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PROCESSING OF TETRAPHENYLBORATE PRECIPITATES IN THE SAVANNAH RIVER SITE DEFENSE WASTE PROCESSING FACILITY (U)

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A paper proposed for presentation and publication at the

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INTRODUCTION

The mission of the Savannah River Site has been the production of special nuclear materials for the Department of Energy. As a result of these operations, the Savannah River Site has generated 77 million gallons of high level radioactive waste since the early 1950's. By 1987, evaporation had reduced the concentration of the waste inventory to 35 million gallons. Currently, the wastes reside in large underground tanks as a soluble fraction stored, crystallized salts, and an insoluble fraction, sludge, which consists of hydrated transition metal oxides. The bulk of the radionuclides, 67 percent, are in the sludge while the crystallized salts and supernate are composed of the nitrates, nitrites, sulfates and hydroxides of sodium, potassium, and cesium. The principal radionuclide in the soluble waste is ^{137}Cs with traces of ^{90}Sr.

The transformation of the high level wastes into a borosilicate glass suitable for permanent disposal is the goal of the Defense Waste Processing Facility (DWPF). To minimize the volume of glass produced, the soluble fraction of the waste is treated with sodium tetraphenylborate and sodium titanate in the waste tanks to precipitate the radioactive cesium ion and absorb the radioactive strontium ion. The precipitate is washed in the waste tanks and is then pumped to the DWPF. The precipitate, as received, is incompatible with the vitrification process because of the high aromatic carbon content and requires further chemical treatment. Within the DWPF, the precipitate is processed in the Salt Processing Cell to remove the aromatic carbon as benzene. The precipitate hydrolysis process hydrolyzes the tetraphenylborate anion to produce borate anion and benzene. The benzene is removed by distillation, decontaminated and transferred out of the DWPF for disposal.

This paper describes the Salt Processing Cell and the chemistry occurring during precipitate processing.

PROCESS DESCRIPTION AND CHEMISTRY

The Salt Processing Cell is designed to remove 90 percent of the aromatic carbon present in the precipitate feed top the DWPF. The process chosen to remove the aromatic carbon is based upon the hydrolysis of tetraphenylborate in the presence of acid, which generates benzene.[1]

Due to limitations imposed by the need to produce a product compatible with the DWPF glass melter and the process materials of construction, formic acid was chosen as the active acid. The general reactions for the removal of the first three phenyl groups can be represented by reactions 1, 2, and 3.

$$(C_6H_5)_4B^- + HC00H \Longrightarrow$$
$$C_6H_6 + (C_6H_5)_3B + HC00^- \qquad (1)$$

$$(C_6H_5)_3B^- + H_20 \Longrightarrow$$
$$C_6H_6 + (C_6H_5)_2BOH \qquad (2)$$

$$(C_6H_5)_2BOH^- + H_20 \Longrightarrow$$
$$C_6H_6 + C_6H_5B(OH)_2 \qquad (3)$$

Initial research on the process demonstrated that the product of reaction 3, phenylboronic acid, is stable and is difficult to hydrolyze. The final phenyl can be removed by adding copper (II) to the reaction system as a catalyst.[2,3] The final product, as shown in reaction 4, is boric acid.

$$C_6H_5B(0H)_2 + H_20 \Longrightarrow$$
$$C_6H_6 + B(OH)_3 \qquad (4)$$
$$Cu\ (II)$$

Based upon these reactions the final product would be benzene, boric acid and alkali formates. Removal of the benzene would be easily accomplished by distillation.

Initial process research demonstrated that benzene is the major product; however, many other products, in smaller quantities, were also produced. These side reactions are due to the complex composition of the tetraphenylborate precipitate feed. Table 1 gives the expected composition of the DWPF precipitate feed.

The primary constituent producing side reactions is the nitrite anion. Nitrite in the feed is produced by radiolysis of nitrate and is also added to the washed feed as a corrosion inhibitor to protect the carbon steel waste tanks. The effect of nitrite on removal of organic material from the feed is shown in Figure 1. For nitrite levels greater than 0.04 molar, organic removals drop below the required 90 percent that the hydrolysis process must produce. However, the nitrite interference can be minimized by adding hydroxylamine nitrate to the hydrolysis process.

