

Thermophysical Properties and Corrosion Behavior of Secondary Coolants

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Introduction

Since 1930, the suitability of non-toxic, chemically inert chlorofluorocarbons - (H)CFC - to function as primary refrigerants is well known. Consequently, traditional refrigerants like sulfur dioxide or ammonia have been almost completely replaced over the following years. Increasing environmental concerns basing on the discovery of CFCs ozone depleting effect in 1974 [1] have led to a global phase-out program of chlorine-containing refrigerants. Although alternatively used hydrofluorocarbons (HFC) have no ozone depletion potential, those substances have become discredited due to their global warming potential.

Direct expansion systems commonly used in supermarket and food processing refrigeration are often charged with considerable amounts of CFCs / HFCs. The *direct* greenhouse effect of such plants is mainly determined by the nature of the refrigerant and the leakage rate, respectively. Compared to DX systems, the content of refrigerant can be reduced enormously in secondary cooling systems, thus making the step back to natural refrigerants like ammonia or propane (ODP, GWP = 0) possible. However, the investment cost for pumps and heat exchangers of the secondary loop must be taken into account as well as the additional cost of electrical energy required for fluid circulation. Generally, the latter factors may significantly affect the economical efficiency of the plant, if the system is not properly designed. An important point in this context is the choice of the appropriate secondary coolant.

This paper contains a survey on water-based secondary fluids as presently used in european supermarket / food processing refrigeration and for special applications like climatic chambers or wind tunnel systems. Thermophysical properties and material compatibility of recently developed media based on potassium acetate and potassium formate are compared to traditional inorganic salt brines and glycol / water mixtures, respectively. Synthetic fluids based on silicone oils or hydrocarbons were not taken into consideration.

Secondary Coolants – Composition and General Demands

Because of outstanding thermal transport properties and numerous other favorable features, water is in general predestined for heat transfer in secondary loops.

However, when it comes to applications below 0 °C, addition of a freezing-point depressing substance is inevitable. A variety of requirements has to be met by such a compound to ensure trouble-free operation of the resulting aqueous solution in a secondary system:

- Good thermal transport properties
- Freezing point max. -60 °C at low C_{comp}
- Compatibility with metals, alloys and sealants
- Long-term stability under operating conditions
- Non-toxicity
- Biodegradability
- Non-inflammability
- Reasonable price

Water-based secondary coolants used today usually belong to one of the following groups:

Inorganic Salt Solutions

Traditional brines consisting of e.g. potassium carbonate or calcium chloride have favorable thermophysical properties. Those salts are furthermore non-toxic, inexpensive, and provide efficient freezing-point depression (29.9 % w/w $CaCl_2$ lowers the freezing point to -55 °C). However, uncontrollable corrosivity at temperatures below 0 °C restricts its application to industrial cooling systems with a relatively simple technical design (no mixing installation, no defrosting cycles possible).

Alcohol / Glycol - Water Mixtures

Monohydric alcohols like methanol or ethanol are effective freezing-point depressants and much better compatible with the construction materials frequently used in secondary cooling systems. The toxicity of methanol, however, excludes this compound from application in food industry. Ethanol's main disadvantage is a low boiling point of 78 °C, that depresses the boiling point of its solutions in water. Compared to monoalcohols, ethylene glycol 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 thermal transport properties, i.e. a very high viscosity, non-toxic food grade propylene glycol is used exclusively for food cooling instead of „injurious-to-health“ classified ethylene glycol.

Organic Salts

Since the early days of refrigeration, the range of available fluids was still limited to inorganic salt brines on one hand, and propylene glycol / water mixtures on the other hand when it comes to choose a secondary fluid for food cooling applications. Modern, high-quality cooling systems, however, demand a medium that provides good thermal transport even at -20 °C and lower in combination with acceptable material compatibility. To provide a way out of this dilemma, the introduction of organic salt based secondary coolants to the European food industry was started in 1994. First use of a corrosion inhibited aqueous solution of *potassium acetate* (brand name: TYFOXIT® 1.20) for low cooling purposes (-35 °C) in a German supermarket [3] generated rapidly increasing interest in this new type of fluid. Consequently, TYFOXIT® found wide-spread application all over Europe during the following years.

