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IMPACT OF THE PROPYLENE GLYCOL-WATER-BORAX COOLANT ON MATERIAL RECOVERY OPERATIONS

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INTRODUCTION

The reaction of the propylene glycol-water-borax coolant with nitric acid has now been studied in some detail. Many of the experimental particulars have been submitted for publication in our Development Division Technical Progress Report No. Y-2307-7. This document is intended to provide a summary of our results. Our findings are summarized under nine headings. Tests have also been conducted to determine if the new coolant would have any adverse effects on the uranium recycle systems. Experiments were scientifically designed after observation of the production operations so that accurate response to the immediate production concerns could be provided.

EXPERIMENTS AND FINDINGS

A. Based on Both the Technical Literature and Our Own Findings, Formation of Glycol Nitrates is Very Improbable. This is a point that must be considered because propylene glycol dinitrate, a possible product of the nitric acid-propylene glycol reaction, is a potent explosive. The reactions of alcohols with nitric acid have been investigated in detail.[1,2] Formation of appreciable quantities of nitrates requires highly anhydrous media, usually involving mixed acids such as HNO_3-H_2SO_4. This is because the nitration reaction has been proven[2] to depend on the formation of nitronium ions, NO_2^+, according to the reaction:

$$HNO_3 + H^+ \rightleftharpoons H_2O \cdot NO_2^+ \rightleftharpoons H_2O + NO_2^+.$$

The nitronium ion concentration can become appreciable only when the medium is very acidic and anhydrous. In the 9212 Uranium Recovery complex, the very severe conditions required for nitration do not exist.[1]

Our own experiments have been in agreement with the literature. Analyses of the condensed-phase products of the reaction of nitric acid (70%) with propylene glycol showed no evidence of nitrated compounds.

B. The Reaction of Concentrated (70%) Nitric Acid with Pure Propylene Glycol is Very Violent and Hazardous. This is especially true when the ratio of nitric acid-to-glycol is high. Thus, mixtures of 7.00 g HNO_3 (70%) and 3.00 g propylene glycol gave distinct flames and clearly audible explosions about fifteen minutes after mixing. This was accompanied by very dense brown NO_2 fumes. The induction time, which is the time between initial mixing and the onset of the violent reaction, was found to increase as the ratio of HNO_3-to-propylene glycol decreased. It is important to bear in mind that these results were observed for 70% HNO_3 and pure propylene glycol. The behavior of 30% HNO_3 and coolant (<50% propylene glycol) was vastly milder, as described in sections C and E.

After one of the reactions between nitric acid (70%) and propylene glycol had subsided, the volatile materials were pumped away, leaving an oily residue. Analysis of this residue by FTIR showed glycollic acid, lactic acid, and oxalic acid. These are logical oxidation products of propylene glycol, as seen in Fig. 1.

C. Dilution of the Nitric Acid-Glycol Mixture Causes a Drastic Decrease in the Rate and Intensity of the Reaction. The reaction of 1.00 g propylene glycol with 9.00 g of 35% nitric acid did not evolve fumes until about two days after mixing, and the reaction was a very gentle one, with no perceptible bubbling or heating. Other glycol-nitric acid (35%) reactions with a higher ratio of glycol-to-acid were even slower to reach the point where NO_2 evolution was observed.

D. The Mechanism of the Nitric Acid Propylene Glycol Reaction is Autocatalytic in Nitrous Acid. This means that nitrous acid is formed as a product of the reaction, and serves as a catalyst to accelerate the reaction. This has been reported in many other nitric acid oxidation reactions. We demonstrated the autocatalytic effect in the laboratory by adding known amounts of sodium nitrite to HNO_3-glycol mixtures and measuring the induction times. The induction time dropped sharply as the nitrous acid concentration increased. This is an important consideration since some nitrous acid is present as an impurity in almost any nitric acid.

E. No Reaction is Observed Between Coolant and 30% Nitric Acid Unless the Solution is Heated. The standard coolant consists of a solution of borax (90 g/L) in a 1:1 mixture (by volume) of water and propylene glycol. Mixtures of coolant with 30% nitric acid are more dilute than the systems under Sections B and C. There was no evidence of any reaction when coolant and 30% nitric acid were mixed. Addition of $NaNO_2$ gave very slight NO_2 evolution, but no detectable heating or bubbling. Several solutions of coolant in 30% nitric acid were warmed slowly on a hot plate. These began to react when the temperature reached 75°C (or higher if the volume of nitric acid was not substantially greater than that of coolant). The reaction was by no means violent, but rather a gentle boil accompanied by some NO_2 evolution. There was no coolant-to-nitric acid (30%) ratio that gave a reaction that seemed hazardous. The experiments are believed to have covered the range of conditions of temperature, concentration, and nitrite content that would be experienced in the oralloy recovery area.

