Glycol Ethers and Thermal Runaway

Gourbet Reaction:

$$RCH_2CH_2OH + \text{Base}(NaOH \text{ or } KOH) \longrightarrow RCH_2CHO + H_2$$

$$RCH_2CHO \downarrow \downarrow CO + CO_2 + ??$$

Actual Incidents:

1. **Tetrahydrofurfuryl Alcohol Still**

Incident Description

On November 2, 1961, an explosion occurred at the South Charleston Plant during the final stages of a distillation of tetrahydrofurfuryl alcohol from sodium hydroxide. Caustic concentration (NaOH) was eight to nineteen percent. In five minutes, the kettle temperature increased 50°C (252°C to 300°C); the pressure increased from 13 mmHg to greater than 35 psig. The steam had been shutoff and the system was under nitrogen.

Apparent Cause

A caustic-ether decomposition reaction in a batch process.

2. **Ethoxytriglycol Still**

Incident Description

On March 18, 1964, an explosion occurred after ethoxytriglycol recovery was completed. Steam to the calandria was shutoff. The vacuum had been broken with hydrogen-methane gas (6 mm Hg to 218 psia) and transfer of kettle residues to storage had begun. The kettle temperature exceeded 200°C within 15 minutes after pressurizing the column. An initial, small "bump" occurred. Safety valves set at 30 psig blew. Within a few seconds a larger explosion occurred. The incident report claims air was drawn into the column between the two explosions. The kettle residue represented 0.7% of the original charge and contained at least 40% base (as NaOH).

Apparent Cause

A caustic-ether decomposition reaction in a batch process.

3. Ethoxytriglycol

Incident Description

Laboratory experiments, designed to explore the hazards of ethoxytriglycol plant distillations employed synthetically prepared mixtures of crude ethoxytriglycol (5.25% CARBITOL, 81.8% ethoxytriglycol and 13.0% ethoxytetraglycol) containing one to three percent sodium hydroxide. These experiments showed the decomposition appears to initiate at kettle temperatures of 195°C to 200°C. The final caustic residue content in these laboratory distillations range from six to 11.5% sodium hydroxide. In another distillation study of crude ethoxytriglycol, a spontaneous increase in kettle temperature was observed at 195°C. Calculations indicate the base level as sodium hydroxide was 3.1% at this time.

4. UCAR Solvent 2LM (Methyl DIPROPASOL) Still

Incident Description

On February 19, 1973, an explosion occurred at the end of a distillation from caustic residues. Six consecutive batches had been refined. Sufficient heavies had accumulated in the kettle and a final "tails cut" before discarding these residues had been completed. One hour prior to the incident, the operator noted that the head pressure (10 mmHg to 130 mmHg) and the kettle temperature (120°C to 195°C) had increased during the preceding hour. The operator turned off the calandria steam. The explosion occurred an hour later. The caustic level was 22% to 26%, calculated as sodium hydroxide, and the soluble iron concentration was 0.31% (3100 ppm) at the time of the explosion. In the laboratory, one sample, obtained from the Still before the incident, was stripped of all volatile material up to 190°C simulating the kettle contents at the time of the explosion and submitted for a thermal stability test. This sample underwent a strong exothermic reaction at 195°C. In one minute, the temperature reached 426°C and the pressure in the closed system increased 400 psig.

HAZARDS IN PROCESSING ALKALINE CRUDE GLYCOL ETHER STREAMS

1. PROCESSING THESE ALKALINE STREAMS AT ELEVATED TEMPERATURE MAY RESULT IN UNCONTROLLED EXOTHERMIC RUNAWAY REACTION WITH CONCURRENT PRODUCTION OF NON-CONDENSABLE GAS.

2. THE RESULTING TEMPERATURE INCREASE AND/OR GAS PRODUCTION CAN RAPIDLY LEAD TO DANGEROUS OVERPRESSURE AND SUBSEQUENT RUPTURE OF PROCESSING EQUIPMENT IF ADEQUATE SAFETY RELIEF IS NOT PROVIDED.

