NITRATION

1.0 INTRODUCTION

A **manufacturing chemist** is concerned with **industrial processes** in which **raw materials** are charged or separated into **useful products**. In any case, the products themselves may serve as the starting materials for further changes and thus may not be the end products but only the intermediates.

Any commercial **production of chemicals** is usually a combination of **physical** and **chemical** changes **e.g.** cracking of petroleum involves transportation of liquids and solids, distillation into various fractions of a definite boiling range and the chemical reactions resulting in cracking of big molecules into small ones etc. Thus the cracking process involves both the physical and chemical changes.

The process of manufacture of common salt from seawater involves the following steps; Transportation of brine (aqueous solution of common and other salts), heat transfer, evaporation, crystallization, sieving etc. None of the steps in the sequence involves any chemical change. Thus the process here consists of only physical **unit processes** changes.

For the systematic study of chemical process industries the **physical** and **chemical changes** which are important for the **manufacturing processes** have been **classified** as **unit operation** and respectively

Any piece of equipment used in industry would involve doing something (operations) and hence analysis of the operation to be performed by the equipment into fundamental terms would simplify and unify the treatment of all processes because the **unit operations** are **identical** in fundamentals.

1.0.1 1 Unit operation

They may be **defined** as **major physical changes** useful to chemical industries. Important **unit operations are** heat transfer, flow of fluids, material handling, filtration, distillation, extraction, drying etc. Relatively few of the unit operations are required in any particular process. In **majority of cases**, operations are to be done to set up the condition to carry out chemical changes. Thus very important classification of various changes useful to chemical industries was needed to be done. This was called Unit Processes.

1.0.2 Unit process

Unit processes may be **defined** as **major chemical transformations** which are important to the chemical industries **e.g.** Nitration, halogenation, sulfonation, oxidation, reduction etc.

The **study of these processes** includes

- The basic knowledge of a particular chemical reaction
- Equipment for the reaction
- Running the reaction so as to get the purest product in minimum time and at minimum possible cost

The classification of unit operations is more systematic than that of unit processes due to the diversity and complexity of the latter. However the regularities emerged from the study of a particular process can be useful in setting up condition for the manufacture of a new chemical which may include one or more such unit processes. **E.g.** For the unit process nitration (i) The reaction is always almost exothermic (ii) The physicochemical principles of equilibrium and chemical kinetics are similar (iii) Material of construction and the equipment for the process can be predicted.

The principles of widely varying sequence of making up a chemical process do not depend upon the nature of the materials being worked upon and other characteristic of the system under study. If the step of process is recognized, the process can be designed in such a way that each step to be used can be studied individually, illustration of

Unit operations	**Unit processes**
Distillation, drying, evaporation, Heat-exchange, mixing, size-reduction, transportation, separation etc.	Alkylation, animation, dehydration, diazotization, coupling, electrolysis halogenation, nitration, sulphonation, oxidation, reduction etc.

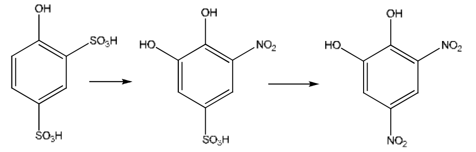
In both unit operations and unit processes the **similarities** within any unit operation or unit process are **separated and studied**; thus drawing attention to the like qualities of a given physical change, as in distillation or chemical change as in hydrogenation. The emphasis thus place upon the similarities led to unifying theories and to expression by rules and formulas of those like aspects and these in turn led to a clearer understanding of the function and thus to improved design of the necessary equipment: This is the **scientific** and **engineering approach**. The ultimate study by this method of the technical changes culminated in chemical engineering formulas and laws for using the classified observations in each unit operation or unit process. These **formulas** and **laws** are the **tools** for the **industrial chemist** uses in designing or operating a distillation column or a hydrogenation.

In **conclusion**, it may be stated that the unitary concept as applied to both physical and chemical changes, has been useful and has emphasized the fundamental systems and principles rather than technical details.

1.1 NITRATION

Nitration is the **process of introduction** of **one** or **more nitro groups** in a reacting molecule (called substrate), e.g.

$R\text{-}Cl + AgNO_2 \longrightarrow R\text{-}NO_2 + AgCl$
Silver nitrite
$R\text{-}Cl + AgNO_3 \longrightarrow R\text{-}O\text{-}NO_2 + AgCl$
Silver nitrate



Phenol-2,4-disulfonic acid

Picric acid
Powerful explosive

1.2 USES OF NITRO-COMPOUNDS

The nitro compounds find applications as solvents, dyestuffs, pharmaceuticals, explosives and as intermediate for the preparations of amines which are prepared by the reduction of the corresponding nitro compounds.

1.3 NITRATING AGENTS

A **variety of nitrating agents** can be used depending upon compound to be nitrated

- Dilute, concentrated or fuming **nitric acid** can be used.
- HNO_3 **dissolved in** acetic acid, H_2SO_4, acetic anhydride, $CHCl_3$, H_3PO_4
- **Mixed acids**: This is a mixture of HNO_3 and H_2SO_4. The HNO_3 may be concentrated or fuming
- **N_2O_5** and **N_2O_4**

1.3.1 Functions of H_2SO_4

- It **removes** the **water** produced during nitration.
- Being a stronger acid than nitric acid, it **protonates nitric acid** to form a **nitryl ion** which is **strong** nitrating agent.

$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

1.3.2 Evidence to support the formations of nitryl ion in the mixed acid

$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

- From the **freezing point depression** van't factor of HNO_3 in H_2SO_4 is found to be 4 which indicate that the **ionization** of HNO_3 can be represented by the above equation.
- Solution of HNO_3 has **three different UV spectra**. In **dilute aqueous solution**, its spectrum is that of NO_3^- (nitrate ion). In an **inert weakly polar solvent** e.g.$CHCl_3$, the spectrum is the same as that of ethyl nitrate, indicating that HNO_3 exists as unionized HNO_3. A **3rd spectrum** is characteristic of H_2SO_4 solution of HNO_3 and its esters, indicating that here that HNO_3 does not exist as NO_3 ion or as unionized nitric acid. The **Raman spectrum** of HNO_3 in H_2SO_4 is even more informative. Solution of HNO_3 in H_2SO_4 and in perchloric acid have only one Raman line owing to HNO_3 which occurs at $1400 cm^{-1}$ and which is polarized.
- **Electrolysis of solution** of HNO_3 in H_2SO_4 posses **positively charged ions** migrating towards the cathode.
- Several **crystalline nitryl salts** have been isolated and characterized. e.g. NO_2^+ ,NO_3^- $NO_2^+ClO_4^-$ and $NO_2^+HS_2O_7^-$.

1.4 AROMATIC NITRATION

$ArH + HONO_2 \longrightarrow ArNO_2 + H_2O$

1.4.1 Orientation

Nitration is an **electrophillic substitution reaction** i.e. NO_2^+ is an electrophile. Therefore the substituent which raises the electron density on the ring carbon towards the nitration reaction forms o-, p-nitro products.

1.4.2 Kinetics and mechanism of aromatic nitration

Kinetics
Rate =K(HNO_3) (ArH)
1 1
Overall rate = 2
Generally accepted mechanism which is compatible with the data is

$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (Fast) Step - 1
$ArH + NO_2 \longrightarrow ArHNO_2^+$ (Slow: Rate determining step) Step – 2
$ArHNO_2^+ + HSO_4^- \longrightarrow ArNO_2 + H_2SO_4$ Step - 3

1.5 NITRATION IN ORGANIC SOLVENTS

In the **organic solvents** like nitromethane or acetic acid, with HNO_3 in large excess, the **kinetics** of the nitration process **depends** upon the **aromatic compound** being **nitrated**. **Compounds** such as nitrobenzene or ethyl-benzoate with **strongly deactivating group** are nitrated at a **rate** which is **proportional to** the concentration of the **substrate** i.e. the reaction is first order. **Compounds** which are **more reactive than benzene** such as toluene, xylene and p-chloranisole react at a rate which is independent of concentration of the substrate i.e. the reaction is **zero order**. The rate of reaction with all substrates which show zero-order kinetics is the same.

The results may be interpreted in the following manner.

$2HNO_3 \longrightarrow H_2NNO_3^+ + NO_3^-$

$H_2NO_3 \longrightarrow H_2O + NO_2^+$ (nitryl ion)

This **1st step** which represents the transfer of proton from one nitric acid molecule to another is very rapid. The rate at which the **2nd step**, the formation of nitryl ion takes place **depends** upon the **medium**. In a **strongly acidic** and **highly polar solvent** like concH_2SO_4 this takes place **very quickly**. In **less strong acidic media** such as acetic acid or nitromethane this step can be **relatively slow**. The zero order kinetics shown by highly reactive substrate in these solvents indicates that the nitration step is fast compared with rate of formation of NO_2.

