Hello, I welcome all the students. My name is Abhijeet.

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and Science, Farmagudi, Ponda-Goa. Today, we're going to discuss

about the topic nitration and in that we're going to look into

the module benzene to

nitrobenzene and m-Dinitrobenzene

in this module we are going to learn about preparation of

nitrobenzene and preparation of m-dinitrobenzene

The learning outcomes will be the student will be able

to learn the industrial methodologies for the

preparation of nitrobenzene and m-dinitrobenzene

and they will be also able to understand the

mechanism for the synthesis of nitrobenzene and

m-dinitrobenzene.

This is the mechanism for the preparation of Nitro

benzene from benzene. In this, we're going to take benzene and

along with benzene we are using the nitrating mixture that is

concentrated H2SO4 and concentrated nitric acid below

the temperature of 55 degrees Celsius to get Nitro benzene in

the first step you can see on the slide nitric acid attacks

the sulfuric acid and it takes a proton from it.

And then it forms an intermediate and then the

negative charge attacks onto the single bond to form a

double bond, and then there is formation of nitronium ion and

water. Then there is reaction between benzene and nitronium

ion where there is formation of intermediate and

then it reacts with water to give you.

Nitrobenzene

preparation of nitro benzenenitrobenzene can be manufactured

by two methods. The first one is by nitration with mixed acid.

In this use of cycle acid is essential, particularly when the

problem of heat transfer has been satisfactorily so the

operation commenced by delivering the delivering to the

nitrator sufficient cycle acid that is spent acid from a

previous charge in which some Nitro benzene and nitric acid

are still present.

Amount of such acid required depends on the type of the

nitrate are used in the sleeve and propeller type. It should

cover the cooling units in the whole nitrator. It must cover and

overflow through the parts of the machine.

Cold water is then circulated through the heat exchange medium

when the temperature is 50 degrees Celsius or lower, the charge of benzene is pumped from the scale tank into the nitrator. The mixed acid can be fed on the top of the hydrocarbon or under surface. The temperature of nitration for benzene may vary within moderate limits. When no cycle acid acid is used, the temperature below 50 degrees Celsius is kept.

Fortified spent acid is employed. The nitration temperature may be kept between 50 degrees Celsius and 55 degrees.

Separation and neutralization.

The Separation of nitrobenzene is done in large conical bottomed lead tanks, each capable of holding one or more charges. The nitrator charge is settled here for about four to 12 hours.

When the spent acid is drawn off from the bottom of the lead tanks and delivered to the spent acid tanks for additional setting or for the treatment with benzene next to be nitrated in order to extract the residual nitrobenzene. The Nitro benzene is then delivered to the neutralizing house.

The neutralizing tub maybe either a large lead conical shape tube containing an air spider which is used for agitating the charge of nitrobenzene during the washing process or a standard cast iron kettle similar to the nitrator with sleeve and propeller agitation, the neutralizing vessel is prepared with heel of warm water which is delivered from an adjacent vat, and the nitrobenzene is blown into it.

The charge is thoroughly agitated and warm with live stream for about 30 minutes or until neutral to Congo and then allowed to settle for a similar period. The supernatant acid water is then run through the side outlets into the labyrinth where practically all the immersed nitrobenzene will settle out. The charge is now given a neutralizing wash.

At 40-50 degrees Celsius with warm sodium carbonate solution until alkaline to phenolphthalein.

When the Nitrobenzene is intended for aniline production, this may be followed by a wash with aniline water from the Reducer House, if any has to be worked with.

Otherwise, a final washing with a small quantity of warm water is made. The Nitrobenzene then delivered to its storage tanks, where it is again settled to remove the final traces of water. The crude product can now be distilled for commercial use.

Or used directly for the preparation of aniline some plants where the nitrobenzene is used almost exclusively in the aniline plants, the neutralizing and subsequent washes are omitted. No harmful effects on the equipment are noticeable if the acidity is kept below 0.5%.

Next, the second one is continuous nitration with fortified spent acid.

Hot sulfuric acid at about 90 degrees Celsius is run from the heat insulated storage tank into one of a battery of nitrator under vigorous agitation. Sufficient that is about 63% nitric acid is added to the nitrator to produce a mixed acid containing 4% $HNO3$.