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HAZARDS IN PROCESSING ALKALINE CRUDE GLYCOL ETHER STREAMS

3. THERMAL DECOMPOSITION STARTS WITH THE NET OXIDATION OF THE GLYCOL ETHER TO THE CORRESPONDING ALDEHYDE AND HYDROGEN.

4. COMPLEX SUBSEQUENT REACTIONS THEN OCCUR TO FORM ACIDS, OTHER ALDEHYDES AND CONDENSATION PRODUCTS, WHICH EVENTUALLY LEAD TO AUTOCATALYTIC FREE RADICAL DECOMPOSTION!

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DEFINITIONS

ARC = ACCELERATED RATE CALORIMETRY.

ONSET TEMPERATURE = THE TEMPERATURE AT WHICH A REACTION SOLUTION REACHES A 0.02°C PER MINUTE EXOTHERMIC REACTION RATE.

RO-/ROH = MOLAR RATIO OF GLYCOL ETHER ANION TO FREE GLYCOL ETHER IN ALKALINE GLYCOL ETHER STREAMS.

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IMPORTANT GENERALIZATIONS ABOUT THE EXOTHERMIC DECOMPOSITION OF ALKALINE GLYCOL ETHER STREAMS

1. THE ONSET TEMPERATURE OF THE EXOTHERMIC DECOMPOSITION REACTION DECREASES AS THE ALKALINITY INCREASES.

2. THE ADIABATIC TEMPERATURE RISE FROM EXOTHERMIC DECOMPOSITION AS WELL AS THE RATE OF THE TEMPERATURE RISE INCREASES AS THE ALKALINITY INCREASES.

3. POTASSIUM ALKALINITY IN GLCYOL AND GLYCOL ETHER STREAMS RESULTS IN SIGNIFICANTLY LOWER ONSET TEMPERATURES THAN SODIUM ALKALINITY AT EQUIVALENT LEVELS.

4. SOME EVIDENCE SUGGESTS SOLUBLE IRON OR INSOLUBLE IRON AS RUST AT LEVELS OVER 1000 PPM MAY LOWER THE EXOTHERMIC DECOMPOSITION ONSET TEMPERATURE 10-15°C.

5. THE POSSIBILITY OF CONCENTRATING IRON TO OVER 1000 PPM IS MUCH HIGHER IN BATCH SYSTEMS, PARTICULARLY AFTER EXPOSURE OF THE SYSTEM TO AIR AND/OR WATER DURING SHUTDOWNS AND TURNAROUNDS.

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IMPORTANT GENERALIZATIONS (CONTINUED)

6. THE STABILITY OF THE STREAMS IS SUBSTANTIALLY IMPROVED BY COMPLETE NEUTRALIZATION OF THE ALKALINITY WITH PHOSPHORIC ACID TO pH 7.0 AND COMPLETE REMOVAL OF THE INSOLUBLE PHOSPHATE SALTS.