$NO_2^+ + ArH \longrightarrow ArNO_2 + H^+$

This is supported by the fact that all these **highly reactive compounds** are nitrated at the **same rate** which is the rate of **formation of nitryl ion**. In the nitration of aromatic substrates of low reactivity, the formation of the nitryl ion is fast relative to the nitration step which is rate determining. Each compound in this class reacts at its own characteristic rate. In the nitration of compounds of intermediate reactivity, both steps occur at comparable rate.

1.6 EFFECT OF HNO2 ON NITRATION: HNO2 (NITROUS ACID)

HNO_2 or NO_2 inhibits or in some cases **catalyses** the process of nitration: The **inhibiting effect** is observed in the nitration of compounds having **no activating groups**, where reaction are carried out either in strong HNO_3 or in mixed acid. In these media the nitrous acid forms the nitrosyl ion (NO^+) and thus reduces the reaction rate.

$HNO_3 + HNO_2 \longrightarrow H_2O + NO^+ + NO_3^-$

$HNO_2 + 2H_2SO_4 \longrightarrow NO^+ + H_3O^+ + 2HSO_4^-$

The **catalytic effect** is observed in the nitration of **reactive substrates** such as anisole or dimethyl aniline which are nitrate in relatively weak HNO_3 where the nitryl ion concentration is low. The catalysis is done to form a nitro compound according to the following equation.

$ArH + NO^+ \longrightarrow ArNO + H^+$

$ArNO + HNO_3 \longrightarrow ArNO_2 + HNO_2$

Because of nitorsyl ion (NO^+) which is much weaker electrophillic reagent than nitryl ion (NO_2^+), it is able to react only with very reactive aromatic compounds such as anisole or dimethylaniline. **Two conditions** are necessary for catalysis by nitrous acid.

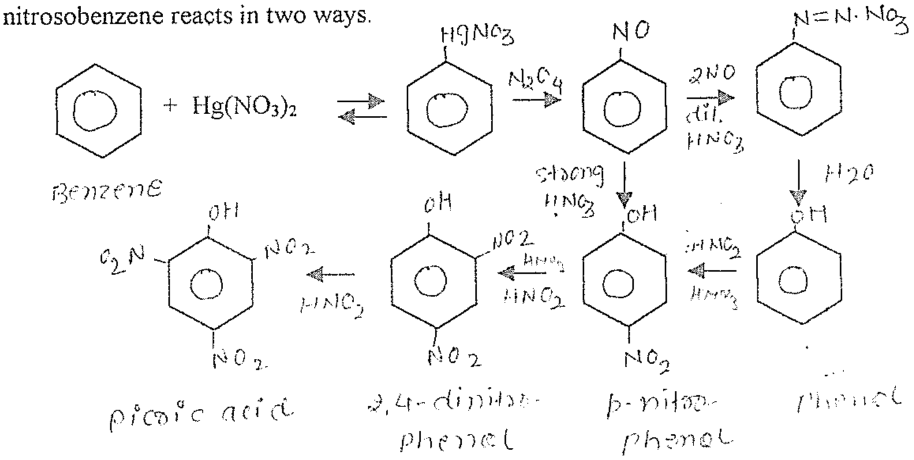
1. The **substrate** must be **sufficiently reactive** so that it can be easily attacked by nitorsyl ion (NO^+)
2. The **reaction medium** must be such that the concentration of nitryl ions is very low, thus allowing the nitrosyl ions to complete favourably for the substrate.

1.7 OXYNITRATION

An interesting reaction occurs between benzene and 50% HNO_3 containing 0.2 molar $Hg(NO_3)_2$ (Mercuric nitrate) which yields up to 85% dinitro phenol and picric acid. This **process** includes both **oxidation** and **nitration**. Hence it is called **oxy-nitration**. Benzene is initially converted to phenyl mercuric nitrate which reacts with nitrogen dioxide to form nitrosobenzene. Each of these intermediates has been isolated from reaction mixture. The nitrosobenzene reacts in two ways

1. In **nitric acid weaker than 50%,** it reacts with 2 moles of nitric oxide to from phenyl diazonium nitrate. The diazonium salt is converted to phenol by water which is nitrated in steps to from final product.
2. In **nitric acid of greater 50%** concentration, the nitrosobenzene is converted directly to p-nitrophenol which is than nitrated to give final product.

nitrosobenzene reacts in two ways.



1.8 NITRATION OF PARAFFINIC HYDROCARBON

They are inert to electrophillic reagent. It is not an electrophillic substitution reaction. It is a **free radical reaction**. **Classification** is done as

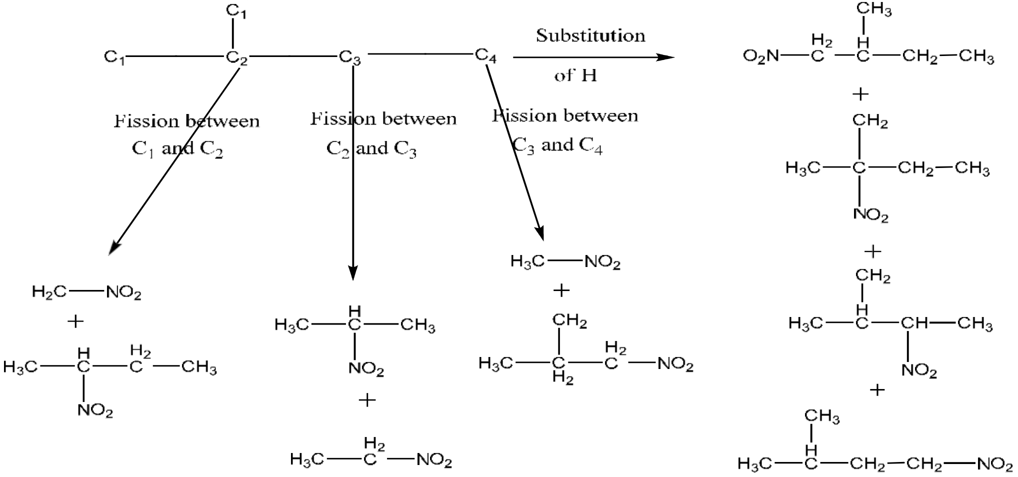
- Gas-phase nitration and
- Liquid-phase nitration,

1.8.1 Gas-phase nitration

Paraffins are quite inert to electrophillic reagent such as the nitryl ion. The paraffins are attacked by certain atoms and free radicals. **Nitration** of these compounds is carried out in industries in **vapour phase** at 350 – 450^{0}C. It is free radical reaction. Nitric acid of strength 70% or less is generally used. We can also use NO_2

1.8.1.1 Nitration products of iso-pentane

A characteristic feature of reaction involving alky radical is the great variety of product formed. This is indicated by **nitration of 2-methyl butane**. This gives all possible **mono- nitration products** that might be formed by **breaking any one** of the **bonds** presents and **introducing** a **nitro group** at the point of cleavage. The products are as under.



More due to nitration, mostly mono nitro compounds are formed. In otherword **poly-nitration does not occur** to significant extent.

Although C – C bond breaks during the reaction no rearrangement of carbon skeleton occurs.

1.8.1.2 Facts as a result of systematic study

- There is **optimum temperature** at which highest yield is obtained.
- The **addition of oxygen** increases yield based on HNO_3 but also increases oxidation of alkane.
- **NO_2 also reacts** with paraffin to yield nitro-paraffin.
- **Bromine** has **beneficial effect** on both yield and conversion to nitro-paraffin using HNO_3.
- **Highly branched hydrocarbons** undergo **less fission** during nitration than to their less branched isomer. Correspondingly substitution is favoured when highly branched structures are nitrated.
- **Temperature coefficient** for H substitution are in order is 1° > 2^0 > 3°
- **Rate of substitution** is in reverse order at low temperature i.e. $3^0 > 2^0 > 1^0$.

