# Corrosion Inhibitors in Antifreeze Coolants

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# What are antifreeze coolants?

- Heat transfer fluids in internal combustion engines and heat exchange systems
- Main function is to keep the thermal balance of the system
- Additional functions:
  - Protect the system from freeze
  - Protect the system from overheating
  - Protect the system from corrosion

# Composition of antifreeze coolants

- Water
- Freezing point depressant
- **Corrosion inhibitors**
- Antifoams, defoamers
- Stabilizers
  - To prevent scale formation, flocculation or polymerization of inhibitors
    - Anti-scaling agents
    - Silicate stabilizer
- pH buffers

# Composition of antifreeze coolants
## Corrosion inhibitors

- Since the strongly corrosive characteristic of water, addition of corrosion inhibitors is needed
- Corrosion inhibitor is a chemical substance added to the coolant to **reduce the corrosion rate** of one or more metals in the cooling system
- Most common molecular mechanisms:
  - **Passivation** of the metal or reinforcement of the passive metal oxide layer
  - Formation of a **thin barrier** of the inhibitor on part or all of the full metal or metal oxide surface by varying the extent of physi- and/or chemi-sorption.
  - The formation of **thick barriers** of inhibitor or inhibitor metal reaction product

## Composition of antifreeze coolants
## Classification of corrosion inhibitors

- **Passivators**
  - **Cause a large anodic shift of the corrosion potential, forcing the surface into the passivation range**
  - **Stabilize passive oxide layer**
  - **Repair damaged oxide layer**
  - **Reinforce the passive layer by incorporation**
  - **Hinder the absorption of aggressive ions**

# Composition of antifreeze coolants
## Passivators

- **Direct passivators or oxidizers**
  - **Anions that react with metal surface**
  - **Generate or reinforce passive layer**
  - **Do not require the presence of oxygen**
    - **Chromate, nitrite, nitrate**
  - **Require the presence of oxygen or stronger oxidizer**
    - **Molybdate**
  - **Toxic**
  - **Powerful oxidizers**
  - **Unwanted side reactions and rapid depletion**

# Composition of antifreeze coolants
## Passivators

- **Indirect passivators**
  - **Improve the absorption of dissolved oxygen**
  - **Effective only if dissolved oxygen or a direct passivator is present**
  - **Alkaline substances**
  - **React with absorbed hydrogen**
  - **Locations become available for the absorption of oxygen**
    - **Phosphate (hard water stabilized), hydrogen phosphate, borate**
    - **Benzoate and benzoate derivatives**

- Composition of antifreeze coolants
  Classification of corrosion inhibitors
- **Thin Barrier Inhibitors**
  - **Form a layer on metal or metal oxide surface**
    - **Total surface**
    - **Anodic regions**
    - **Cathodic regions**
  - **One or two layers of inhibitor molecule**
  - **Mechanisms of adsorption can vary from physisorption to salt like chemical bond**

- Composition of antifreeze coolants
  Thin barrier inhibitors
- **General barrier inhibitors**
  - **Adsorption to the total surface**
  - **Surface is cleaned of water**
  - **Solvatation of metal ions is impossible**
  - **Absorption of protons or oxygen can be prevented**
    - **Triazole compounds**
    - **Silicate**