However, on-going research activities with focus on further lowering of viscosity at operation temperatures down to -60 °C have been undertaken. The development of TYFOXIT® F, now based on chemically related, likewise non-toxic and readily biodegradable *potassium formate*, was finished in the end of 1995. The product is available as ready-to-use formulations F15, F20, F30, F40, F50, and F60, where the numbers indicate the cooling limits. Hence, provided specific requirements regarding system design and material selection (see below) are taken into consideration, these fluids can serve as highly efficient secondary media for food cooling as well as for modern wind tunnel systems to generate ambient temperatures from -55 to +70 °C.

Table 1 displays some main features of calcium chloride, ethylene glycol (EG), propylene glycol (PG), potassium acetate (K-Ac.), and potassium formate (K-F). Note the different substance concentrations that are necessary to achieve similar freezing points of -40 °C!

	Inorg. Salt	Glycols		Organic Salts	
	CaCl ₂	EG	PG	K-Ac.	K-F
Antifreeze	28.3 %	50 %	54 %	39 %	41 %
Heat transfer	excellent	regul.	poor	good	excell.
Viscosity	very low	high	very high	low	very low
Corrosivity	very high	low	low	moderate	moderate
Toxicity	food-safe	toxic	food-safe	food-safe	food-safe
Costs	very low	low	high	low	low

Tab. 1: Properties of water-based secondary coolants

Thermophysical Properties

Favorable thermophysical properties allow to keep the capital and operating costs of secondary refrigeration on a low level. The following comparison of food-safe se-

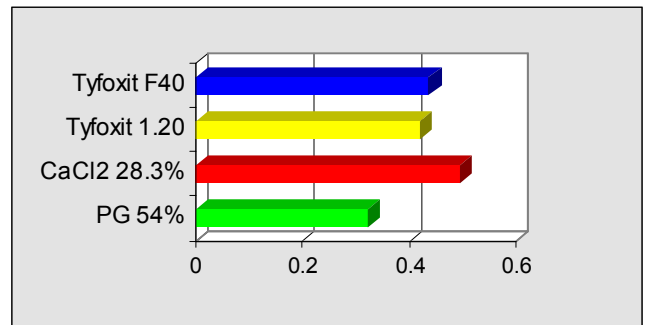
condary coolants set to a freezing point of -40 °C, i.e. aqueous solutions of potassium formate ≈ 41 % (TYFOXIT® F40), potassium acetate ≈ 39 % (TYFOXIT® 1.20), calcium chloride 28.3 %, and propylene glycol 54 % reveals tremendous differences in energetic efficiency.

The energetic performance of a secondary fluid is mainly governed by its volumetric heat capacity $C_p \cdot \rho$, the thermal conductivity λ , and the kinematic viscosity ν .

High volumetric heat capacity is desired because it lowers the volume flow for a given refrigeration capacity. The lower the volume flow, the smaller the sizes of pumps and the diameters of pipework can be.

Assuming an operation temperature of -30 °C, K-formate has the highest value of 3593 kJ/m³•K, closely followed by propylene glycol (3590 kJ/m³•K, 0.1 % less), K-acetate (3515 kJ/m³•K, 2 % less), and calcium chloride (3448 kJ/m³•K, 4 % less). However, the differences are small, and propylene glycol is absolutely competitive.

Things change when thermal conductivity is compared. A high thermal conductivity increases the fluid's heat transfer performance by decreasing the temperature difference between the liquid and the tube wall. As shown by figure 1, now calcium chloride possesses the highest value (0.493 W/m•K), followed by TYFOXIT® F40 (0.436 W/m•K, -12 %), TYFOXIT® 1.20 (0.418 W/m•K, 15 % less), and finally propylene glycol (0.323 W/m•K, 35 % less).