1.8.1.3 Steps involved in nitration of paraffin

$HONO_2 \longrightarrow OH + NO_2$

Alkyl Radical formation

$R\text{-}H + {}^\circ OH \longrightarrow R^\circ + H_2O$
$R\text{-}H + NO_2 \longrightarrow R^\circ + HNO_2$

Nitro paraffin formation

$R^\circ + NO_2 \longrightarrow R\text{-}NO_2$

Oxidative and cleavage steps

$R\text{-}CH_2^\circ + NO_2 \longrightarrow R\text{-}CH_2O^\circ + NO$
$R\text{-}CH_2O^\circ + NO_2 \longrightarrow R\text{-}CHO + HNO_2$ R-
$CH_2O^\circ \longrightarrow R^\circ + CH_2O$
$RCHO + NO_2 \longrightarrow RCO^\circ + HNO_2$
$RCO^\circ \longrightarrow R^\circ + CO$
$CH_2O + NO_2 \longrightarrow NO^\circ + H_2O + CO$

Olefin formation (unsaturation)

$$RCH_2CH_2^{\circ} + NO_2 \longrightarrow HNO_2 + CH{=}CH_2$$
$$2RCH_2CH_2^{\circ} \longrightarrow RCH{=}CH_2 + RCH_2CH_3$$

1.8.2 Liquid phase nitration

The reaction is **less important** than the gas-phase nitration **because**

- Low yields
- Low conversions
- Unwanted side reaction occurs. (Oxidation and decomposition)

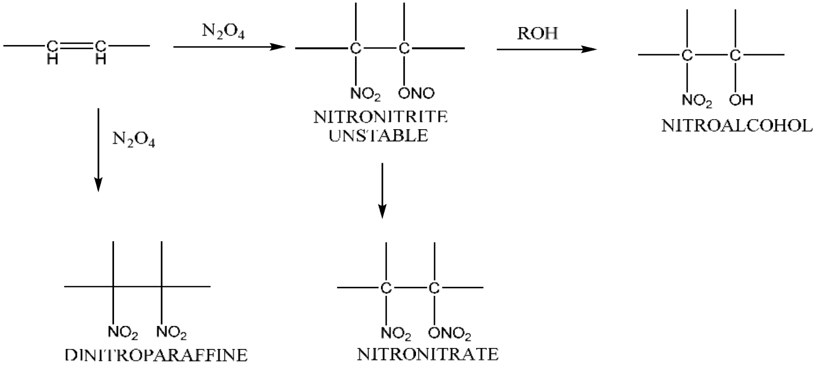
In this reaction, **hydrogen** atom is **replaced** by **nitro** group. The **alkyl groups** are **not replaced.** The **rate of formation of product** is in following **order** $3^0 > 2^0 > 1^0$ nitro-paraffin. The **reaction** is **slow** because of **low mutual solubility** of paraffin and nitration medium. Because of **higher boiling point**, higher hydrocarbons can be **nitrated** at **high temperature**.

The initially formed **mononitroparaffin** is **more soluble** in the HNO_3 than in hydrocarbon and undergoes further reaction **to yield** polynitroparaffins and **decomposition** and **oxidative** products including fatty acids, alcohols and oxides of carbon.

The oxidation which occurs along with the nitration reduces HNO_3 to elementary nitrogen, which cannot be usefully utilized. This makes the process expensive.

1.9 LIQUID PHASE NITRATION OF OLEFINS

NO_2 is **nitrating agent** and **air** is added to oxidize any nitric oxide to dioxide.



REACTION OF OLEFINS WITH NITROGEN DIOXIDE

The **initia**l **products** are **dinitroparaffin** and **nitronitrite**. The latter is unstable and is partially oxidized to stable nitronitrate. The remaining nitronitrite is converted into nitroalcohol by **treatment** of reaction product with **H_2O or ethanol** before distillation.

The reaction is carried out by slow addition of olefin to nitrogen dioxide at temperature **-10 to 25^{0}C**.

The **use of ether** as solvent **minimizes** the oxidative **side reactions**. Ethylene reacts slowly but higher olefins react more rapidly and molar equivalent can be made to react completely in **1 to 2 hrs**. Total **yield** of separated products are **65 - 85%.**

1.10 THERMODYNAMICS OF NITRATION

Nitration reaction is **highly exothermic**. The heat released e.g. in nitration of 1lb of benzene is comparable to that released on condensation of 1lb of steam. The heat problem is much more important because of heat of dilution of nitrating acid and low heat capacity of medium. We must know how to develop and **use thermodynamic data** in **designing** nitrating **equipment** and providing **safe** and **efficient operation**. Since nitration is exothermic, its enthalpy change (ΔH) will be -ve.

1.10.1 Heat of nitration

The **nitration** reaction must be **controlled** by **systematic cooling design** to withdraw the heat energy evolved. When all the energy set free by an exothermic reaction is forced to appear as **heat**, the **quantity** of it **lost** to the cooling mechanism equals the **decrease** in **enthalpy** i.e. **$Q = -\Delta H$** where Q = heat of reaction, represent the total amount of heat lost by the reacting system from the start of reaction till the products return to initial temperature and pressure of the system.

1.102 Thermal properties of nitration acid

- **Heat of solution**

To determine the heat evolved during nitration of hydrocarbon by mixed acid, it is necessary to consider not only the heat of nitration but also various heats of solution.

- **Heat of dilution**

This is the quantity of heat evolved where dilution of mixed acid is carried out.

1.103 Integrated heats of nitration

In nitration of hydrocarbon by means of a mixture of concentrated HNO_3 + H_2SO_4, **total heat liberated** is **equal to** heat of solution of initial mixed acid **minus** heat of solution of final spent acid **minus** heat of solution of the nitric acid entering into the reaction **plus** heat of nitration reaction

Although **heats of nitration** are relatively large, the **control of reaction** is closely related to **heats of dilution** of nitrating acid. The simplest way to integrate heat effect involved is to **sum up the enthalpies** on the both sides of complete reaction equation by the use of heats of nitration and other experimental data.

1.104 Thermal data relating to the preparation and use of nitro compounds

It indicates that when nitration occurs, a considerable amount of **heat is generated**. It has been found that **heats** of nitration **decreases** with **increase** in the number of **nitro groups**.

1.11 PROCESS FOR TECHNICAL NITRATION

Technical nitration can be discussed as batch processes and continuous process.
Each kind of process has advantages peculiar to itself.

1.11.1 Advantage of batch process compared to continuous processes.

- **Flexibility**

Batch process equipment posses general usefulness because each batch of material passing to the process is separate or nearly separate from batches which have proceeded. It is usually **easier to introduce process variations** into a batch process than into a continuous process. Furthermore batch-process equipment is often of such general applicability that a given plant may be readily converted from **production** of **one nitrated material to another**. **Beginning production** of new compound or **pilot production** is conveniently done by the batch process because of operating flexibility, even though a use of continuous of process may be planned for completely developed process.

- **Labour usage**

For high rates of production when **large batches** are used, the labour efficiency of a batch process may be **equal to** a **continuous process** e.g. large scale industrial production of nitro glycerine and nitro toluene.

1.11.2 Advantage of continuous processes compared to batch processes

- **Lower capital cost**

For a given rate of production, the **equipment** needed for a continuous process is **smaller** than batch process. This is the most striking difference between two types of processes.

It is **not** necessary to **accumulate material** in a continuous process anywhere and therefore vessels are designed with the capacities detected by the rate of reaction process step which they must accommodate. Alternatively, because of the relatively **small size** of continuous process equipment, it is often possible and advantageous **to use materials** of **construction** which could be **very high in cost**. If stainless steel is used there is no corrosion problem.

- **Safety**

Because of relatively **small size** of continuous process equipment, there is **less material** in process at any time, than at certain times in a comparable batch process. **E.g.** at the completion of a batch process nitration and during its normal separation of the product from the spent nitrating acid, the entire batch of an often hazardous compound will be present in the material need be present in hazardous condition as needed to gain sufficient reaction or process time. In case of high explosives made by nitration such as nitroglycerine, this safety factor of a continuous process is very attractive.

- **Labour usage**

A continuous process is usually a **more efficient labour user** than a batch process. This is particularly true for small or medium scale production and for hazardous products, since continuous processing **minimizes** the **amounts of material** in the process on the average, it is possible to handle operation at one place that required physical separation in batch process and hence requires additional labour. This discrepancy in labour efficiency disappears as scale of operations increases.

1.12 BATCH NITRATION

1.121 Construction, working and safety measures of batch nitrator

Nitration is usually done in **cast iron** or **steel vessel**. Now a day's **mild carbon steel** is used. When nitrating with **mixed acid** ($HNO_3 + H_2SO_4$), the life of such nitrator is satisfactory and any shot like failure is due to more water or to low actual HNO_3 content in the waste acid. It has been found that during manufacture of mononitrotoluene, as the **water content** of the waste acid increases above **26%** or the **actual nitric** falls below **2.5%,** the rate of **corrosion** on mild steel becomes **very rapid** because alloy steels are preferred for construction the nitrator

Nitrator consists of an upright **cylindrical vessel** with **cooling surfaces**, a means of **agitation**, **feed inlet** or inlets and **product outlet** lines. Most nitrators also have a large diameter thick **dumping line** for emergency use. If the reaction goes out of hand or the temperature rises because of failure of agitation, cooling or otherwise. In such an emergency the contents of nitrator may be dumped rapidly into a large volume of H_2O contained in a **"drowning tub".** A common accessory for a nitrator is **suction line** in the vapour space above the liquid charge to remove the acid fumes and oxides of nitrogen which may be liberated.

The **two factors** of prime importance in the **design of nitrators** are

- The degree of agitation
- The control of temperature.

Agitation in general must be **very efficient**, even violent, in order to obtain smooth reactions and to avoid local over-heating which could occur in strangle sports were to exist

in nitrator is quickly and thoroughly mixed reactant which could lead to local overheating do not occur.