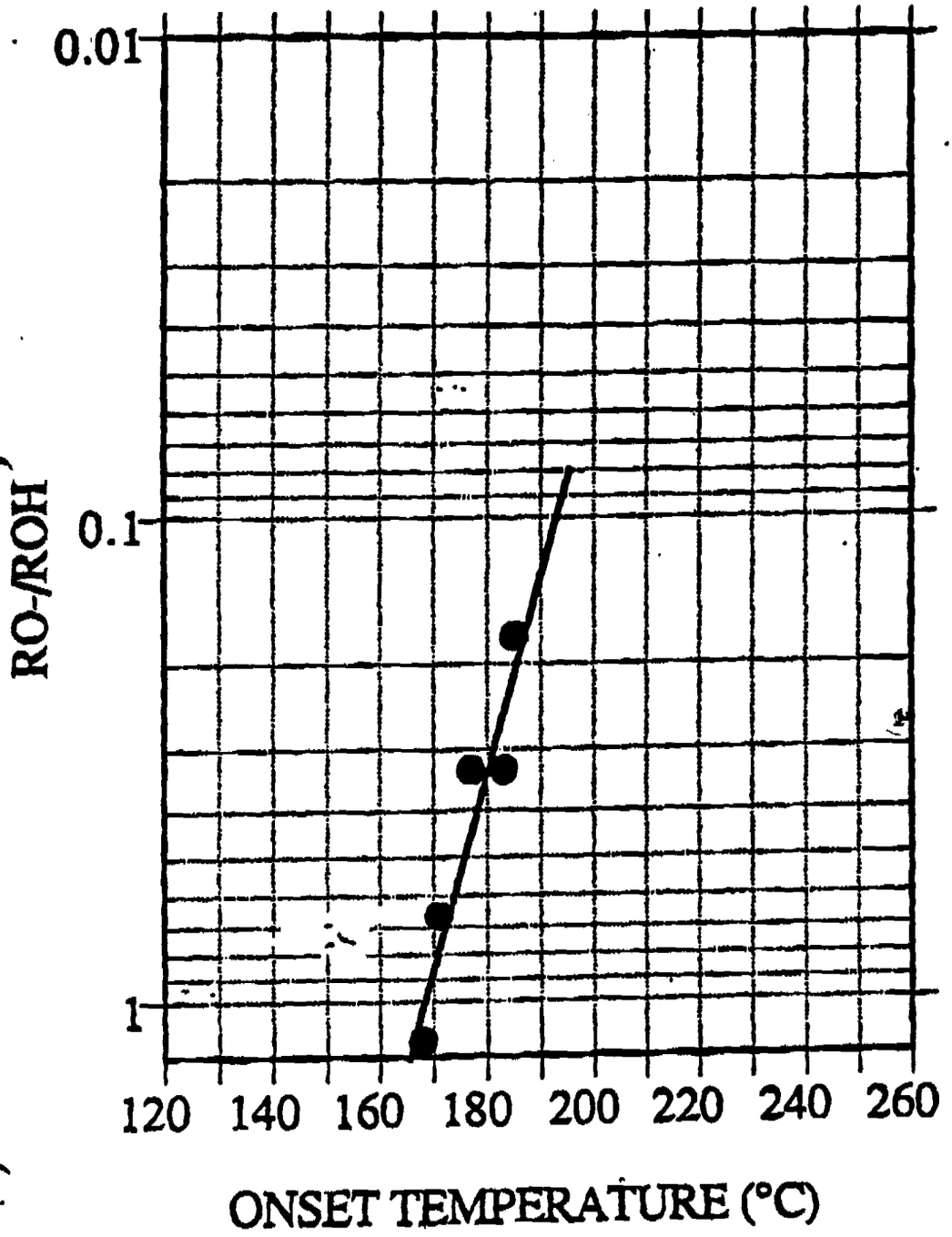
7. THERMAL STABILITY TESTING HAS ALSO SHOWN THAT EXCESS PHOSPHORIC ACID SIGNIFICANTLY, ALTHOUGH TO A LESSER DEGREE, LOWERS THE THERMAL STABILITY OF THESE STREAMS, THUS CAREFUL NEUTRALIZATION IS REQUIRED.

