NITRIC ACID

- PRODUCTION IN PAKISTAN AS COMPARED TO WORLD
- PRODUCTION COMPANIES IN PAKISTAN
- ► PROCESS FLOW DIAGRAM (PFD)
- MANUFACTURING
- ► USES
- PHYSICAL PROPERTIES

► CHEMICAL PROPERTIES

► INTRODUCTION



Introduction

 Nitric acid (HNO3). A colorless liquid that is used in the manufacture of inorganic and organic nitrates and nitro compounds for fertilizers, dye intermediates, explosives, and many different organic chemicals. Continued exposure to vapor may cause chronic bronchitis; chemical pneumonitis may occur.

(From Merck Index, 11th ed)

NITRIC ACID, RED FUMING is a pale yellow to reddish brown liquid generating red-brown fumes and having a suffocating odor. Very toxic by inhalation. Corrosive to metals or tissue.

(Physical Description from CAMEO Chemicals)



PHYSICAL PROPERTIES

- Appearance: Colorless, yellow or red
- Odor: Acrid, suffocating
- ► Density: 1.5129 g cm-3
- ► Melting point: -42 °C (-44 °F; 231 K)
- Boiling point: 83 °C (181 °F; 356 K)
- Solubility: Completely miscible
- Vapor pressure: 48 mmHg (20 °C)



CHEMICAL PROPERTIES

Stability : Pure nitric acid is not very stable. Even at ordinary temp. in presence of sunlight it undergoes slight decomposition.

 $4 \text{ HNO}_3 \rightarrow 2 \text{ H}_2\text{O} + 4 \text{ NO}_2 + \text{O}_2.$

Oxidizing properties: Nitric acid is a strong oxidizing agent as shown by its large positive E^o values.

> NO3- (aq) + 2H+ (aq) e- \rightarrow NO2 (g) + H2O (I) E $^{\circ}$ = 0.79 V NO3- (aq) + 4H+ + 3e- \rightarrow NO (g) 2H2 (I) E $^{\circ}$ = 0.96 V

CHEMICAL PROPERTIES

Reactions with metals: Nitric acid dissolves most metals including iron, copper, and silver, with generally the liberation of lower oxides of nitrogen rather than hydrogen. It can also dissolve the noble metals with the addition of hydrochloric acid.

 $CU + 4HNO3 \rightarrow CU(NO3)2 + 2NO2 + 2H2O$

Reactions with nonmetals: Reaction with non-metallic elements, with the exception of silicon and halogen, usually oxidizes them to their highest oxidation states as acids with the formation of nitrogen dioxide for concentrated acid and nitrogen oxide for dilute acid.

 $C + 4HNO3 \rightarrow CO2 + 4NO2 + 2H2O$

USES:

- As a starting material in the manufacture of nitrogen fertilizers such as ammonium nitrate & ammonium etc. Large amounts are reacted with ammonia to yield ammonium nitrate.
- It is commonly used in science laboratories at schools for experimenting when specifically testing for chloride
- As a nitrating agent in the preparation of explosives such as TNT, nitroglycerine, cellulose poly-nitrate, ammonium picrate.
- > It is used as a medicine to remove chancres and warts.
- > Used in fibers, plastics and dyestuffs industries
- Used in metallurgy and in rocket fuel production.
- > It is used in calorimetric test to distinguish between heroin and morphine.

MANUFACTURING OF NITRIC ACID

INDUSTRIALLY NITRIC ACID IS PREPARED BY FOLLOWING 3 METHODS:

- CHILE SALTPETRE METHOD BY NANO3
- BRIKLAND EYDE'S METHOD BY USING AIR
- OSTWALD'S METHOD BY AMMONIA SOLVEY PROCESS

CHILE SALTPETRE METHOD (By NaNO₃)

It is the first commercial process of manufacture of nitric acid from sodium nitrate extracted

from Chile saltpeter. The process is now become obsolete since second decade of nineteenth century.

► <u>Raw materials</u>

Basis: 1000kg Nitric acid (95% yields) Sodium Nitrate = 1420kg Sulfuric acid = 1638kg

► <u>PROCESS</u>:

Equal weight of sodium nitrate (or potassium nitrate) and sulfuric acid is charged to cast iron retort having outlet provided at bottom to take out solution of sodium bisulfate. The reactants are heated to about 2000C by the hot furnace gases. The furnace gases are produced by combustion of coal in the furnace. Then the vapour of nitric acid are cooled and condensed in water cooled silica pipes. The cooled acid is collected in stoneware receiver. The un-condensed vapours are scrubbed with water in absorption tower which is packed with stone ware balls and cooled by cold water. The dilute acid is re-circulated till it becomes concentrated. The residual sodium bisulfate is removed by outlet provided at the bottom of retort.

Reaction:

NaNO3 + H2SO4→NaHSO4 + HNO3



Figure: Manufacture of nitric acid from chile saltpetre or nitrate

BRIKLAND EYDE'S METHOD (Arc Process)

Raw materials

Basis: 1000kg Nitric acid (98% yield)

Air = 198kg

Water = 145kg

Process:

 CO_2 and dust free air is heated in an arc furnace at 3000 °C. Nitric oxide is formed. Gases coming out from the furnace are cooled at 1000 °C by passing through cooler then gases are passed in a boiler and cooled at 150°C. Cold water is circulated around the boiler to cool the gases. Gaseous mixture is now passed through aluminum tubes. The temperature of gaseous mixture becomes 50°C.