Cooling or other temperature control in nitrators is accomplished by **coils of tubes** through which **cold water or brine** for cooling may be circulated or **hot water or steam** is passed for **heating**. For **control of temperature** in nitration, a wall jacket is not usually efficient enough except in the case of vessels of very small capacity. The need for large cooling surface and for high velocity of cooling medium and nitrator contents past the surfaces dictates use of cooling tubes.

The most common type of **agitating system** used in nitrator has **vertical shaft** with one more **propellers** mounted on it. This shaft propeller is mounted in the cylindrical shape center of one or more banks of cooling coil. An actual **cylindrical sleeve** is sometimes mounted in the center of coil banks to **assure** that **circulation** of nitrator content is **as desired**. When **reactant feed** to the nitrator is **from** the **top** into the **center** of agitator sleeve, circulation by the propellers is usually down through the center and around and up through the cooling coils. When the fed is beneath the liquid level, at the bottom of the sleeve and **cycle acid** is **used**; circulation is up through the sleeve and around and down through the banks of coil. **Good mixing** and **efficient heat transfer** is obtained by this **sleeve and propeller** arrangement. When **cycle acid** is **not used**, circulation is down through the sleeve so that the hydrocarbon fed into the sleeve near the bottom is quickly disperses in mixed acid and immediately passed over the cooling coils.

1.122 Batch nitration of hydrocarbons

Batch nitration of hydrocarbon such as benzene toluene, it has been common past practice **to nitrate** by **using** a **cycle acid**. Here the common practice involved **charging** a sleeve and propeller agitator with **cycle acid** to **above** the level of the **top of cooling coils**. **Hydrocarbon** was than **floated** in on **top of** cycle acid. Nitrating acid was fed into the nitrators in the cycle acid with continuous stirring near the bottom of sleeve under the propeller. This **fortified cycle acid** then reacted at the inter phase of the hydrocarbon and acid in top of the nitrator. Nitration was then completed by allowing the temperature to rise and eventually to emulsify nitrated products and acid. More **modern practice** for this type of hydrocarbons involves **no cycle acid** but consists of feeding the hydrocarbon under the surface of nitrating acid in the bottom of sleeve where agitation is very thoroughly. This is called **direct nitration** and is more satisfactory than the older "indirect' nitration method.

1.13 CONTINUOUS NITRATION

Continuous nitration is carried out in the **same** type of **vessels** as those used for **batch nitration** with the **exception** that an **overflow pipe** or **weir arrangement** is provided for continuous withdrawal of the products and that continuous feed of all the reactants is provided. **Schmid nitrator** and **Biazzi nitrator** are continuous nitrator.

1.131 Schmid nitrator

This nitrator has been designed for the German Schmid Meisener system.

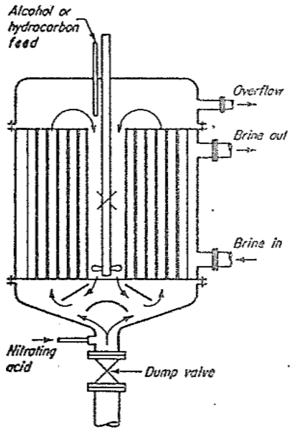


Figure: Schmid nitrator

In this nitrator, the material to be nitrator is fed from top of nitrator and immediately drawn down through sleeve and intimately and thoroughly mixed with the spent acid and reacting materials. In bottom of nitrator, fresh mixed acid is fed and is immediately mixed with the other reactants by means of high flow rate caused by the agitators and baffles. The reacting materials then pass upward with the high velocity through the tubes surrounded by refrigerated brine circulating in the jacket. Products and spent acid are withdrawn continuously from the nitrator through the overflow line.

1.132 Biazzi nitrator

It is designed by Swiss form of M. Biazzi. There is a turbine type agitator provides intensive agitation. A vortex is formed in the center about the agitator shaft. The reactants, both of which are fed in nitrator through the top are immediately drawn into this vortex, thoroughly mixed and circulated down through the center of bank of cooling coils and back up through and around the coils. The high velocity makes mixing and heat transfer very efficient.

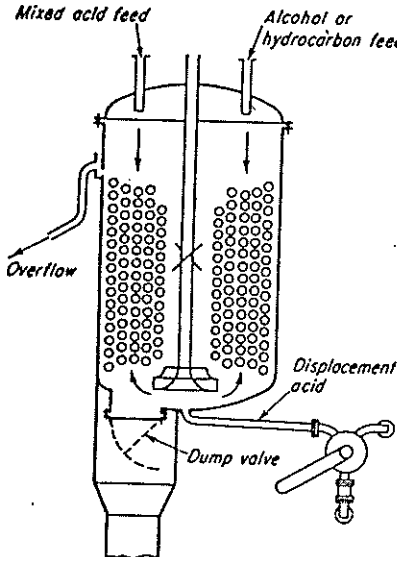


Figure: Biazzi nitrator

In any **continuous equipment**, the designer must be careful to assure that **no stagnant areas** can exist. Also it is quite general to specify **high finishes** on the **interior surfaces** with complete **freedom from** surface **pits** or **pockets** which could trap the product. It is also important that the apparatus must be **completely drainable** so that if the contents must be dumped no product contaminated with acid remains. Alternatively upon shut down of equipment, it is common to displace all products from the apparatus by filling the nitrator from the bottom with spent or cycle acid. Only if the apparatus is completely free of traps or pockets can this displacement procedure be carried out with assurance that no nitrated product will be trapped and remain behind in the nitrator.

Safety measures are similar for both continuous and batch processes. It is common to provide for **automatically stopping feed** of the material to be nitrated **in the event of** an undue temperature rise in the nitrator, a failure of the refrigeration or brine circulation or a failure of agitation. Continuous observation of the nitrator temperature is necessary. The feed of reactant can be controlled by a **"dead man valve"** which can be kept open only by manual pressure. **Solenoid operated controls** which "fail-Safe" are also commonly used. This means that the operation can be carried out only when all necessary services such as power, refrigeration or agitation are functioning.

1.14 MIXED ACID COMPOSITIONS FOR NITRATION

From the technical stand point of using mixed acid, there are two primary conditions that must be met. These are:

1. The **amount of 100% HNO_3** present in nitration must be enough to satisfy stoichiometric requirement of the reaction. It is usually present in excess to maintain reasonably fast overall rate of reaction (nitration).
2. The **amount of 100% H_2SO_4** with dissolved SO_3 (i.e. Oleum, $H_2S_2O_7$) if needed must be sufficient to promote the desired reaction regardless of mechanism of reaction.

Two values which are calculated from reaction stoichiometry in one case and determined in process development in the other case are practical controlled yardsticks. Those values are D.V.S. (dehydrating value of sulfuric acid) and the nitric ratio.

- **D.V.S.:** It is ratio of H_2SO_4: H_2O present at the end of reaction.
- **The nitric ratio (R):** It is the ratio of wt. of 100% HNO_3: wt. of material being nitrated.

The accumulation of water, as a result of nitration reaction would be objectionable, in nitrating medium and the function of sulfuric acid is to make it ineffective.

1.141 Relation between D.V.S. and stability of the nitrator charge

An important consideration in nitration of glycerin and related compounds is the stability of the nitrator charge or product in contact with its own spent or partially spent acid. Any condition which lowers the stability is increasing the hazards because of firing in the nitrator. High D.V.S. favours high stability of nitrator charge. Decrease in D.V.S. results in lower stability.

1.15 NITROBENZENE

Nitrobenzene can be manufactured by

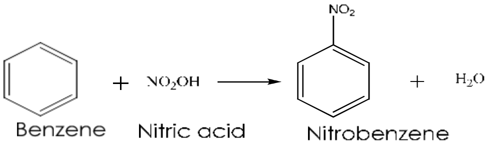
- Batch Nitration with mixed acid
- Continuous nitration with fortified spent acid

1.16 BATCH NITRATION WITH MIXED ACID

1.16.1 Raw Materials

Benzene: 10000lb
Mixed acid: 23300lb
Nitric acid ratio: 1.04

1.16.2 Reaction



1.16.3 Manufacture

Use of cycle acid is not essential, particularly when the problem of heat transfer has been satisfactorily solved. The operation commence by delivering to the nitrator sufficient **cycle acid**, i.e. spent acid from a previous charge in which some nitrobenzene and nitric acid are still present, The **amount** of such **acid** required depends on the type of nitrator used. In the **sleeve and propeller** type, it should cover the cooling coils; in the **Hough 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^{0}C** or lower, the charge of **benzene** is pumped from the scale tank into the nitrator. The **mixed acid** for nitration can be fed on the top of the hydrocarbon or under surface.

The temperature of nitration for benzene may very within moderate limits. When **no cycle acids** used, the temperature **below 50^{0}C** is kept, when **fortified spent acid** is employed the nitration temperature may be kept **between 50^{0}C** and **55^{0}C**.