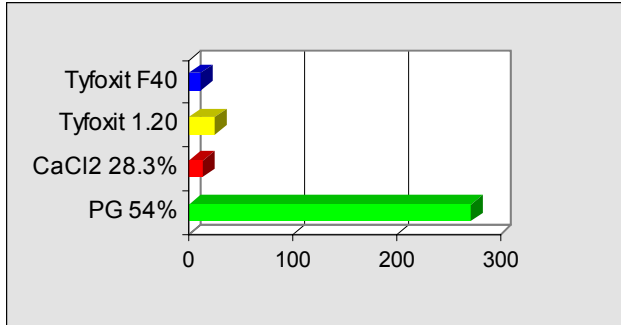


F1: Thermal conductivity [W/m•K] of secondary coolants, operation temperature -30 °C / freezing point -40 °C

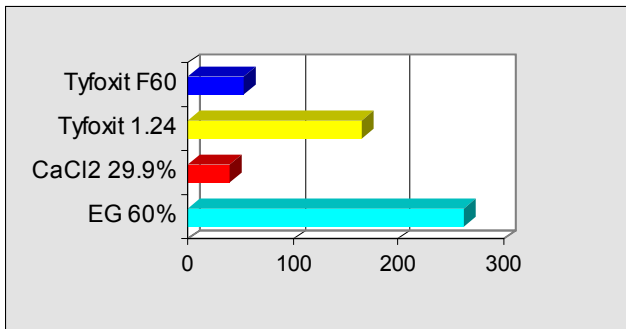
Low viscosity has a very positive effect on the pressure drop at flow in the piping system as well as on the amount of pumping power that is necessary to maintain turbulent flow in the heat exchanger. The favorable viscosity of potassium formate is demonstrated by figure 2. The value of 10.3 mm²/s is even slightly lower than that of calcium chloride (11.9 mm²/s). K-acetate's viscosity (23.9 mm²/s) is about 130 percent higher. A roughly 25 times higher viscosity (272 mm²/s) is a serious disadvantage of propylene glycol and restricts its economical use in refrigeration to normal cooling (down to -10 °C).

K-formate's thermophysical properties allow its use at temperatures down to -60 °C, as in some cases required for special applications like climatic chambers or wind tunnels. Due to propylene glycol's unacceptable viscosity, ethylene glycol (EG) was chosen to be compared with the above discussed media, now set to a

freezing point of $-55\text{ }^{\circ}\text{C}$. Figure 3 shows the viscosities of potassium formate $\approx 50\%$ / TYFOXIT[®] F60 ($54\text{ mm}^2/\text{s}$), potassium acetate $\approx 45\%$ / TYFOXIT[®] 1.24 ($166\text{ mm}^2/\text{s}$), calcium chloride 29.9% ($40\text{ mm}^2/\text{s}$), and ethylene glycol 60% ($262\text{ mm}^2/\text{s}$). Again it becomes evident that only the potassium formate based TYFOXIT[®] F60 is competitive to calcium chloride.



F2: Kinematic viscosity [mm²] of secondary coolants, operation temperature $-30\text{ }^{\circ}\text{C}$ / freezing point $-40\text{ }^{\circ}\text{C}$



F3: Kinematic viscosity [mm²] of secondary coolants, operation temperature $-50\text{ }^{\circ}\text{C}$ / freezing point $-55\text{ }^{\circ}\text{C}$

Above discussed factors can be used to evaluate the energetic efficiency of secondary fluids by calculating the pumping power per length P_p/L , and the heat transfer value Φ , respectively.

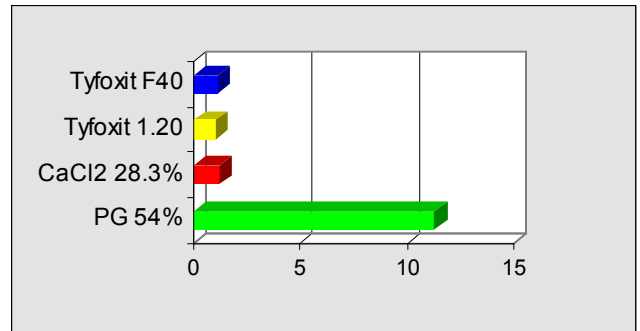
The pumping power per length expresses the amount of energy that is required for the secondary loop to overcome the pressure loss caused by fluid friction. For turbulent flow it is given by

$$P_p/L = V \cdot \lambda / d \cdot \rho \cdot w^2 / 2$$

V = Volume flow [m ³ /s] λ = pipe friction number = $0.3164 \cdot 1 / 4 \sqrt{\text{Re}}$ d = tube diameter [m] ρ = fluid density [kg/m ³] w = fluid flow velocity [m/s]
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The pumping power required at $-30\text{ }^{\circ}\text{C}$ (refrigeration capacity 10 kW , tube diameter DN 35×1.5) is about 1 W/m for TYFOXIT[®] F40, calcium chloride, and TYFOXIT[®] 1.20. The difference to propylene glycol (11.3 W/m) is enormous, as shown by figure 4. Increased values result when those media are compared at $-50\text{ }^{\circ}\text{C}$:

TYFOXIT[®] F60: 2.6 W/m , TYFOXIT[®] 1.24: 2.4 W/m , 29.9% calcium chloride: 2.3 W/m , and 60% ethylene glycol: 10.2 W/m . The advantages of the organic and inorganic salt based fluids are again easy to recognize.



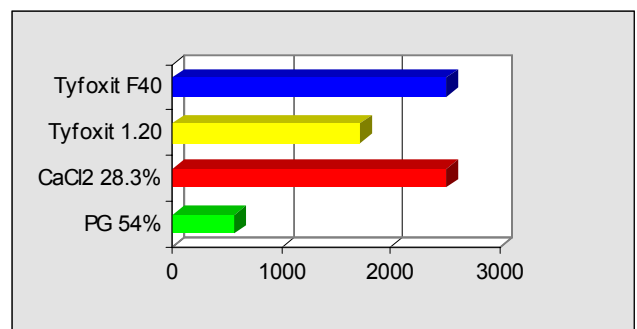
F4: Pumping power / length [W/m] of secondary coolants, operation temperature $-30\text{ }^{\circ}\text{C}$ / freezing point $-40\text{ }^{\circ}\text{C}$

The fluid's heat transfer capacity directly affects the evaporation temperature and consequently the energy consumption of the primary loop. The heat transfer value Φ can be calculated by the following equation:

$$\Phi = \lambda^{0.6} \cdot C_p^{0.4} \cdot \rho^{0.8} / 10\eta^{0.4}$$

with $\alpha \approx 0.22 \cdot w^{0.22} \cdot d^{-0.2} \cdot \Phi$ λ = thermal conductivity [W/m•K] C_p = specific heat capacity [kJ/kg•K] ρ = fluid density [kg/m ³] η = dynamic viscosity [mPa•s]
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Figure 5 displays the heat transfer values for the various fluids at $-30\text{ }^{\circ}\text{C}$. TYFOXIT[®]F40 ($2514\text{ W}\cdot\text{s}^{0.8}\cdot\text{m}^{0.6}/\text{m}^2\cdot\text{K}$) reaches the heat transfer capability of calcium chloride, whereas potassium acetate (32% less) and in particular propylene glycol (87% less) have unfavorably lower Φ .



F5: Φ [W•s^{0.8}•m^{0.6} / m²•K] of secondary coolants, operation temperature $-30\text{ }^{\circ}\text{C}$, freezing point $-40\text{ }^{\circ}\text{C}$

A comparison at $-50\text{ }^{\circ}\text{C}$ gives best value for calcium chloride ($1371\text{ W}\cdot\text{s}^{0.8}\cdot\text{m}^{0.6}/\text{m}^2\cdot\text{K}$), followed by TYFOXIT[®] F60, 6% less), TYFOXIT[®] 1.24, 44% less) and ethylene glycol, 60% less).

As a summary it can be said that only potassium formate based products can compete with calcium chloride in view of heat transfer efficiency.

Corrosivity and Corrosion Control

Besides good antifreeze and heat transfer properties, material compatibility is another essential demand that water-based secondary refrigerants must meet. Unfortunately, one main disadvantage of water is its corrosivity to metals. Factors that strongly govern the grade of corrosivity are: the content of oxygen, pH value, temperature, and furthermore the nature and concentration of dissolved ions. The latter point is of great importance regarding the practical suitability of „pure“ aqueous solutions of freezing point depressants: the corrosivity of such mixtures is in general enormously enhanced, as discussed in the following. At least in case of glycols and organic salts, this effect can be compensated by inhibitors that prevent corrosive attack predominantly by forming thin layers on the metal surfaces.

