Handling of circuits with counterfeit R134a

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Background

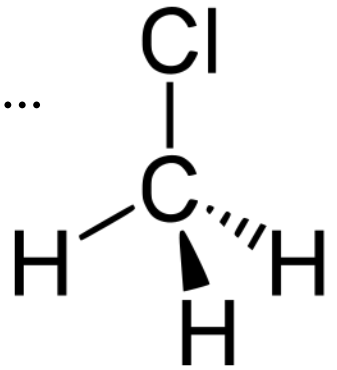
- Why counterfeits?
- Why should we worry? **R40**, side reactions, …

Content

- History of R40 as refrigerant
- Toxicity, flammability and known reaction products
- Observed phenomenon in AC circuits
- Procedures for safe refrigerant recovery
- Proposal about procedure to deactivate reaction products
- Observed effects in AC circuits
  - Metal parts
  - Seals, hoses, thermoplastic parts
- Summary & conclusions

History of R40 as refrigerant & more

- Used in AC and refrigeration system up to the late 1930s
- Several severe and fatal injuries have been documented
- Typical composition of the current refrigerant counterfeit: 60% R22, 40% R40, traces of R142b, R30, …



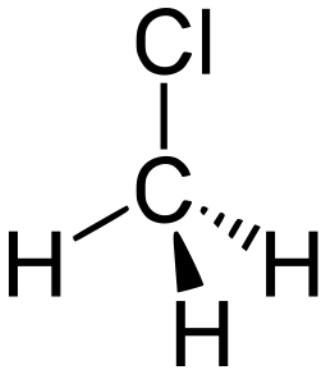
Methyl chloride poisoning

An investigation by the American Medical Association found 29 cases of methyl chloride poisoning and ten deaths in Chicago, alone, during 1929. All except three cases (which occurred in a methyl chloride refrigerator factory) were as a result of leaks in the refrigerating system.

Source: ACR News July 2011

History of R40 as refrigerant & more

- First appearance as component of a refrigerant counterfeit observed in 2009 (southern Europe, public transport company)
- Affected industries: reefer industry, automotive, refrigeration
- Difficulties in analyzing and handling of contaminated systems
- Source of the counterfeit still not safely known

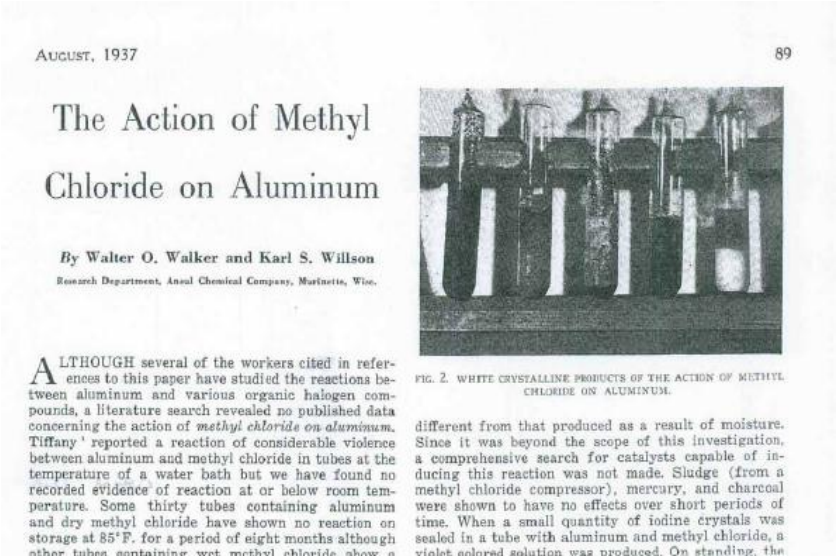


R40 – toxicity, flammability

- **Toxicological aspects:**
  - LTEL: 50 ppm (below smelling “border”!!!)
  - LD50/1h: 8300 ppm
- **Raw estimated calculation:**
  - *Assumptions:* *11 m³ passenger compartment, 2.4 kg counterfeit R134a (= 1 kg R40)*
  - *Exceedances:* ***LD50/1h: factor 5 (!!!)***
    LTEL: factor 830 (!!!)
- **Further aspects from MSDS about R40**
  - Carcinogenic, damaging to central nervous system
  - Self-contained breathing apparatus suggested
  - Tends to form explosive mixtures

R40 - analytics and known reaction products

- **Halide flame test:**
  - Sensitivity: ca: 350 ppm
  - Indicates all chlorinated substance
- **Refrigerant identifiers:**
  - no safe detection possible due to measuring principle



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The Action of Methyl Chloride on Aluminum

By Walter O. Walker and Karl S. Willson

Research Department, Ansul Chemical Company, Marinette, Wisc.