1.16.4 Separation and Neutralization

The **separation** of the nitrobenzene is done in large **conical bottomed lead tanks**, each capable of holding one or more charges. The nitrator charge is **settled** here for **4** to **12 hrs.,** when the spent acid is drawn off from the bottom of the lead tanks and delivered to the **spent acid tanks** for additional settling or for treatment with benzene next to be nitrated, in order to extract the residual nitrobenzene. The **nitrobenzene** is then delivered to the **neutralizing house**. The **neutralizing tub** may be either a large lead conical shaped tubecontaining 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 **warmed** with live steam for **30 min**. or **until neutral** to Congo and then allowed to settle for a similar period. The supernatant acid water is then run off through side outlets into a labyrinth where practically all the immersed nitrobenzene will settle out. The charge is now given a **neutralizing wash** at **40-50^{0}C** with a 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 up; otherwise, a final washing with a small quantity of warm water is made.

The nitrobenzene is then delivered to its **storage tanks**, where it is again **settled** to remove final traces of water. The **crude product** can now be **distilled** for commerce or used directly for the preparation of aniline. In some plants where the nitrobenzene is used almost exclusively in the aniline plant, the neutralizing and subsequent washes are omitted. The nitrobenzene delivered to the reducer house it, consequently acid. No harmful effects on the equipment are noticeable, if the acidity is kept below 0.5 percent.

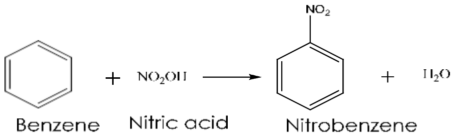
1.17 CONTINUOUS NITRATION WITH FORTIFIED SPENT ACID

Methods for the continuous nitration of benzene have been proposed by **Castner and Mares**. Both processes are base on the recognition that a slightly HNO_3 - fortified spent acid constitutes a satisfactory nitrating agent for a limited quantity of hydrocarbon. For large scale production, it is necessary to circulated relatively large quantities of acid of low nitric acid content high heat capacity and to remove the water of nitration continuously in an integrated evaporator operating under reduced pressure. When the heat of sulfuric acid hydration and the chemical heat of nitration are evolved in separate vessels by adding nitric acid to prepared mixture of benzene, sulfuric acid and water, the hazards of nitration are further reduced and it is feasible to operate safely at relatively high temperatures and to utilize the sensible heat in effecting the subsequent removal of water from the spent acid.

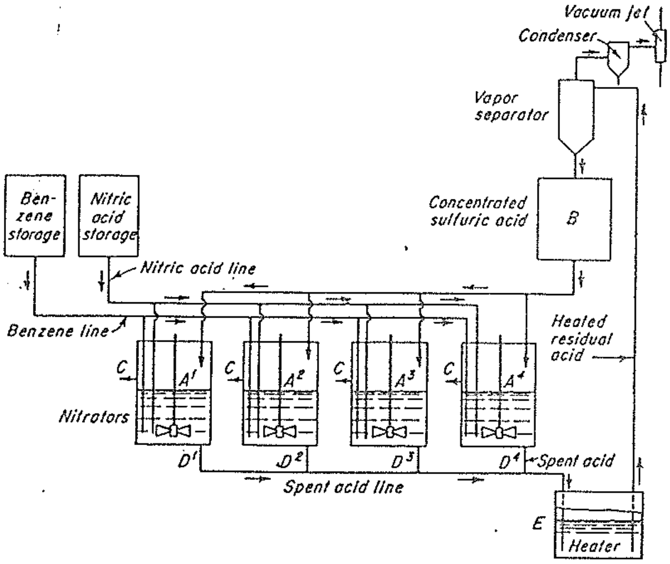
1.17.1 Raw materials

Benzene, Nitric acid, sulfuric acid are the main raw material for continuous nitration.

1.17.2 Reaction



1.17.3 Manufacture



Hot **sulfuric acid** at **90^{0}C** is run from the heat insulated **storage tank (B)** into one of a battery of **nitrator (A_1 to A_4).** Under vigorous agitation, sufficient **63% nitric acid** is added to the nitrator to produce a mixed acid containing 4% HNO_3. 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 min**. 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 off through **side outlets C** on the nitrator and sent to the **neutralizer**. The **spent acid** which is free of nitric acid but contains small amounts of nitrobenzene is drawn off in operating sequence at the **outlets (D_1 to D_4)** located at the base of the nitrators.

The spent acid is first directed to the **acid heater (E)** which is heated by low pressure steam to maintain the sensible heat of the spent acid (72 percent H_2SO_4) and delivered to the vapour 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 (75 percent) strength. The small quantity of nitrobenzene found with the water in the condenser is separated and added to the crude charge.

1.18 m - DINITROBENENE

1.18.1 Raw materials

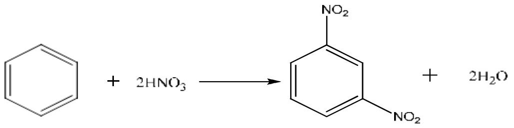
Benzene

Mixed acid composition

(1) For mono-nitration		(2) For di-nitration
60.0%	H_2SO_4	75.0%
32.0%	HNO_3	20.0%
08.0%	H_2O	05.0%
03.52%	D.V.S.	07.36

01.01 Nitric ratio 01.

1.18.2 Reaction



1.18.3 Manufacture

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 nitrobenzene. At the conclusion of the first nitration, the spent acid is run off from the base of the machine and is replaced by a storage nitrating acid for the **second stage** of nitration. The composition of the nitrating acids for the both stages of nitration is as shown above.

It is readily seen from compositions that the **second nitration** required a **more concentrated acid**. Moreover, the reaction must be controlled at a higher temperature i.e. **90-100⁰C**. 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 this nitration.

In the combined operations **2,200Kgs of spent acid** from a dinitration (about 80% H_2SO_4) is retained in a **jacketed cast-iron nitrator** of 8 cu. ft. (2,112 gal) capacity that is provided with a lead cooling coil and sleeve in which a stirrer operates at 110 rpm. To this added **1900Kgs mixed acid** analyzing 88 percent HNO_3, 11% H_2SO_4 and 1% H_2O. Then **2200Kgs benzene** is introduced over a period of **4 hrs** while controlling the temperature initially at **25⁰C** and finally at **40⁰C**. The temperature is then raised to **60⁰C in 1 hr**. The charge

is permitted to stratify and the spent acid is discharged to a lead lined washer with stirrer where it is **washed with** either benzene or nitrobenzene.

To the nitrobenzene retained in the nitrator, there is **added** over a **3 hr.** period **5,000- 6000 Kg.** of **mixed acid** (Approx 33 % HNO_3, 67% H_2SO_4) permitting a temperature **rise** from **25⁰C to 40⁰C**. The temperature is then raised to **90⁰C** and maintained there for **1 hr** or until free of nitrobenzene by the steam distillation test. The charge is settled and the spent acid run into a large **washer**, where several batches are washed with nitrobenzene. The dinitrobenzene is delivered to a tile lines or stainless steel washer, provided with a lead cover and stirrer. Here, it is **washed** first with **4,000 liters** of **hot water**, then with **caustic soda** solution until neutral and finally with water.

About **4,500kgs** of crude molten **dinitrobenzene** (85% m-, 13% o-, 2% p-) obtained from each nitrator charge is purified by mixing thoroughly with **3,000 liters** water at **80⁰C** in a jacketed cast iron vessel. The contents are allowed to cool without heat exchange, until about **70⁰C** when pelleting begins. Then **650kgs sodium sulfite**, which converts the para and ortho derivatives to nitramines, is added at a rate of 100kgs/15 minutes. During this period, temperature rises to **78⁰C**. **Stirring** is continued for **3 hrs**, when a **solidification point** on a washed and filtered sample should **not** be **less** than **88.5⁰C**; if lower 25-50kgs more sodium sulfite is added.