Mainly due to cost reasons, supermarket refrigeration systems commonly consist of different construction materials like copper, brass, solder, steel, grey cast iron, and aluminum. Unfortunately, there is no universal inhibitor available hitherto. Thus several organic and inorganic compounds with metal-specific protective capability have to be combined to form an efficient, low-toxic and environmentally friendly *inhibitor package*. Typical components used today are e.g. triazoles (for yellow metal protection), salts of carboxylic acids, borax (protect steel and cast iron from corrosion), and silicates (specific for aluminum). Formerly used components like nitrites, amines, or phosphates are to be avoided with respect to environmental concerns. Water hardness stabilizers, defoamers, and buffering compounds are other inevitable ingredients of a modern inhibitor system.

Although the substances with anti-corrosive potential are well known in general, some important points are to be taken into account when it comes to development of a powerful inhibitor system. For example, a package found to be excellent to decrease the corrosivity of a propylene glycol / water mixture does not automatically work for potassium formate solutions. Furthermore, unfavorable

inhibitor combination may lead to negative synergisms or formation of hazardous substances.

Anti-corrosive properties of secondary coolants can be compared and evaluated by several standardized tests. A likewise fast and inexpensive method providing valuable information about the performance of inhibitor systems is based on ASTM D 1384 [4]. In the course of this test, metals and alloys present in refrigeration systems are immersed in aerated fluid for two weeks at +88 °C, hence conditions that accelerate corrosion significantly. Inhibitor formulations that have proven to stand the test can be selected to undergo further evaluation in the course of more comprehensive lab and field tests.

The cleansed and weighed specimens - copper SFCu, soft solder WL30, brass MS 63, steel HI, cast iron GG 26, and cast aluminum (GAlSi6Cu4) - are arranged on an insulated screw held by two brass legs in the above mentioned order. Insulating spacers are used between the first brass leg and copper, followed by brass spacers between copper, solder and brass. Another insulating spacer separates the „yellow metal bundle“ from the following three specimens that are electrically connected by steel spacers. Finally, an insulating spacer is mounted between aluminum and the second brass leg. The unit is set into the solution for 336 h at 88 °C under permanent aeration (rate: 100 ml/min). At the end of the test, the specimens are at first subject to visual evaluation. A tarnished surface can be tolerated, whereas blooming, pitting corrosion, or formation of metal coverings (e.g. corroded copper that deposits on the less noble iron metal specimens) are not admissible. Subsequently, the coupons are cleansed and weighed. The corrosion rate, expressed in mm/year, can be calculated from the weight loss of the specimens.

Figure 6 displays the specimens as obtained after test run in not inhibited 41 % K-formate compared to those immersed in TYFOXIT® F40. It is clear from the appearance in particular of the ferrous metals and aluminum, that only *inhibited* fluids should be used in practice.



F6: Appearance of Metal Specimens after Corrosion Test acc. ASTM D 1384

This fact is underlined by the results of a comparative test that was carried out on „pure“ aqueous solutions of calcium chloride, propylene glycol, potassium acetate and potassium formate (set to a freezing point of -40 °C) and the corresponding inhibited formulations. Table 2 gives the corrosion rates for the several metals and alloys. The limit was set to an annual corrosion rate of less than 0.01 mm, as indicated by a green background. It can be recognized that corrosion rates are significantly lower in case of inhibited propylene glycol (brand name: TYFOCOR® L). TYFOXIT® F40 and TYFOXIT® 1.20 provide full protection for all materials except in case

of soft solder, whereas even inhibited calcium chloride remains too aggressive to all materials.

	CaCl ₂ 28.3 %		PG 54 %		K-Acetate 39 %		K-Formate 41 %	
	Pure	Inhibited	Pure	Tyfo- cor L	Pure	Tyfo- xit 1.2	Pure	Tyfo- xit F40
Copper	0.02	0.015	0.02	0.0007	0.07	0.003	0.07	0.005
Soft Solder	1.39	1.02	0.43	0.0004	0.37	0.20	0.66	0.19
Brass	0.11	0.06	0.02	0.0003	0.08	0.001	0.03	0
Steel	0.32	0.22	0.52	0	0.18	0	0.90	0
Cast Iron	1.04	0.73	0.83	0	0.13	0.002	0.88	0.007
Cast Alu	1.25	0.98	0.38	0.002	0.19	0.002	0.21	0.003

Table 2: Corrosion rates in mm/year. Limiting value: 0.01 mm/a

Application Guidelines for Organic Salt based Secondary Coolants

The life-span of refrigeration 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 fluid and installation must be optimally adapted to each other.