ALTHOUGH several of the workers cited in references to this paper have studied the reactions between aluminum and various organic halogen compounds, a literature search revealed no published data concerning the action of *methyl chloride on aluminum*. Tiffany [1] reported a reaction of considerable violence between aluminum and methyl chloride in tubes at the temperature of a water bath but we have found no recorded evidence of reaction at or below room temperature. Some thirty tubes containing aluminum and dry methyl chloride have shown no reaction on storage at 85°F. for a period of eight months although

FIG. 2. WHITE CRYSTALLINE PRODUCTS OF THE ACTION OF METHYL CHLORIDE ON ALUMINUM.

different from that produced as a result of moisture. Since it was beyond the scope of this investigation, a comprehensive search for catalysts capable of inducing this reaction was not made. Sludge (from a methyl chloride compressor), mercury, and charcoal were shown to have no effects over short periods of time. When a small quantity of iodine crystals was sealed in a tube with aluminum and methyl chloride, a

R40 - analytics and known reaction products

- **Tube detectors:**
  - potential cross reactions unknown)
- **GC / MS (gas chromatography / mass spectrometry):**
  - big effort, experience required
  - not available in the field

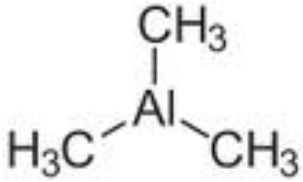
Nach SPENCER und WALLACE und den bestätigenden Versuchen in den Laboratorien der Ansul Chemical Co.[3] kann Aluminium mit CH_3Cl direkt reagieren nach der Formel

$$2\,Al + 3\,CH_3Cl \rightarrow AlCH_3Cl_2 + Al(CH_3)_2Cl. \quad (168)$$

Dabei bilden sich zunächst Aluminiummethyldichlorid und Dimethylaluminiumchlorid, die beide brennbar sind. Diese reagieren weiter unter Bildung von Aluminiumchlorid und Trimethylaluminium

$$AlCH_3Cl_2 + Al(CH_3)_2Cl \rightarrow AlCl_3 + Al(CH_3)_3. \quad (169)$$

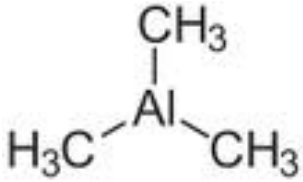
[1] BOPP, J. D.: Ansul News Notes, Juni 1951, S. 13.
[2] SPENCER u. WALLACE: J. chem. Soc. Bd. 93 (1908) S. 1827.
[3] Ansul Chemical Co.: Ansul News Notes Bd. 1 Nr. 2, S. 2.



Observed phenomenon in AC circuits

- **Conditions under which TMA (trimethyl aluminum) can be formed in circuits are not all known**
- **Several severe accidents known (explosions of circuits while being serviced, in operating and non operating states)**

  ⟶ TMA suspected to play a role



- **Known effects:**
  - Heavy corrosion especially of aluminum alloys
  - Decomposition of elastomer and thermoplastic parts

Observed phenomenon in AC circuits

- **Working hypothesis:**
  - Intensity of formation of TMA depends on oil type (POE, PAG, PVE) – POE type oils are suspected of stimulation extensive TMA formation
  - Potentially, further components of the counterfeit refrigerant could be involved (eg. silanes)
  - TMA is highly flammable and tends to decompose when of traces of air and moisture are present

Procedures for safe refrigerant recovery

- **Condensing and keeping cool:**
  - Establishing an oxygen free suction line on the service valves of the circuit (evacuating and purging with dry nitrogen) – 3-way system
  - Adapting an evacuated recovery vessel
  - Cooling the recovery vessel with dry ice and removing the refrigerant from the circuit through condensation
  - Purging the circuit with dry (!) nitrogen

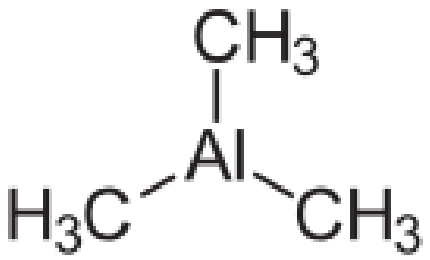
Procedures for safe refrigerant recovery

- **Remarks:**
  - Composition of the refrigerant in suspected circuit is not known precisely
  - Compressors in standard servicing equipment work with POE oils and are not protected against explosions

ATTENTION: Risk of decomposition of TMA is not eliminated at this point. Possible existing amounts of TMA still need to be deactivated! Avoid air and moisture!

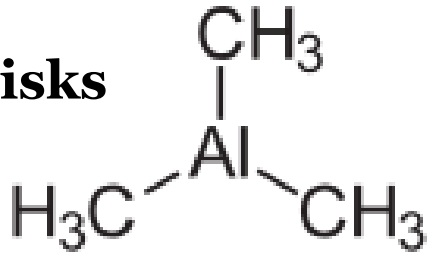
How to deactivate TMA?