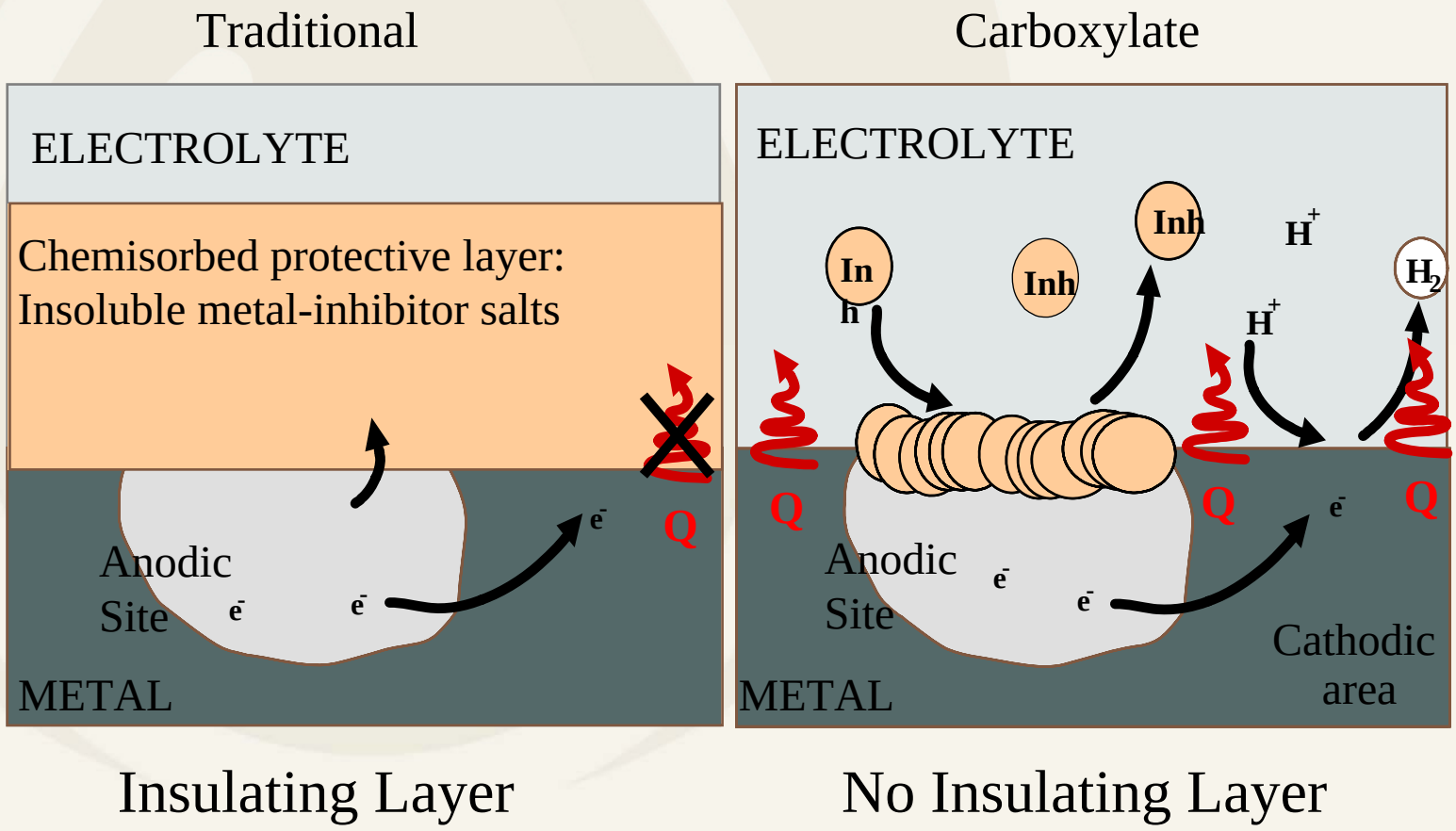
## Composition of antifreeze coolants
Thin barrier inhibitors

- **Anodic barrier inhibitors**
  - **Selectively absorbed at the anodic spots**
  - **Basis of Organic Additive Technology (OAT)**
  - **Salts of organic acids**
  - **Forming strong metal-carboxylate bond**
  - **This shielding of the anodic spots makes the release of metal ions impossible.**

# Organic Additive Technology
## Organic inhibitors

- Slow depletion
- **„Extended Life Coolants”**
- Combination of di- and mono-carboxylic acids
  - Efficiency depends on the hydrophobic tale
  - Aliphatic monobasic acid
    - 2-ethylhexanoic acid
  - Aliphatic dibasic acids
    - Sebacic acid
    - Dodecandioic acid
  - Alkyl benzoic acids
    - PTBBA
    - Benzoic acid
- Hydrocarbon triazoles
  - Tolyltriazole
  - Benzotriazole