If a carefully composed inhibitor formulation is used, organic salt based secondary fluids are compatible with most of the metals and alloys common in refrigeration. Nevertheless it must be mentioned that a mixing installation poses a higher corrosion risk - due to distinct electrochemical potentials - than a system consisting of one single material. Different metals have to be combined and assembled in a proper way to keep the danger of galvanic corrosion as low as possible. Take into account that great differences in electrochemical potential as occurring in case of direct combination of copper and aluminum cannot be compensated even by the most efficient corrosion inhibitors.

As shown above, soft solder is not resistant when exposed to organic salt based secondary coolants. Copper or silver brazing solders therefore must be used on joints.

Metal corrosion is in general accelerated under acidic conditions, i.e. at pH values below 7. Secondary coolants are therefore adjusted to an alkaline level. Zinc, however, is rapidly corroded under alkaline conditions. Galvanised heat exchangers or piping consequently must not be used, otherwise the zinc will be rapidly detached under sludge formation that might lead to deposits, flow obstruction and corrosion. If fluid is spilled on external galvanised surfaces during maintenance or deaeration, it must be washed away with water instantly.

Organic salt based media generally do not chemically affect the elastomers used for sealants. However, the temperature range of application given by the manufac-

turer must be adhered to. Materials that have proven to be compatible are among others:

Butyl rubber (IIR), Polyethylene s,h (LDPE/HDPE), Ethylene-propylene-diene-rubber (EPDM), Polyethylene, cross-linked (PE-X), Epoxide resins (EP), Polypropylene (PP), Polytetrafluorethylene (PTFE), Nitrile rubber (NBR), Polyvinylchloride (PVC), Polyamide (PA), Styrene-butadiene-rubber (SBR), Acrylonitrilebutadiene styrene (ABS), Chloroprene rubber (CR), Aromatic polyamide (Aramid), Polyphenylene oxide (PPO).

Because of the much better wetting power of organic salt based fluids compared to water, connections must be carried out very accurately to prevent leakages.

Thorough cleansing of the installation is mandatory before the fluid can be filled in. Dirt, packing material, scale, rust or welding slag will otherwise automatically lead to malfunction of pumps and valves. Such abrasive particles may furthermore damage the protective layer that was formed on the metal surfaces by the inhibitors. Scale and encrustations also hinder the formation of homogeneous inhibitor films, thus causing accelerated local corrosion in those areas.

Tap water can be normally used for cleansing without difficulties. There is only one but important purity requirement: the content of very aggressive chloride ions must not exceed a limit of 100 mg/l, otherwise risk of pitting corrosion in particular of stainless steel can be incurred. After cleansing and leak test, the water must be removed from the system as completely as possible. The filling of the system must follow immediately even in case that the plant will be put into operation at a later date to ensure comprehensive corrosion protection.

Excessive dilution of organic salt based secondary coolants by cleansing water is to be avoided for two reasons. One the one hand, these fluids usually contain distilled water to keep aggressive ions like chlorides, sulfates, and water hardness constituents out of the pro-

duct. Additional water on the other hand lowers the concentration of inhibitors and raises the fluids freezing point. It is essential in this context, that products like TYFOXIT® F15-F60 must on no account be mixed with traditional brines or glycol / water to avoid precipitation of solid material and chemical reactions of different inhibitor systems.

