, de mesurer ses propriétés physiques et de mettre au point un additif qui permette une protection encore plus efficace contre la corrosion. Des tests en laboratoire et en situation réelle ont démontré que le mélange d'eau et de bétaïne pouvait servir de fluide caloporteur dans l'industrie de la climatisation. Il en a résulté un nouveau produit pour l'industrie protégé par un brevet d'invention et qui s'applique à des températures allant de –45°C à +110°C (de -49 F à +230 F)