- **Foregoing consideration:**
  - TMA can be deactivated with steric alcohols, but this procedure has bee tested in lab scale only
  - Reactivity of TMA strongly depends on temperature, moisture and air – depending on environmental temperature specific deactivator might be required



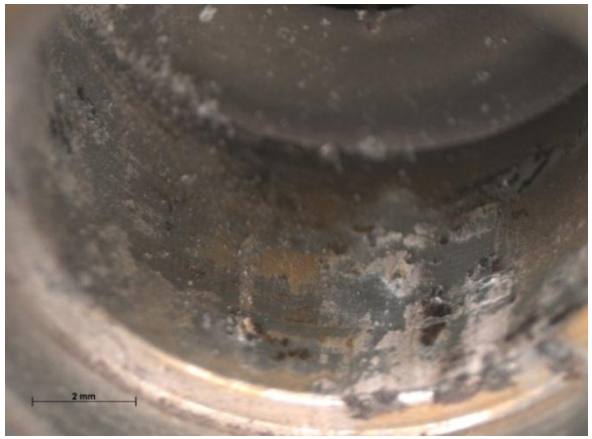
How to deactivate TMA?

- **Proposal (ATTENTION – keep safety distance):**
  - Evacuate the circuit with a diaphragm pump and keep low pressure
  - Introduce deactivator using nitrogen
  - Monitor the circuit for increased temperature and increasing pressure – continue evacuation
- **Procedure only tested once – severe remaining risks**
  - Is all TMA deactivated?



Observed effects in AC circuits – metal parts

- **Shown effects seen in a circuit with ca. 10% R40 and PAG oil**
  - General corrosion of metal parts
  - High amounts of particles and residues
  - No flushing technology currently available

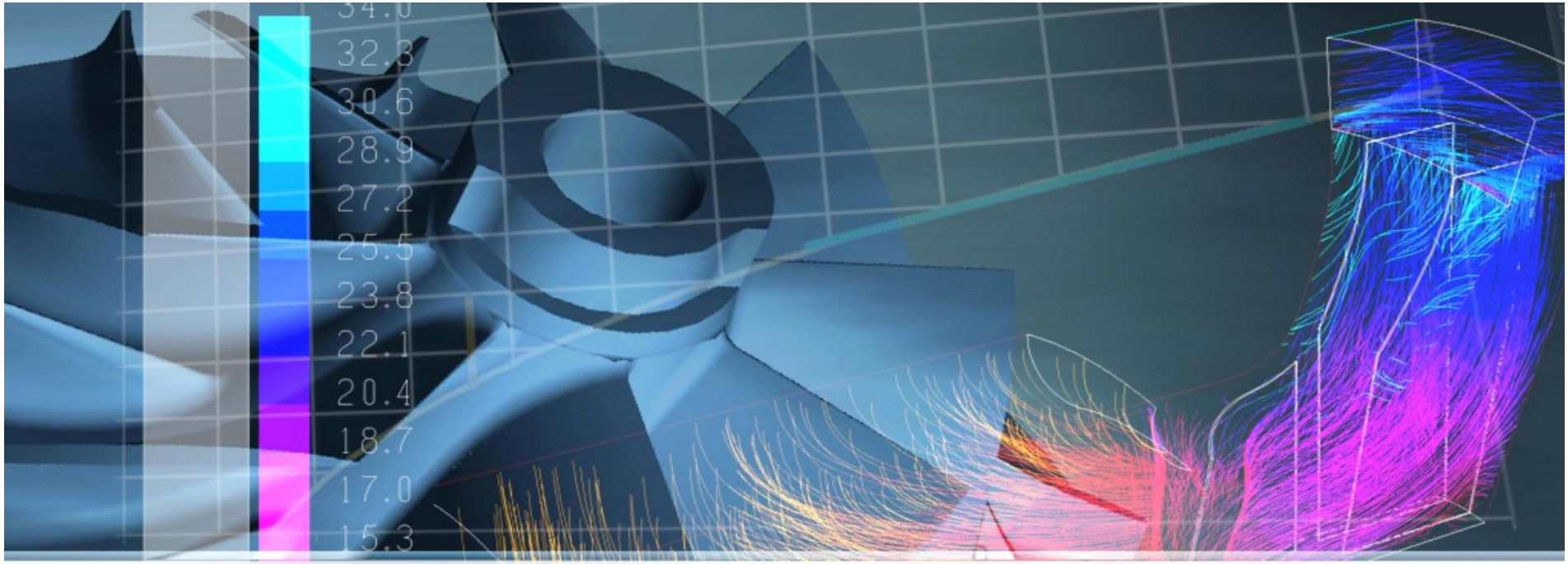


Observed effects in AC circuits – seals & hoses

- **Shown effects seen in a circuit with ca. 10% R40 and PAG oil**
  - Extrusion of O-rings observed – total failure
  - Hoses delamination
  - Effects strongly depend on R40 amount
  - ATTENTION: possible failure of suction line during operation

Summary and conclusions

- Currently not all chemical effects in contaminated circuit understood
  - *TMA can be deactivated by lab scale procedures only*
  - *Possible further components of counterfeit refrigerants unknown*
- Especially AC circuits with POE oils have very high risk of forming TMA (electrically driven compressors / circuits!)
- R40 affected AC circuit components are expected to be replaced completely
- Cooperative research initiative to handle the risk sholud be considered



Thanks for your attention!

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