Sufficient benzene is then delivered from its storage tank to react with all the nitric acid in the nitrator. Upon completion of the reaction that takes about 10 minutes, the agitation is stopped and the charge is permitted to settle. While the separation of nitrobenzene and spent acid proceeds, another nitration is started, thus providing a continuity of operations.

The crude nitrobenzene is drawn through the side outlets on the nitrator and sent to the Neutralizer. The spent acid, which is free of nitric acid but contains small amount of

nitrobenzene, is drawn off in operating sequence at the

outlets located at the base of

the Nitrator. The spent acid is first directed to the acid

heater, which is heated by low pressure steam to maintain the

sensible heat of spent acid that is around 72% of sulfuric acid

and delivered to the vapor

separator. The evaporator operating under vacuum of 29

inch, effectively removes the water of nitration by virtue of

the sensible heat of the spent acid, and returns the sulfuric

acid to the system at its original. That is, 75% strength.

The small quantity of Nitrobenzene found with the water in

the condenser is separated and added to the crude charge.

This is now the preparation of m-Dinitrobenzene. Here you can see

that Nitrobenzene is made to react with concentrated nitric

acid and concentrated sulfuric acid and then it will give you M

dinitrobenzene or 1,3-dinitrobenzene. The first step

here remains the same as of the earlier example and in the

second step you can see the double bond attacks

the nitronium ion.

To form an intermediate where the water will attack the hydrogen ion and then there will be a double bond

formation here giving rise to M dinitrobenzene and H3O plus.

Now we'll look into its industrial process. Preparation

of M Dinitrobenzene, the preparation of M dinitrobenzene

from benzene is usually accomplished in two stages of

nitration. Both may be made in the same vessel. The first stage

is carried out under the conditions of nitration of

benzene to form Nitro benzene. At the conclusion of the first

nitration, the spent acid is runoff from the base of the

machine and is replaced by a Storage nitrating acid for the second stage of nitration, the

composition of nitrating acid for both stages of nitration is

Shown above. It is readily seen from the composition that

the second nitration requires a more concentrated acid.

Moreover, the reaction must be controlled at a higher

temperature that is 90-100 degrees Celsius, although the heat of

nitration for the second Nitro group is not so great As for the

introduction of the first. The operation is nevertheless much

slower on account of the lower specific heat and greater

integral heat of dilution of the more concentrated acids that are

used. Since the rate of feed and time of reaction are determined

By the efficiency of agitation and heat exchange. These are matters of special importance in the nitration. In the combined operations, 2200 KG of spent acid from a dinitration that is about 80% of sulfuric acid is retained in the jacketed cast. Iron nitrator of 8 cubic feet that is around 2112 gallon capacity that is provided with a lead cooling coil and a sleeve in which stirrer operates at 110 RPM. To this 1900 KG of mixed acid is added that is about 88% of HNO3 11% of sulfuric acid and 1% of water. Then 2200 KG of benzene is introduced over a period of four hours while controlling the temperature, Initially at 25 degrees Celsius and finally at 40 degrees Celsius. The temperature is then raised to 60 degrees Celsius in one hour. The charge is permitted to stratify and the spent acid is discharged to a lead line washer with stirrer where it is washed with either benzene or nitrobenzene. To the nitrobenzene retained in the nitrator, That is added over a 3 hour period 5000 to 6000 KG of mixed acid having a concentration of. 67 percent H2SO4 and 33% HNO3 approximately. A temperature rise from 25 degrees Celsius to 40 degrees Celsius. The temperature is then raised to 90 degrees Celsius and maintained there for about one hour or until free of nitrobenzene by the steam distillation test. The charge is settled in. The spent acid is run into Large Washer where several batches are washed with nitrobenzene. The dinitrobenzene is delivered to a tile lines or stainless steel washer provided with the lead cover and stirrer. It is washed first with 4000 liters of hot water and then with caustic soda solution until neutral and finally it is washed with water and about 4500 KG of. Crude molten dinitrobenzene that is 85% of meta, 13% of ortho and 2% of para is obtained from each nitrator charge is purified by mixing thoroughly with 3000 liters of water at 80 degrees Celsius in a jacketed cast iron vessel. The contents are allowed to cool without heat exchange until about 70 degrees Celsius when the pelleting begins and then 650 KG of sodium sulfide, which converts the para and ortho derivatives to Nitramines, is added at a rate of 100 kg per 15 minutes. These Are the references.

Thank you.