8. STRONG ALKALINITY CAN BE REGENERATED IN SITU FROM NEUTRAL SALTS DURING A PROLONGED BATCH DISTILLATION.

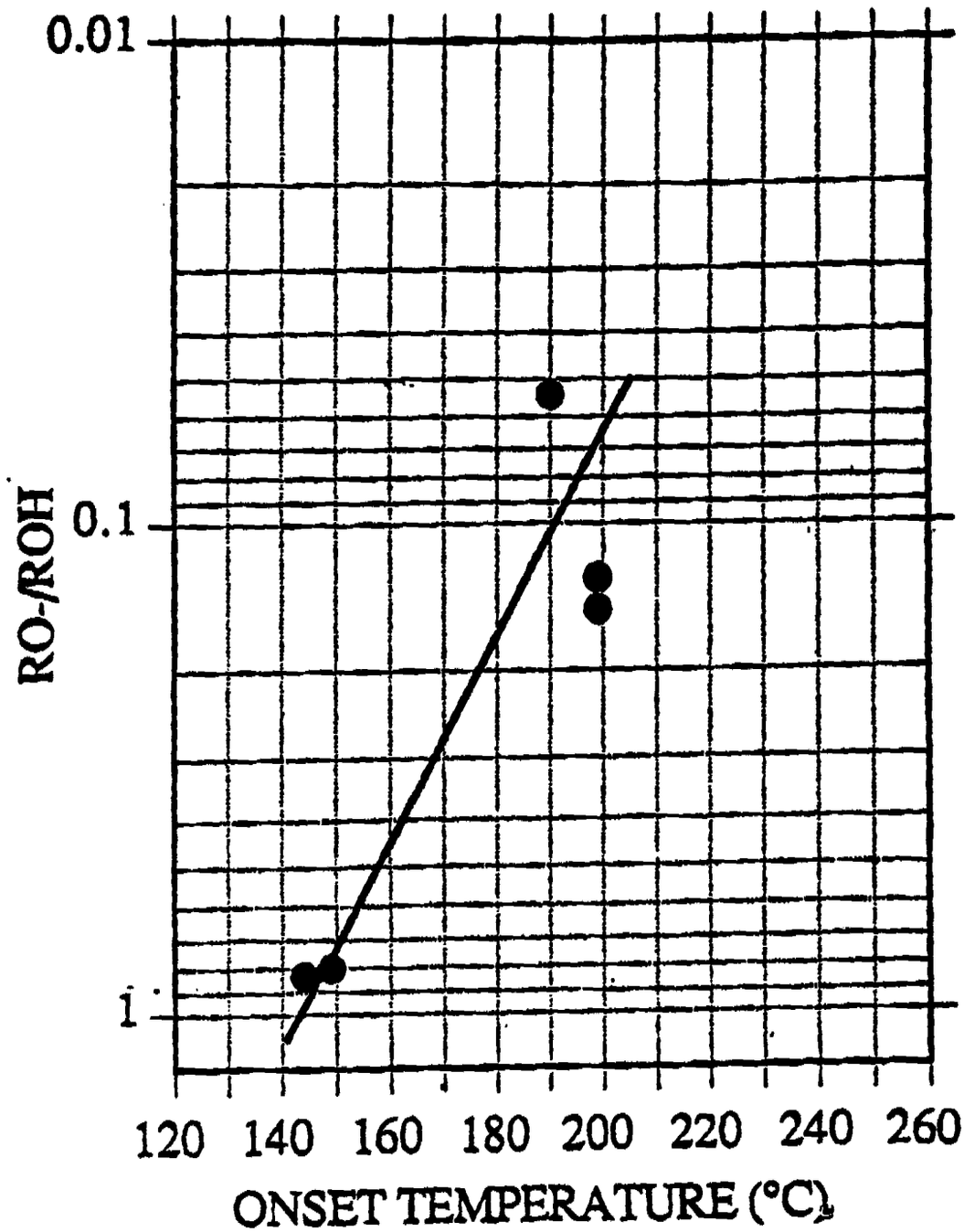
9. AT LEAST TWO EXOTHERMS EXIST IN ALL CASES. THE TEMPERATURE RISE PRODUCED BY THE FIRST EXOTHERM CAN BE SUFFICIENT TO INITIATE THE SECOND MORE SEVERE EXOTHERM.

10. PURE GLYCOL ETHERS WILL EXHIBIT EXOTHERMIC THERMAL DECOMPOSITION WITH ONSET TEMPERATURES AS LOW AS 290°C.

BUTYL DIPROPASOL SOLVENT SODIUM ALKOXIDE



BUTOXYTRIGLYCOL POTASSIUM ALKOXIDE



BUTOXYTRIGLYCOL SODIUM ALKOXIDE