The process developed for the Salt Processing Cell combines a nitrite destruction step with tetraphenylborate hydrolysis to minimize side reactions and achieve the required organic removal. Figure 2 is a flow diagram of the DWPF Nitrite-Destruction Precipitate Hydrolysis Process. First, the precipitate reactor is charged with formic acid and hydroxylamine nitrate and heated to 50°C. Tetraphenylborate slurry is then pumped into the reactor while the reactor temperature is maintained During this addition the nitrite in the slurry is converted to nitrous oxide by means of reaction 5.

$$NaNO_2 + NH_20H{\cdot}HN0_3 \Longrightarrow N_2O + 2H_20 + NaNO_3 \qquad (5)$$

During feeding approximately 30 percent of the phenyl groups are removed by the initial hydrolysis reactions. After precipitate feeding is complete, copper (II) formate or copper (II) nitrate is added and the reactor is heated to achieve aqueous boiling (101-102 °C) and maintained for five hours. During this period, the hydrolysis reactions are completed, and the benzene is distilled into the Precipitate Reactor condenser/Decanter. The organic phase in the decanter is continuously decanted to the Organic Evaporator, and the aqueous phase returned to the reactor for additional boiling and organic steam stripping. After five hours of boiling, the reactor is cooled, sampled, and transferred to the Chemical Processing Cell for blending with sludge and glass frit. The organic product is distilled a second time to provide the required radioactive decontamination, sampled and transferred out of DWPF for final disposal. The vapors from both condensers pass through a chilled vent condenser (10°C) to minimize benzene emissions.

The addition of a nitrite destruction step has allowed the hydrolysis process to achieve the necessary organic removal with up to 0.2 molar nitrite in the feed. The maximum nitrite level in SRS precipitate will be less than 0.2 molar. the combined process has tested at the Savannah River Lab on both glassware and semi-works (1/5 scale) levels. Tables 2 and 3 give the aqueous and organic product compositions obtained for a typical run at 0.18 molar nitrite. Table 4 lists the major process operating parameters.

Hydrolysis of tetraphenylborate, without the other feed components present, produces an organic product that is 99 percent benzene with traces of phenol and biphenyl. When nitrite is present in the feed an extensive list of side products is produced. a partial list is given in Table 5. The compounds range from polar, water-soluble organics to non-polar, high-boiling organics. The major side products, because of nitrite, are aromatic amines, including diphenylamine and aniline. Removal of the side products from the aqueous product is a function of the aqueous/benzene solubilities and volatility of the compounds.

Nitrite reacts in formic acid to generate nitrous acid and nitric oxide by reactions 6 and 7.

$$NO_2^- + HCOOH \Longleftrightarrow HNO_2 + HCOO^- \qquad (6)$$

$$HNO_2 \xrightarrow[\text{Heat}]{} 2NO + NO3^- + H^+ \qquad (7)$$

The pKa for formic acid and nitrous acid are nearly equal, therefore, a significant fraction of the nitrite in a formic acid solution is present as nitrous acid. Both nitrous acid and nitric oxide can attack the carbon-boron intermediates to generate the side reactions.

Elimination of the side reactions requires removal of the nitrite before the hydrolysis reactions become significant. After testing several reducing or oxidizing agents for removing the nitrite, hydroxylamine nitrate was chosen because the reaction was compatible with the DWPF process and happens as fast as the nitrite is added.

The side reactions are also impacted by the presence of the copper catalyst. Copper not only accelerates the hydrolysis of phenylboronic acid, but it also accelerates the other hydrolysis reactions and the side reactions involving nitrite. Initial tests in the semi-works facility includeed a 20 percent heel of the previous batch product carried over into the current batch. The heel included a proportionate amount of copper catalyst and resulted in the production of an increased amount of side products; this was despite the presence of the nitrite scavenger. The aqueous product contained much less organic residues when the heel was reduced to a negligence amount.