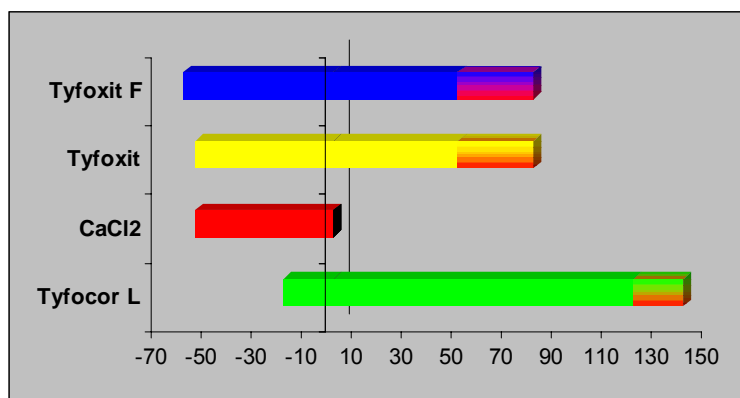
As it is well known, the presence of oxygen in water-based fluids increases its aggressivity enormously by corroding the materials on one hand and affecting the inhibitor concentration on the other hand. Secondary loops should therefore be preferably designed as closed systems. Filling the system at its lowest point and installation of deaerators at the highest point are further good measures to minimize the oxygen content of the fluid.

Last but not least, temperature is a very important factor that significantly influences the corrosivity of secondary fluids. According to van't Hoff's rule it can be said in general that a temperature rise of 10 °C accelerates the velocity of chemical reactions and hence that of corrosion processes by the factor 2-3.

Figure 7 gives the temperature ranges within the above discussed fluids should be operated. Note propylene glycol's (TYFOCOR® L) high upper temperature, allowing its application as a heat transfer fluid for thermal solar heating. With respect to corrosivity, the upper limit for calcium chloride must not exceed 0 °C. If all the above discussed points are carefully taken into consideration, TYFOXIT® and TYFOXIT® F15-F60 can be utilised for commonly designed food processing and supermarket cooling plants in a range from -60 (-55) to short-termed +50 °C. If, as for wind tunnels or climatic chambers, higher temperatures of up to +80 °C are required, the choice of construction materials will be restricted to stainless steel and copper. Supplementary use of a nitrogen blanket has proven to be a worthwhile precautionary measure for such installations to avoid access of oxygen.

The state of the secondary fluid should be regularly monitored. Check of parameters like appearance, density, freezing point, pH value, inhibitor concentration, content of foreign matter, and metal ions allow evaluation of the fluids performance and its anticorrosive properties. Hidden corrosion will be indicated by a change of inhibitor or metal concentrations, and countermeasures can be taken immediately if need be.

Table 3 gives an example of a regular lab check program that was carried out for a wind tunnel system over a period of four years until now. The operation temperature range is -48 to +60 °C, construction materials are copper and stainless steel grades, and the total volume of TYFOXIT® „F55“ (a special formulation) is about 10 cubic meters. Despite an initially occurred dilution which slightly shifted the freezing point to -55.6 °C, the fluid parameters remained almost constant. Start corrosion as indicated by the copper and iron content came to an end when the oxygen contained in the coolant was fully consumed. Until today no further adjustment of the medium, e.g. by topping up the concentration of one of the inhibitors was necessary.



F7: Operation temperatures of water-based secondary fluids [°C]

	Start	11/97	11/98	11/99	11/2000
Appearance	clear, colorless	clear, colorless	clear, colorless	clear, colorless	clear, colorless
Density [g/cm ³]	1.372	1.364	1.364	1.364	1.364
Freezing pt. [°C]	-58.2	-55.6	-55.5	-55.2	-55.3
C _{inhibitors} [%]	100	86	83	82	80
C _{Copper} [mg/l]	0.92	0.90	0.75	0.74	0.76
C _{Iron} [mg/l]	0.61	0.56	0.52	0.53	0.51

Table 3: Monitoring of TYFOXIT® „F55“ / Wind Tunnel, operation temperature -48 to +60 °C

Summary

Recently developed secondary coolants based on food-safe, environmentally friendly organic salts combine advantageous thermophysical properties of inorganic salt brines with good material compatibility of glycol / water mixtures. TYFOXIT® F15-F60 in particular is suitable for application in low food cooling and wind tunnel / climatic chamber secondary loops. Except soft solder and zinc, all construction metals and alloys normally used in refrigeration engineering are compatible, if the recommendations regarding material choice, plant design, and temperature limits are accurately observed.

Organic salt based media reduce investment and operational costs of secondary systems and thus competitive power of indirect cooling compared to DX is increased. Development of K-formate based secondary coolants like TYFOXIT® and TYFOXIT® F15-F60 may be seen as one step forward to further HCFC reduction.

Literature

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