The molten charge is cooled by means of the water jacket to 20 - 25⁰C. Then, while water is introduce, the mother liquor is pumped off through a filter basket until the color of the wash changed from dark red to clear yellow. The first wash waters are discharged and sufficient yellow water is retained for washing the next batch. After as much water as possible has been removed via the basket, the charge is heated to 95⁰C, settled for half hour and the oil run into a cylindrical steel steam jacked vacuum drier that is fitted with steam heated run off cocks. The residual water is retained for the next batch. Over all **yield** on benzene **81.9%.**

1.19 p-NITROACETANILIDE

1.19.1 Raw material

In the nitration of acetanilide, it is important in order to prevent hydrolysis, to conduct the nitration at 3-5^{0}C. To ensure a maximum yield of product, use is made of cycle acid, which in this instance is water-white 66 Be sulfuric acid

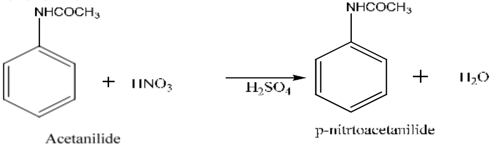
1.19.2 Raw materials

Acetanilide: 1000lb

Mixed acid of composition

HNO_3	33 %	H_2O	20 %
H_2SO_4	47 %	HNO_3 ratio	1.015

1.19.3 Reaction



1.19.4 Manufacture

In to **4,000 lb** of **sulfuric acid** free of nitrous acid, **1,000 lb** of dry **acetanilide**/mp 133^{0}C) is added very slowly. During these **3-4 hrs**., the **temperature** is maintained at **25^{0}C**. The charge is cooled to **2^{0}C** and **1,450 lb** of **mixed acid** of the composition as above is then slowly run into the nitrator. The **rate of feed** being regulated by the capacity of the brine coil to control the temperature at 3-5^{0}C.

Agitation is continued for 1 hr longer, the entire operation consuming **10-12 hrs**. When the temperature rises above 5^{0}C during nitration, there is a distinct tendency towards the formation of the ortho isomer. To **test for complete nitration**, a sample is drawn from the nitrator and poured on ice and the p-nitroacetanilide washed with cold water. The precipitate is hydrolyzed in a test tube with boiling dilute (caustic), and the resulting p-nitro aniline should yield a clear yellow solution with hydrochloric acid. If the acetanilide has not been completely nitrated, the odour of aniline may be detected.

The batch is run from nitrator on to a **suction filter** containing **600 gal of water** and **sufficient ice** (or a brine coil) to keep the temperature **below 15^{0}C**. It is provided with a stirrer that is set in motion just prior to receiving the charge form the nitrator. The temperature should be kept close to **5^{0}C** otherwise, the weak mineral acid present will **hydrolyze** some of the p-nitroacetanilide and the mixture will turn yellow owing to the formation of p-nitro anilinesulfate. The p-nitroacetanilide, which is brown as it runs from the nitrator is changed to milky-white mass as it comes into contact with the cold water.

When the p-nitroacetanilide is to be sold, it is **twice washed** on the filter with cold water until practically **free of acid** and then with minimum of 3 percent caustic soda or sodium carbonate solution. The neutralized cake is finally washed to remove the excess of alkali and then it is removed and dried.

The **yield** of p-nitroacetanilide is **88- 90%** of theory or **160-162 lb** per **100 lb acetanilide** taken.

AMINATION BY REDUCTON

1.20 INTRODUCTION

Amination by reduction involve the synthesis of amines by reductive methods. **Amines** can be **produced by reducing** nitro, nitroso, hydroxylamino, azoxy, azo and hydrazo compounds as well as oximes, amides, nitriles and azides. In each case, a carbon to nitrogen bond already exists. Amines may also be formed by **reacting compounds** containing certain **labile groups** (e.g. halogens, hydroxyl and sulfonic) with ammonia.

1.21 METHODS FOR THE PREPARATION OF PRIMARY AMINES

- ¾ The **reduction of** nitro, nitroso, hydroxylamino, azoxy, azo and hydrazo compounds.
- ¾ The **reduction of** nitrites, amides, oximes and azides.
- ¾ The **replacement of labile groups**, such as nitro, halogen, hydroxyl and sulfonic acid by reaction with ammonia or ammonia progenitors such as urea.
- ¾ **Intramolecular replacement** of (a) hydrazobenzenes and hydroxylamines (b) amides and (c) secondary and tertiary amines.
- ¾ The **hydrolysis** of N-substituted amides.
- ¾ **Direct amination** by means of hydroxylamine and sulfuric acid.

First four are the most important methods from chemical engineering point of view.

1.22 USES OF AMINES

Amines are of very great importance **as intermediates** in the chemical process industries. They are used in **production of** dyes, rubber chemicals, nylon, pharmaceuticals, gasoline additives, surfactants, textile auxiliaries, photographic chemicals, chelating agents, sweetening agents, agricultural chemicals, polyurethanes, inks, plastics etc.

In recent years, the production of diamines by reductive methods has become increasingly important. **Hexamethylenediamine** is a prime intermediates, together with adipic acid, in the production of nylon 66. **m-phenylenediamine** is used as a crosslinking agent in epoxy resin. **Toludenediamines** are intermediates in the production of toluene disocyanates, from which are made polyurethane foam, rubbers, coatings and adhesives.

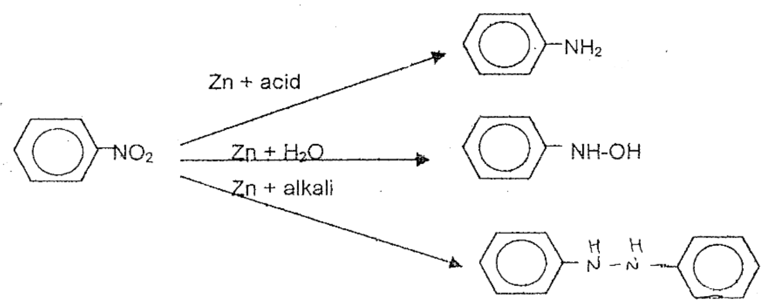
1.23 METHODS OF REDUCTION

A great variety of reduction methods have been used for the preparation of amines. Among these are:

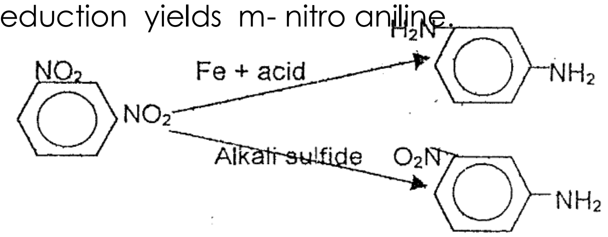
1. **Metal and acid:** Iron and acid (Bechamp method) is the major example in this category, but other metals (tin, zinc) have also been employed. Generally, hydrochloric acid is preferred, but sulphuric acid, acetic acid and formic acid have also been used.
2. **Metal and alkali:** This method is used mainly for the production of azoxy, azo and hydrazo compounds. The latter are important in the manufacture of the benzidine series.

3. **Metal hydrides**
4. **Catalytic:** This method involves the use of hydrogen (or hydrogen - containing gases) and a catalyst such as nickel, copper, platinum, palladium or molybdenum sulfide.
5. **Sulfide:** This is used mainly for the partial reduction of polynitro aromatic compounds to nitro-amines and for reduction of nitro-anthraquinones to amino- anthraquinones.
6. **Sulfite (Piria method):** The reaction of sodium sulfite and bisulfite on an aromatic nitro compound leads to a mixture of amine and aminoaryl sulfonic acid.
7. **Sodium hydrosulfite** (hyposulfite).
8. **Electrolytic**
9. **Sodium and sodium alcoholate**.
10. **Strong caustic oxidation-reduction**.
11. **Hydrogenated quinolines and naphthalene**.

By a **proper selection** of reducing agent and careful **regulation of** the **process**, reduction may often be stopped at intermediates states and **valuable products** other than amines **obtained**. **Metal and acid** reduction is most vigorous and usually yields amines as end products. When nitrobenzene is treated with zinc and a mineral acid, the resultant product is aniline. When an **alkaline solution** is employed, hydrazobenzene is generally obtained, but very vigorous conditions sometimes result in the formation of aniline. When **zinc dust** and **water** are used, reaction product is phenyl hydroxylamine as shown below.



When the compound to be treated contains **more than one nitro group**, the product of **reduction depends** upon the agents used. Thus, m-phenylenediamine is obtained by the iron and acid reduction of m-dinitrobenzene, while the alkaline sulfide reduction yields m- nitro aniline.



With certain compounds containing acid or alkali sensitive groups (e.g. ester or amides), it is necessary to adjust the pH carefully to avoid decomposition and side reactions. In such reductions on the acid side, it is generally advisable to replace the normally used mineral acids with organic acid like acetic acid. An example of the latter is the reduction of nitroanilides, for here the presence of mineral acids would tend to hydrolyze the anilide to an amine.

The **method** to be **used** will therefore, **depend upon** the degree of reduction desired, the sensitivity to the process of both starting material and final product, the need for avoiding contaminants and the overall economics.

The reduction of nitro compounds involves the progressive removal and replacement by hydrogen of the oxygen in the -NO_2 group. The **intermediate products** in the reduction of nitrobenzene, whose **interrelationships** are shown in the following figure are obtained by control of the reduction potential of the system.