The other reactions occurring in the precipitate reactor include acid-base reactions of formic acid with hydroxide and carbonate, excess hydroxylamine nitrate decomposition reactions and diphenylmercury reactions. The decomposition of hydroxylamine nitrate generates ammonium ion and nitrous oxide depending on whether the hydroxylamine nitrate is reduced or oxidized. diphenylmercury is generated in the waste tanks due to reaction 8 during the precipitation process.[4]

$$B(C_6H_5)_4^- + 2Hg^{+2} + 3H_2O) ===> 2\,(C_6H_5)_2Hg + 3H^+ + B(OH)_3 \qquad (8)$$

Since diphenylmercury is not soluble in water, it is filtered with the tetraphenylborate and Transferred from the waste tank to the DWPF and the Salt Processing Cell. During the hydrolysis process, the diphenylmercury reacts with formic acid by reaction 9.

$$(C_6H_5)_2Hg + HCOOH ====> Hg + C_6H_6 + CO_2 \qquad (9)$$

The mercury accumulates in a sump in the reactor and is periodically transferred to a purification process within the DWPF. A small amount of diphenylmercury is team stripped from the precipitate reactor and ends up in the organic product.

PROCESS SAFETY

The primary process hazard for the Salt Processing Cell is the generation of flammable mixtures during precipitate processing. The nitrite destruction portion of the process produces nitrous oxide by reaction 5 at the same time that some benzene generation is occurring. since nitrous oxide can serve as an oxidant and support combustion, both a fuel and an oxidant are produced at the same time.

The method chosen in the DWPF to prevent the formation of a flammable N_2O/C_6H_6 mixture was the dilution of the oxidant to 50 percent of the minimum oxidant required to support combustion, referred to as MOC. An extensive standard bomb explosion testing program was to determine the MOC for dilution with nitrogen and with carbon dioxide. Figure 3 is the general flammability diagram obtained for nitrous oxide/benzene/nitrogen mixtures. For a system composed of nitrous oxide/benzene/carbon dioxide and sufficient air due to leakage to give 2 percent oxygen, the MOC is 28 percent. Control of the rate of generation of nitrous oxide is based upon the precipitate feed rate to the reactor since the nitrite destruction reaction is fast under all conditions. The process is interlocked to shut off precipitate feed if the nitrous oxide content exceeds 60 percent of the MOC. After the vapors exit the chilled vent condenser, the strategy for control of flammability shifts to dilution with air to reduce the benzene concentration to less than 60 percent of the lower explosive limit for a benzene/air mixture.

CONCLUSION AND SUMMARY

The Salt Processing Cell of the DWPF has been designed to effectively remove more than 90 percent of the aromatic carbon in the tetraphenylborate precipitate by hydrolysis. The benzene product is distilled and decontaminated in a safe manner.

Current research is aimed at reducing the quantity of residues produced by the hydrolysis reactions, identifying alternative nitrite scavengers that only generate nitrogen gas as a product, and elucidation of the side reactions that occur within the hydrolysis process. Large scale testing to examine operability of the process and test alternate processing strategies will continue.

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TABLES

Table 1. Tetraphenylborate Precipitate Composition

Compound	Weight Percent
Water	88.5
Potassium Tetraphenylborate	7.6
Ammonium Tetraphenylborate	0.4
Cesium Tetraphenylborate	0.095
Sodium Nitrite	1.11
Phenol	0.34
Sludge Solids	0.3
Phenylboronic Acid	0.28
Biphenyl	0.24
Sodium Titanate	0.2
Potassium Hydroxide	0.2
Sodium Hydroxide	0.11
Phenylphenols	0.05
Terphenyls	0.035
Other compounds	0.54

Table 2. Salt Processing Cell Aqueous Product

Compound	Weight Percent
Water	92.8
Nitrate Salts	2.3
Formate Salts	2.2
Boric Acid	1.4
Phenol	0.3
Sodium Titanate	0.26
Formic Acid	0.15
N-Phenylformamide	0.05
Aniline	0.05
Terphenyls	0.03
Diphenylamine	0.02
Biphenyl	0.01
2-Phenylphenol	0.01
4-Phenylphenol	0.01
Other compounds	0.4