# Organic Additive Technology
## Prevention mechanism of OAT inhibitors



# Organic Additive Technology
## Corrosion protection

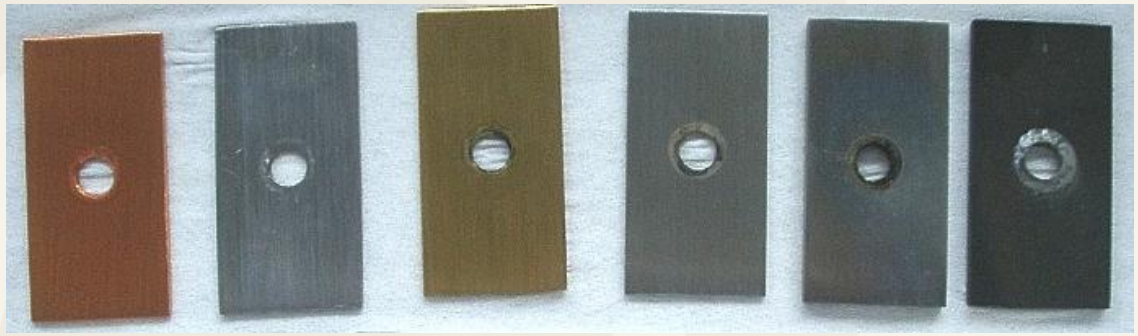
| Test conditions | |
|---|---|
| Duration: | 504 h |
| Pressure: | 2,5 bar |
| Flow: | 3,5 l/min |
| Temperature: | 115°C |
| Concentration: | 20 vol.% |

| Weight loss (g/m2) | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Al | AlMn | Cast iron | Steel | Cu | CuZn | Solder |
| **Reference Coolant** | | | | | | | |
| after initial cleaning | 82.10 | 64.02 | -2.19 | -1.68 | 3.62 | 2.90 | 21.45 |
| after final cleaning | 125.01 | 94.33 | -0.36 | 0.11 | 4.99 | 5.66 | 25.83 |
| **OAT coolant** | | | | | | | |
| after initial cleaning | 9.77 | 0.71 | -0.07 | 0.17 | 1.44 | 1.62 | 0.43 |
| after final cleaning | 23.58 | 4.14 | 0.0 | 0.24 | 2.63 | 2.53 | 0.55 |

Reference coolant is a conventional silicate based coolant.