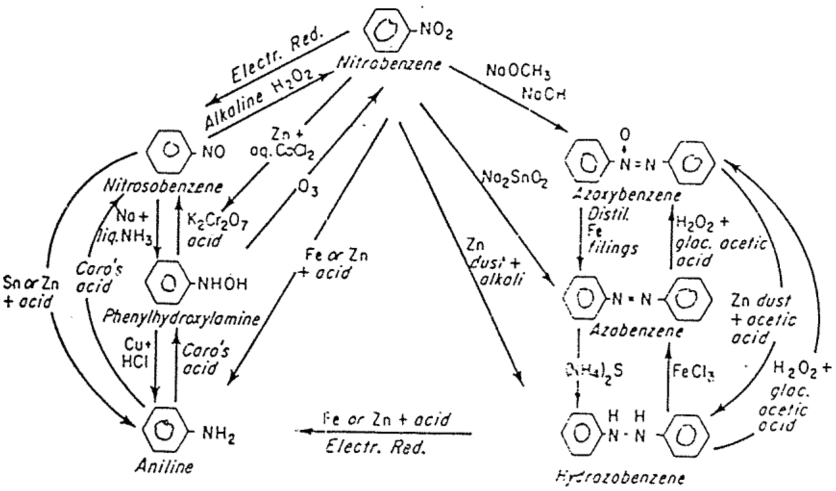


Figure: Reduction products of Nitrobenzene

1.24 IRON AND ACID (BECHAMP) REDUCTION

Bechamp's discovered in 1854 that nitro compounds could be reduced in the presence of iron and acetic acid. **Parkin** applied the reaction in the commercial production of aniline. Technical progress in the application of this reaction was first made by substituting hydrochloric acid for the acetic acid, originally employed. Subsequently, it was discovered that the ferrous functions in such a way that reduction could be carried out with far less than the theoretical quantity of acid.

Reaction: $C_6H_5NO_2 + 2Fe + 6HCl \longrightarrow C_6H_5NH_2 + 2H_2O + 2FeCl_3$

Formula wt.:123 2(55.84) 6(36.45)

In industrial practice, less than 2 % of the amount indicated above is actually used. Operating experience has shown that 3.0 lb of hydrochloric acid (10 lb of 30 % solution) is sufficient to bring about a satisfactory reduction of 100 lb of nitrobenzene to aniline.

The presence of free acid has been shown to be unnecessary. It is demonstrated that nitrobenzene could be reduced with iron powder in alcoholic or aqueous solution, in the presence of magnesium or calcium chloride. The absence of free acid is advantageous. It has been demonstrated that aniline hydrochloride, aluminium chloride, sodium bisulfate or other salts derived from strong acids can be successfully employed. All that is required is a salt that acts like an acid in water solution, liberating hydrogen ion.

1.24.1 Chemical and physical factors

1.24.1.1 Amount of iron

In plant practice, it is customary to use slightly over **2 moles Fe** per mole nitro compound to carry out the reduction process. Under such circumstances, not all the iron is converted to the ferrosoferric oxide, some reducto - active ferrous hydroxide also being present. In plant, practice, it has been found that when **insufficient iron** is present the addition of heat or acid is not effective in carrying the reduction to completion and poorly filtering iron oxide sludge is obtained. The introduction of some finely divided iron under such circumstances brings about a vigorous reaction, which results in the complete reduction of the nitro compound. The range of iron generally used is about **2.5 - 5.0 moles** per mole of nitro compound. This has been found satisfactory for a wide variety of aromatic amines. Some operation prefers to use very **finely divided iron** to finish a reduction and this practice is particularly advisable when the bulk of the iron turnings is not of good quality.

1.24.1.2 Physical condition of iron

The iron fed into the reducer not only supplies the metal absorption surface but also enters into the reactions by providing the iron for the regeneration of the ferrous chloride upon the hydrolysis of the phenyl ammonium chloride (aniline hydrochlorides) and also acts as an oxygen carrier. A clean, finely divided, soft, gray cast iron yields the best results. The **rate of reduction** depends on the **fineness** and **porosity** of the iron particles, the homogeneity of the charge in the reducer, and the degree of etching imparted to the iron by the preliminary acid treatment. To ensure thoroughly **etched iron** it is customary to boil the iron and acid suspension before adding any nitro compound. When this precaution is observed, the reaction proceeds very readily, with no danger of a violent deferred reaction. Iron borings, turnings or shavings are generally used. With coarse particles, the oxidation of the iron is retarded and an excess of it must be provided. It is clear that the use of **finely divided iron shortens** the **time** of reaction.

1.24.1.3Amountofwater

Theoretical considerations indicate the desirability of using 4-5 moles of water per mole of nitro compound treated.

$$4RNO_2 + 9Fe + I6H_2O \longrightarrow 4RNH_2 + 3Fe(OH)_2 + 6Fe(OH)_3 \longrightarrow 4RNH_2 + 3Fe_3O_4 + 12H_2O$$

Owing to the fact that part of the iron hydroxides formed losses water to form the ferrosoferric oxide during the course of the reaction, it is entirely possible that the reduction may be made with less than 4moles of water**.** **Practical problems** relating to (1) the agitation of the reaction mass (2) the promotion or a smooth active reaction and (3) the conservation of the heat of reduction make it advisable to use a slight excess. Where the nitro compound contains a solubilizing group, such as sulfonic or carboxylic residue, and the resulting amine is filtered from alkalinized iron oxide sludge, **much more water** is generally **used (50-100moles)**

1.24.1.4Amountofacid

This reaction required the presence of small amounts of ferrous ion to act as a catalyst. Generally about **0.05 - 0.22** of an equivalent of **acid** is **used**. The acids usually employed in the reduction process are hydrochloric and sulfuric acid.

1.24.1.5Effectsofagitation

A sturdy **sleeve and propeller** or **double impeller type** of stirrer will be superior to the slow moving plow type, speeding up the reaction considerably.

Most aromatic nitro compounds (not containing basic groups) are practically insoluble in faintly acid solution, and through mixing is a factor of major importance. A method involving **use of rotary mills** having freely moving ponderous agitators, such as iron balls for the reduction of nitro, nitroso and azo compounds to amines with iron in aqueous emulsion in order to effect grinding action during the reduction. Such mills are also useful in the distillation of aromatic amines from the iron oxide sludge in vacuum.

1.24.1.6 Reaction temperature

The use of a high catalyst concentration (3 % or more compared to nitrobenzene taken) during reduction results in a finely divided iron sludge which although it is generally a poor filtering sludge, is of possible a commercial value (for removing sulphur compound from illuminating gas). This result can obtain by limiting the quantity of water introduced into the jacketed reducer and utilizing the heat of reaction to carry on the reaction. An obvious advantage arising from operating with such **concentrated solution** is the fact that the charge is easily maintained at the **boiling temperature**. The vigorous reflux that characterizes such as a reduction ensures against the formation of intermediate product of reaction. The reaction is not only rapid but is economical on account of the lower consumption of steam.

1.24.1.7 Additions of solvents

Where a very insoluble and **difficulty reducible** nitro compound is to be reduced, the addition of a **solvent miscible** with **water**, such as ethyl alcohol, methanol or pyridine is often considerable help. This makes for a smoother and more rapid reduction. In carrying out the reduction, the alkalinized iron oxide sludge is filtered off hot and washed with hot solvent. The resulting amine is then isolated from the filtrate. This method is used where reduction in water alone is extremely slow or where the final amine can be isolated only by solvent extraction.

1.24.1.8 Testing for completion

Reduction will **not take place** in the **absence of ferrous ions**, which can be demonstrated by the lack of a black precipitates on spot testing with sodium sulfide solution. The reaction is considered complete when an aliquot no longer increases its take up sodium nitrite on further reduction with a stronger reducing agent, such as zinc and hydrochloric acid.

1.24.1.9 Work up of reaction mixture

Soluble iron is generally precipitated with alkali, using caustic soda, soda ash, lime or magnesia. Where the amine is volatile, it may be isolated by steam distillation or by vacuum distillation from the iron oxide cake after distilling off the water. Where the **final amine** is **soluble in alkaline solution** the iron oxide cake is filtered off and the amine isolated from the filtrate. When the final amine is **volatile** but **sensitive to alkali**, as is the case with some polychloroamine the amine may be steam distilled from the slightly acid mixture.

1.24.1.10 Continuous processing

Although the Bechamp reduction is generally carried out on a batch basis, it has been run continuously. This involves passing an acidified solution or emulsion of the nitro compound through a suitable tower packed with iron shavings or scraps iron and kept at the required temperature.

1.24.1.11 Recovery of by- products

In the technical preparation of amines by catalytic reduction with iron and a soluble salt, it is not customary to **recover and utilize** the dissolved **catalyst**.

1.24.1.12 Yield of amine

In plant, yields in the range of **85-98% of theory** are obtained with the Bechamp reduction.

1.24.2 Equipment

1.24.2.1 Material of construction

Bechamp reduction is usually carried out in **cast - iron vessels** and **alkali reduction** in **carbon steel vessels** of desired sizes. The larger ones (1,600 gal capacity) are favoured by plant engineers because of the possibilities of more economical operation.