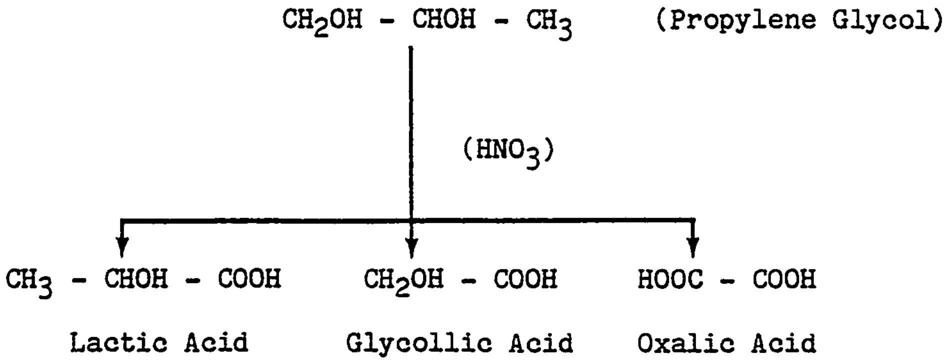

Fig. 1 Oxidation products of propylene glycol.

F. The Coolant Reacts Fairly Vigorously with 55% Nitric Acid After a Concentration-Dependent Induction Time. While 30% nitric acid is the maximum concentration used for oralloy recovery, more concentrated acid (55%) is used in recovering material having other isotopic enrichments. Our laboratory experiments showed that a fairly vigorous fume-off reaction occurs between 55% nitric acid and the coolant. The reaction is preceeded by an induction time, which varied from 36 min to 87 min, depending on the acid-to-coolant ratio. Addition of a small quantity of nitrite catalyst reduced the induction time to about four min.

The reaction of coolant with 55% nitric acid was vigorous enough to be disruptive if large quantities (i.e., gallons) were inadvertently mixed in a production area. On the other hand, the presence of a small amount of coolant on uranium chips that were being cleaned or dissolved in 55% HNO_3 would probably not even have a detectable effect.

G. Experiments Showed that the Dissolution of Uranium Chips that had been Soaked in Coolant Proceeded at About the Same Rate as if the Chips had not Previously Contacted Glycol. To determine if there are any unusual safety hazards associated with dissolving uranium chips coated with the new glycol-water-borax coolant, one batch of depleted uranium chips was dissolved in 30% nitric acid. The chips had been stored in the new coolant for several days. Approximately 500 g of chips were removed from the coolant, allowed to drain for one minute, and then placed in a 4 L beaker. Five milliliters of coolant were added to the beaker to simulate poorly drained chips. Nitric acid (30 wt %) was added stepwise to the uranium chips over a period of five hours. A total of three liters of acid was needed to completely dissolve the chips.

As is normal when dissolving uranium chips in 30% nitric acid, the reaction was exothermic and quite rapid after an initial lag time, resulting in boiling of the acid, the evolution of NO_x fumes and hydrogen gas. There was no indication that the presence of the propylene glycol from the coolant had any effect on the reaction.

H. Thermodynamic Calculations Show that the Enthalpy Change (Heat Liberated) by the Reaction of Nitric Acid (30%) with Propylene Glycol is Smaller than if the Same Amount of Nitric Acid Reacted with Uranium. The calculations were based on high-precision data from the JANAF tables.[3] The reaction with propylene glycol liberates 6.93 Kcal per mole of nitric acid while the reaction with uranium liberates 26.27 Kcal per mole of acid.

I. Effect of New Coolant on Uranium Recycle Operations. Tests were conducted to determine if propylene glycol from the new coolant could extract into the dibutyl carbitol of the uranium recovery system, thereby decreasing uranium recovery and/or carrying the glycol downstream to the evaporator. Various amounts of propylene glycol were added to 9212 raffinate solution and these solutions were contacted with dibutyl carbitol. The carbitol was then analyzed for propylene glycol. There was no detectable glycol in the carbitol. In a final test 10,000 ppm propylene glycol was added directly to the dibutyl carbitol and then this solution was contacted with raffinate solution. There was no glycol left in the dibutyl carbitol.

Based on equilibrium calculations, any propylene glycol that entered the uranium recovery system would end up in the feed stream to the nitric acid recovery distillation column. The glycol will concentrate in the nitric acid product. The glycol would then be destroyed during the ozonation step that removes chlorides. The acid product typically contains about 500 mg/L organic carbon at the present time. The addition of small amounts of propylene glycol would not have any adverse effects on the nitric acid recovery process.

SUMMARY

With a lack of administrative control there is no limit to the number of possible conditions under which nitric acid and propylene glycol could come into contact. The experiments that were run were directed to those conditions that might reasonably be expected to arise under existing controls. We found no problems associated with the use of 30% HNO_3 and the coolant, because the reactions were very mild and occurred after long induction times. There could be a problem in the case of the coolant reaction with 55% HNO_3 if large quantities of the two liquids were inadvertently mixed. If this happened in a well-ventilated area, the result would still not be very serious. The NO_2 fumes that are generated are also a product of the reaction of nitric acid with uranium, so the work area should already have adequate ventilation to cover this problem. Although the reaction of 70% nitric acid is a violent one, it should never occur in either of the uranium recovery areas. This is because neither 70% acid nor pure propylene glycol are used in these areas. Obviously, there are remotely possible circumstances under which serious problems could arise. However, most of the serious situations that can be envisioned are a result of the intrinsic properties of nitric acid, and are not exacerbated by the presence of the glycol-containing coolant.

REFERENCES

1. T. A. Turney and G. A. Wright, Chem. Rev., (1959), 59 497.
2. C. K. Ingold, Structure and Mechanism in Organic Chemistry, p. 238, Cornell University Press, Ithaca, New York (1953).
3. JANAF Thermochemical Tables, second edition, Ed. by D. R. Stull and H. Prophet, U.S. Government Printing Office, Washington, DC, 1971

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