Gaseous mixture is passed in oxidizing tower where NO is oxidized intoNO₂. 2NO + $O_2 \longrightarrow 2NO_2$

NO₂ is absorbed in water in absorption tower then dilute HNO₃ is obtained. $3NO_2 + H_2O \longrightarrow 2 HNO_3 + NO$

Now HNO_3 is not manufactured by this method because consumption of electricity is very high to maintain the temperature 3000 ° C. Even at this temperature 1% NO is form.



Figure: Manufacturing of Nitric Acid by Arc Process

OSTWALD'S METHOD

Principle :

NH₃ is oxidized into NO by air at 800 °C in presence of Pt (Platinum)catalyst.

Raw Materials

Basis: 1000kg nitric acid (100%)

- Ammonia = 290kg
- > Air = 3000Nm3
- Platinum = 0.001kg

- > Water = 120000kg
- Steam credit = 1000kg @ 200psig
- Power = 10-30KWH

PROCESS:

Mixture of NH₃ and O₂ in the ratio of 1:9 is passed through catalyst chamber containing Pt- gauge. Temperature of the catalyst is kept at 800 °C. About 95 % NH₃ is converted into NO.

 $4NH_3 + 5O_2 - 4NO + 6H_2O + 21.6 K.Calorie$

Heat liberated maintains the temperature of the catalyst. The gases coming out are cooled to about 50 °C and mixed with more O_2 . This gaseous mixture is passed in oxidizing tower where NO is oxidized to NO_2 .

 $2NO + O_2 \longrightarrow 2NO_2$

 NO_2 is passed in absorption tower. The dilute solution of HNO_3 is obtained.

 $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$



Nitric Acid Safety and Handling:

Nitric Acid is an extremely corrosive acid capable of causing severe chemical burns very rapidly.

- When handling Nitric Acid in the workplace, it is highly recommended to wear:
- Chemical Safety Glasses.
- Face shield.
- Gloves

As an added safety precaution, eyewash station and washing stations should be easily accessible incase of exposure to nitric acid.

First Aid:

In the event of exposure to Nitric Acid, follow thess first aid guides:

- Inhalation Seek fresh air and immediate medical attention.
- Eye Contact Immediately wash eyes with plenty of water for at least 15 minutes to prevent any further damage and seek immediate medical attention.

Skin Contact - Immediately wash affected area with water for at least 15 minutes and remove any contaminated clothing. Seek medical attention as soon as possible.

Ingestion - Do NOT induce vomiting. Rinse mouth with water and drink a glass of water or milk. Seek medical attention immediately.

NITRIC ACID COMPANIES IN PAKISTAN

- ITTEHAD CHEMICALS LTD.
- INTERNATIONAL PETROCHEMICALS LTD.
- ATTA CHEMICALS PVT LTD.
- FATIMA GROUP
- PAK ARAB FERTILIZERS SUPPLIERS
- THIOGLYCOLIC ACID COMPANY

Production of Nitric Acid in different Regions



Import and Export of Nitric Acid by Region: Imports:



Exports:



The various regional markets for nitric acid are North America, Latin America, the Middle East and Africa, Asia Pacific excluding Japan, Japan, and Europe. Among these, currently Europe holds the major revenue share and is expected to retain its dominance throughout the assessment timeline. The Europe nitric acid market is projected to rise at a CAGR of 3.9% from 2017 to 2022, and is expected to reach a valuation of US\$11,636.1 Mn by the end of the forecast period.

Asia Pacific excluding Japan to Present Lucrative Avenues

Asia Pacific excluding Japan (APEJ) is a prominent market for nitric acid. The APEJ market is projected to create a substantial opportunity of US\$710 Mn during the forecast period. The rising demand for concentrated nitric acid for making explosives and several agrochemicals is a prominent trend expected to fuel the regional market.

Meanwhile, the North America nitric acid market is expected to rise from a valuation of US\$2,093.5 Mn in 2017 to reach US\$ 2,506.3 Mn by 2022 end. The regional market is projected to register a CAGR of 3.7% during 2017–2022.

Competitive Analysis

Some of the key players operating in the market are BASF SE, The Chemours Company, Eurochem Group, Dyno Nobel, Potash Corp, Sumitomo Chemical Co., Ltd., Yara, CF Industries, and OCI Nitrogen. Several prominent companies are focused on expanding their production and distribution facilities to stay ahead of the others. They are seeking to capitalize on lucrative avenues emerging from a rapidly growing end-use industries in various developing and developed regions.

CONCLUSION

- In this presentation we went through the physical and chemical properties of Nitric Acid (HNO₃) as well as its applications and uses.
- Also we have learned the 3 industrial manufacturing processes of Nitric Acid (HNO3)
- ▶ We went through the comparison of our production with the others.
- And at last but not the least we got some information of industries which produce Nitric Acid in our country (PAKISTAN).



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