Table 3. Salt Processing Cell Organic Product

Compound	Weight Percent
Benzene	91.8
Biphenyl	5.8
Diphenylamine	1.2
Phenol	0.93
Nitrosobenzene	0.1
Aniline	0.06
2-Phenylphenol	0.02
o-Terphenyl	0.02
Diphenylmercury	0.009
p-Terphenyl	0.007
m-Terphenyl	0.005
4-Phenylophenol	0.002

Table 4. Compound Produced During Hydrolysis

Phenol
N-Phenylformamide
Nitrosophenol
Nitrobenzene
Biphenyl
Phenylphenols
Nitrodiphenylamine
Quaterphenyl
N-Phenylbiphenylamineses
Aniline
Nitrophenols
Nitrosobenzene
Chlorobenzene
Diphenylamine
Terphenyls
Azobenzene
Triphenylamine
Quinquephenyl

Figures

FIGURE 1

AROMATIC CARBON REMOVAL VS [NO2-]

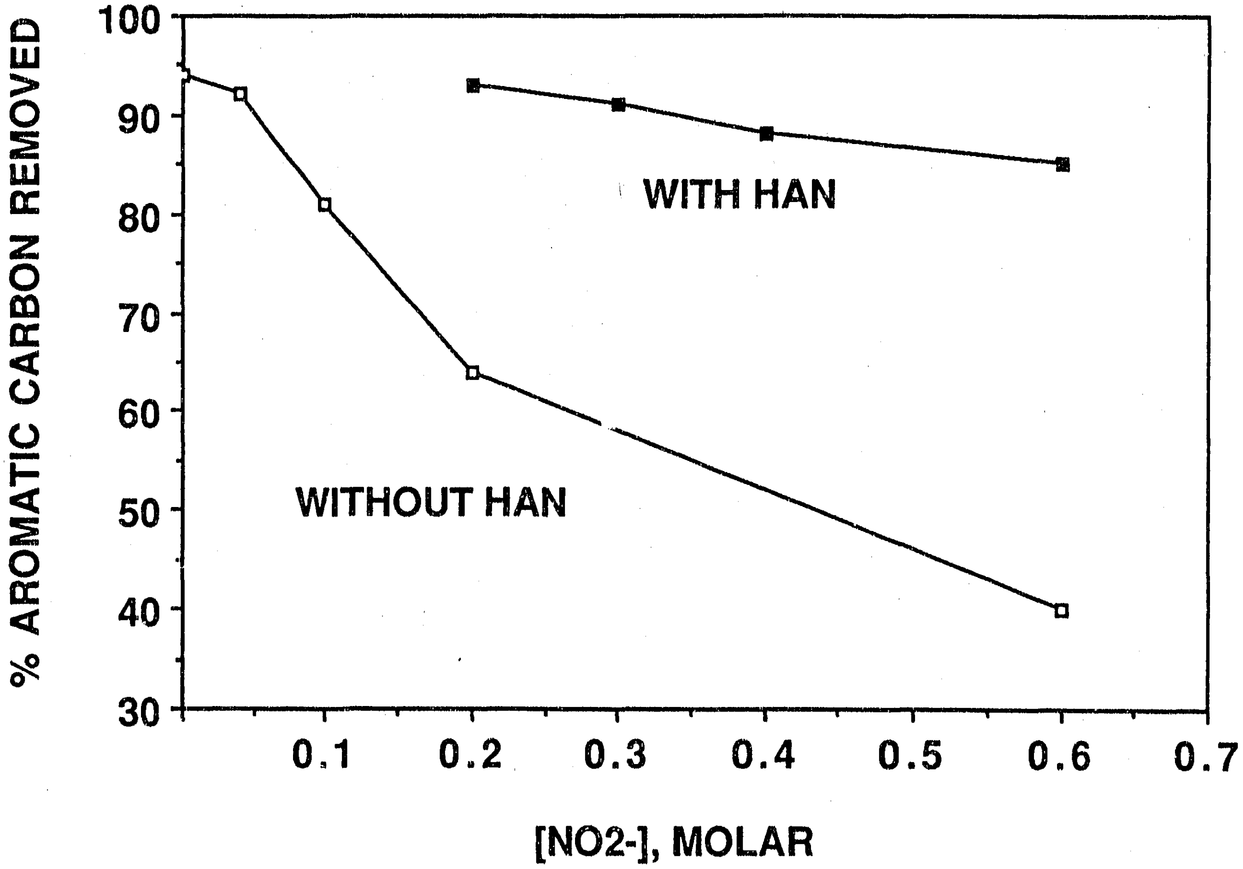


FIGURE 2

NITRITE-DESTRUCTION PRECIPITATE HYDROLYSIS PROCESS

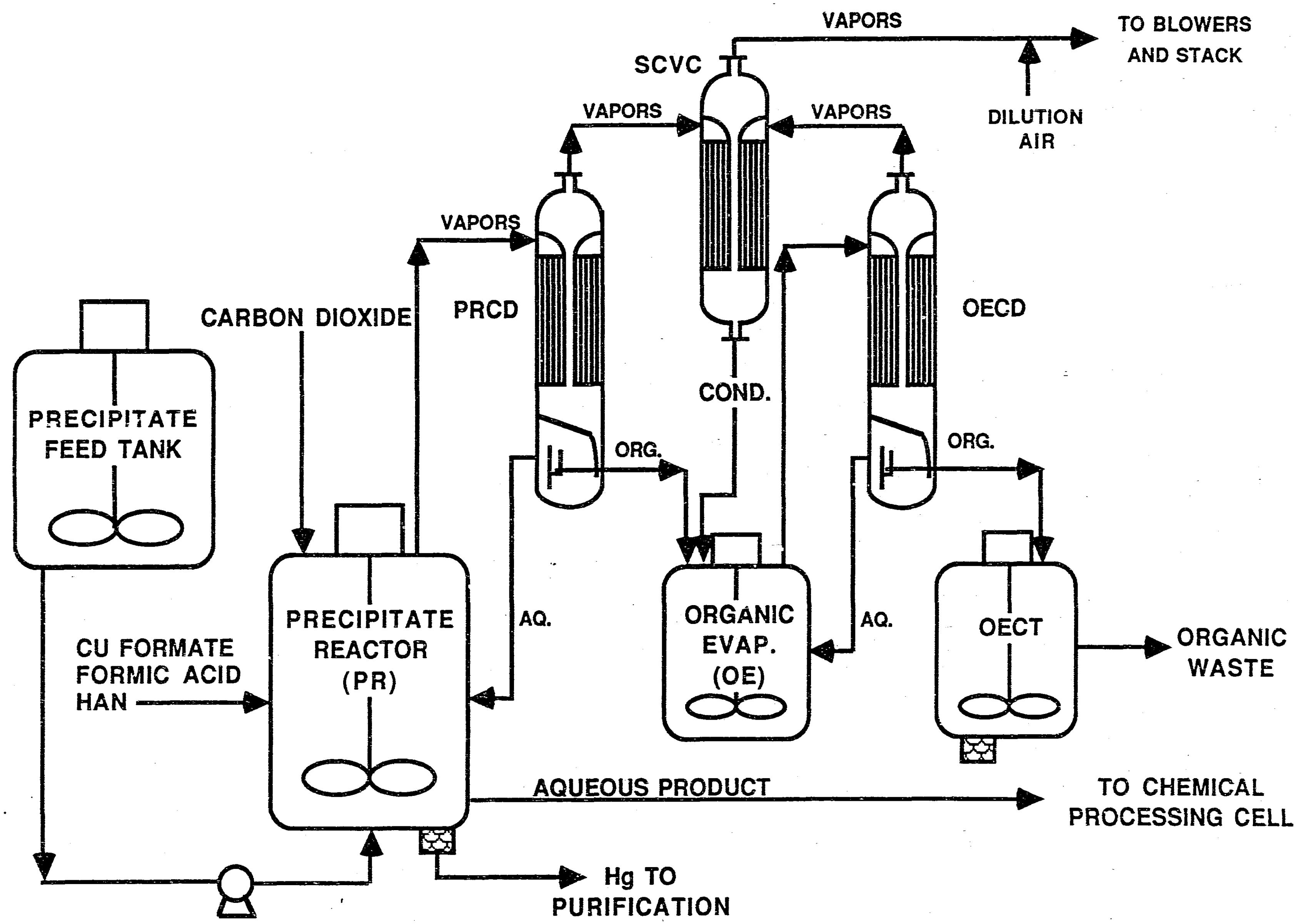
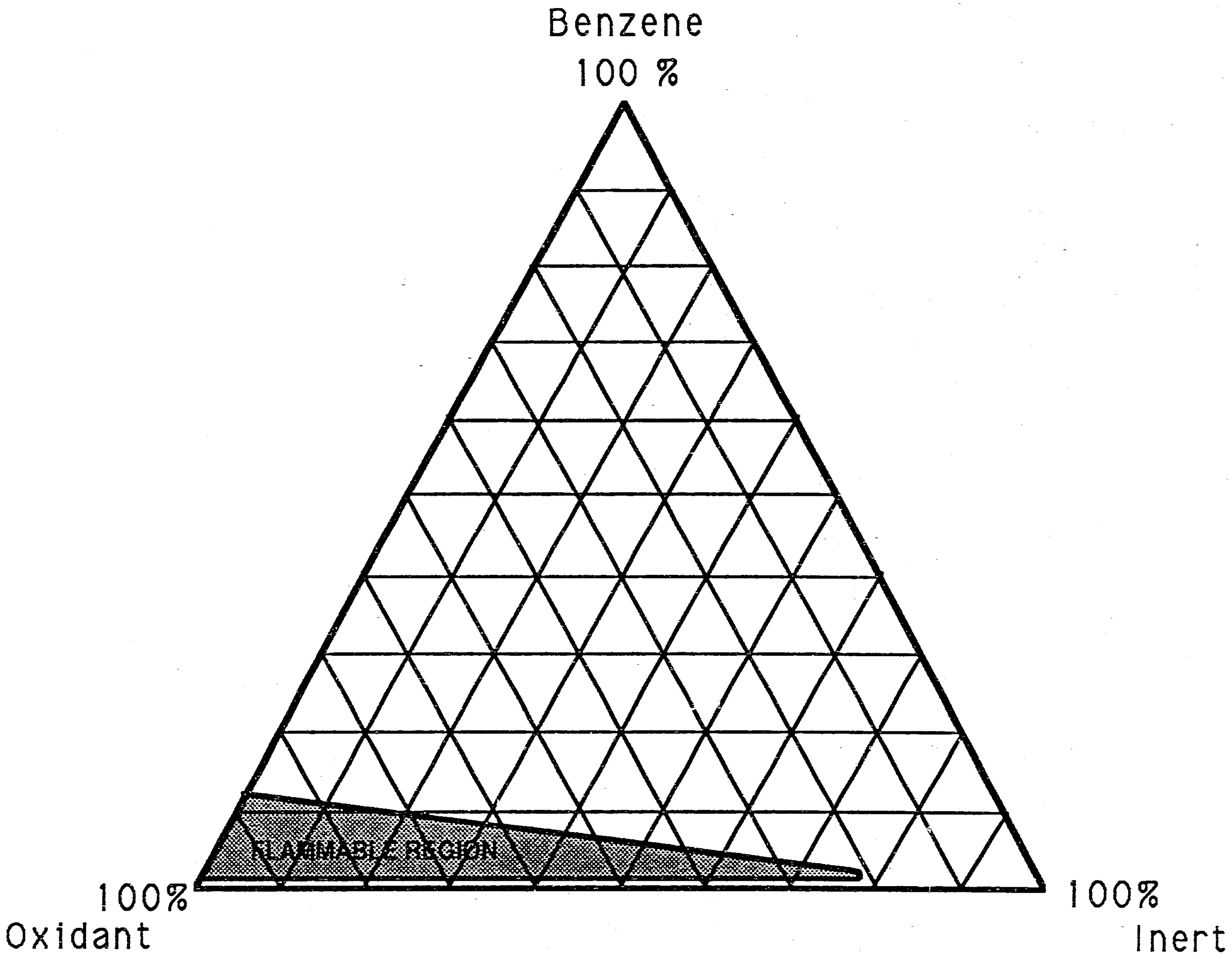


FIGURE 3

Flammability of Benzene/N2O/N2



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