# Organic Additive Technology
## Corrosion protection II.

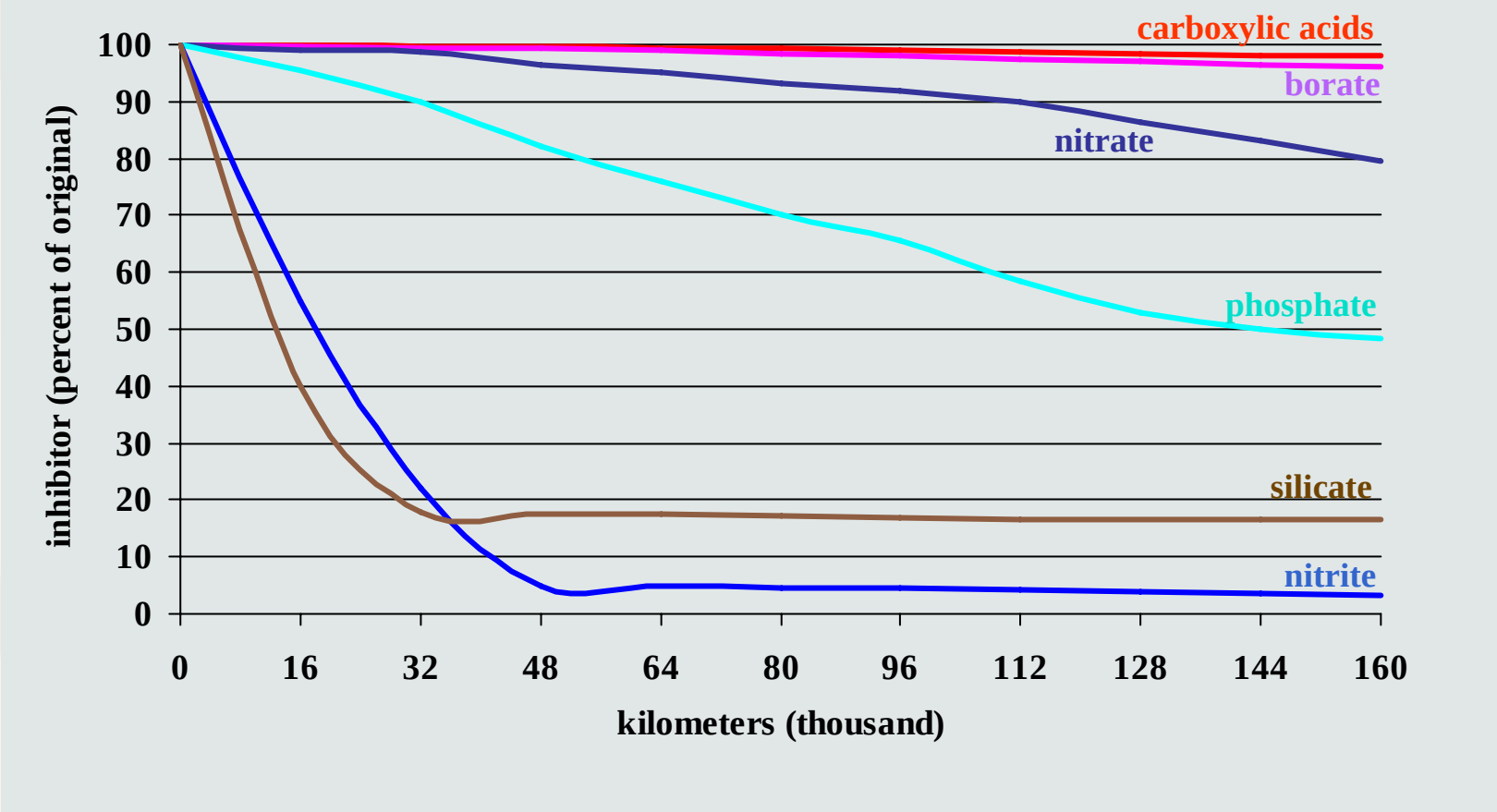
**OAT Coolant**



**Reference Coolant**

# Organic Additive Technology

## Organic inhibitors deplete much slower than inorganic ones



# Benefits of Organic Additive Technology

- Comparison of coolant water manifolds.
- The cooling water manifold on the left clearly shows corrosion, whereas the manifold on the right is still free of corrosion after a similar run time.

**Traditional**

**Carboxylate**

- Composition of antifreeze coolants
  Classification of corrosion inhibitors
- **Precipitation Inhibitors**
  - **General effect over the metal surface**
  - **Form thick, insoluble protective layer**
  - **Blocking both anodic and cathodic spots**
    - **Carbonate**
    - **Unstabilized phosphate, biphosphate**

# Composition of antifreeze coolants
## Classification of corrosion inhibitors

- **Oxygen scavengers**
  - **Removal of available oxygen**
  - **Reduce the rate of corrosion driven by oxygen**
    - $O_2 + 2H_20 + 4e^- \rightarrow 4OH^-$
  - **Sufite, bisulfite, hydrazin**
    - $2\ Na_2SO_3 + O_{2(\text{dissolved ox.})} = 2Na_2SO_4$
    - $N_2H_4 + O_2 = N_2 + 2H_2O$
  - **Not effective in acidic environments:**
    - $(2H^+ + 2e^- \rightarrow H_2)$

# Trend of coolant formulations

- The development of coolant technologies is continuous
- Progression toward more organic additive technologies (OAT) in the three leading regions (United States, Europe and Japan)
- Modern technologies are using OAT backbones or pure OAT in their complex mix of chemicals.
- Current coolants have evolved according to development of cooling systems and demonstrate increased heat transfer characteristics, material and corrosion protection, and longer life estimates even under the more stringent conditions.

Thank you for your attention!