The **reducers** for iron and acid reductions are sometimes equipped with side and bottom **cast - iron lining plates**, which may be reversed or replaced, in order to protect the vessel against the continuous, erosive action of the iron borings. Alternatively the reducers may be **lined partially** or **entirely** with acid resisting brick or tile. **Wooden equipment** is also used, particularly for the reduction of solid nitro compounds such as p-nitro aniline.

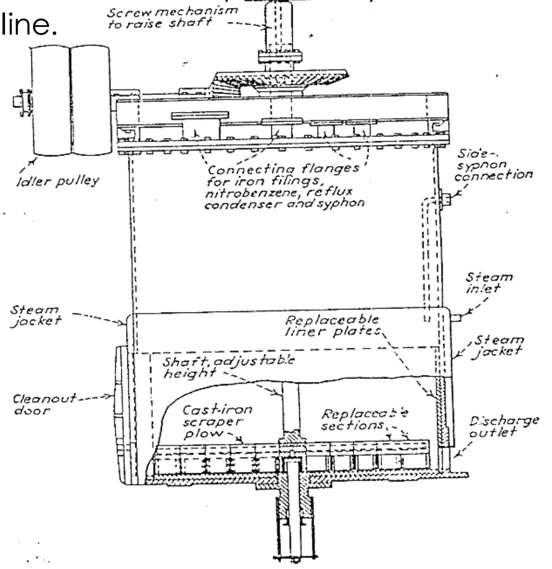


Figure: Jacketed reducer

1.24.2.2 Agitation

In some reducers, a vertical shaft carries a set of **cast iron plows**, which can be removed through the side door to the reactor. These plows travel at the rate of **30-50rpm** and serve to keep the iron particle in suspension in the lower part of the vessel. It will be recalled that the **iron and acid** reduction process is a **four component system** e.g. reducible organic compound, water, acid or metal salts and metal. Obviously, the best results in such a catalytic process can be obtained only when all of the components are in intimate contact.

1.24.2.3 Jacketing of reducers

Practically all the iron reducers employed for the Bechamp reduction of liquid nitro compounds are **equipped** with **jackets**. Although the reduction process is distinctly **exothermic**, the reaction precedes best at slightly elevated temperatures. It is customary, therefore, to warm the reactants at the start.

When jacketed reducers are employed, the heat is applied indirectly and no dilution of the charge occurs. Under such circumstances, the **optimum** quantity of **water** can be delivered during the **"feeding" stage** and the reaction is kept active by regulating the introduction of the reactants.

When the reaction **vessels** are **not jacketed**, as is the case with brick or tile-lined kettles, live steam is introduced to start and maintain the reaction. Care must be taken that the charge does not become unduly diluted. Otherwise, the concentration of acid is lowered and the reaction rate decreased. Yields may also suffer.

1.25 MANUFACTURE OF ANILINE FROM NITROBENZENE BY BECHAMP REDUCTION

1.25.1 Raw materials

Basis: 1 metric ton
aniline Nitrobenzene:
1390 kg Iron borings:
1600 kg
Hydrochloric acid: 125 kg

1.25.2 Reaction

$$4C_6H5NO_2 + 9Fe + 4H_2O \xrightarrow{HCl} 4C_6H_5NH_3 + 3FeO_4 \quad 90 – 95\% \text{ Yield}$$

1.25.3 Manufacture

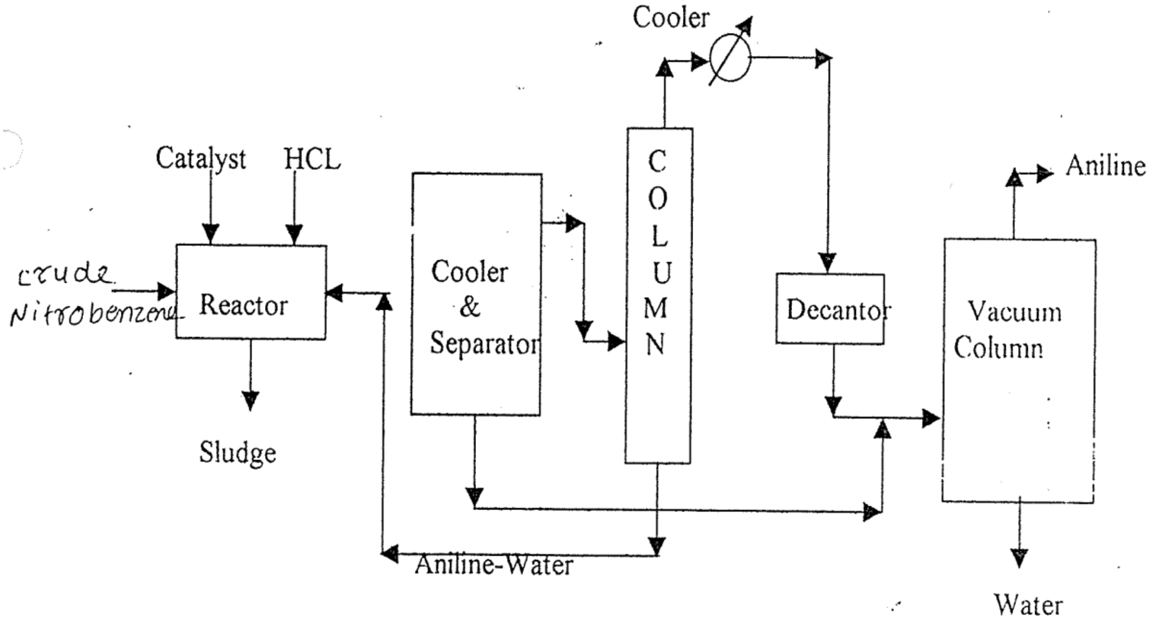


Figure: Manufacture of aniline from nitrobenzene by Bechamp reduction

Crude **nitrobenzene** is charge into a **reducer** (reactor) fitted with an efficient reflux condenser. The reducer is a **steam jacketed cast iron** enclosed cylindrical vessel containing an agitator. **Cast iron** borings (turnings) or powder (free from oil and non - ferrous metals), **water** and **catalyst** are added gradually, in small quantities, to the nitrobenzene.

Generally **10 to 20%** of the total iron is added at the beginning and the mixture is heated by steam to **reflux temperature** (200°C). The remaining iron is added over a period of time at a rate determined by the proper pressure temperature balance. The **addition rate** is fast enough to maintain lively reflux by the heat generated from the exothermic reaction, yet slow enough to prevent excessive hydrogen, pressure build up.

The **water** required for the reaction is generally in the form of aniline water recovered from the **separator** or column and is added to the reducer in bulk at the start or in small quantities along with the iron additions. Dilute **(30%) HCl** acid is added along with the water **as catalyst**. The acid reacts with the iron borings. Forming catalytically active iron salts. Subsequent runs may utilize aniline hydrochloric acid mother liquor as the source of the catalyst and some of the reaction water; the **weight ratio of reactants** is approximately 115 parts of **iron borings**, 0.27 parts of 100% **hydrochloric acid** and 60 parts of **water** per 100 parts of **nitrobenzene**. After the last addition, the reaction is heated with steam to maintain lively reflux.

At the **end of the reduction** (about 10 hrs. for 2250kg charge), the **aniline** is **separated** from the reducer charge by one or more of several methods, The liquid **water aniline mixture** may be separated from the solid iron oxide iron hydroxide sludge by steam distillation, vacuum distillation, filtration, centrifugation or siphoning. For example the finished reduction product may be neutralized with a small amount of sodium carbonate (about equal to the amount of hydrochloric acid in the charge) and allowed to settle. Most of aniline and some water siphoned off and the residual aniline is separated from the sludge by steam distillation. The **sludge** consisting of ferric oxide, water and small amount of ferric oxide is dumped and may be marketed after drying.

The water aniline mixture from the reducer is run to a separator where the lighter aniline separates and is withdrawn from the upper. The top layer, which contains 3 to 5% aniline, is partially distilled until the aniline content in the water is low. The residual aniline water is returned to the reducer for subsequent runs. The aniline in the distillate is separated by decantation and the water layer is redistilled to obtain the remaining aniline. An **alternate procedure** is to extract aniline from the aniline water with nitrobenzene.

The aniline streams from the separator and decanter are united and vacuum distilled to yield purified aniline. The **yield** based on nitrobenzene is approximately **95%** by weight.

1.26 MANUFACTURE OF ANILINE FROM CHLOROBENZENE BY AMMONOLYSIS

1.26.1 Raw materials

Basis:1 ton aniline

Chlorobenzene	= 2,500 lb
Ammonia solution(28%)	= 7,450 lb
Cuprous oxide	= 350 lb

1.26.2 Reaction

$$C_6H_5Cl + 2NH_{3(aq)} \longrightarrow C_6H_5NH_2 + NH_4Cl\ (soln)$$

96% yield

1.26.3 Manufacture

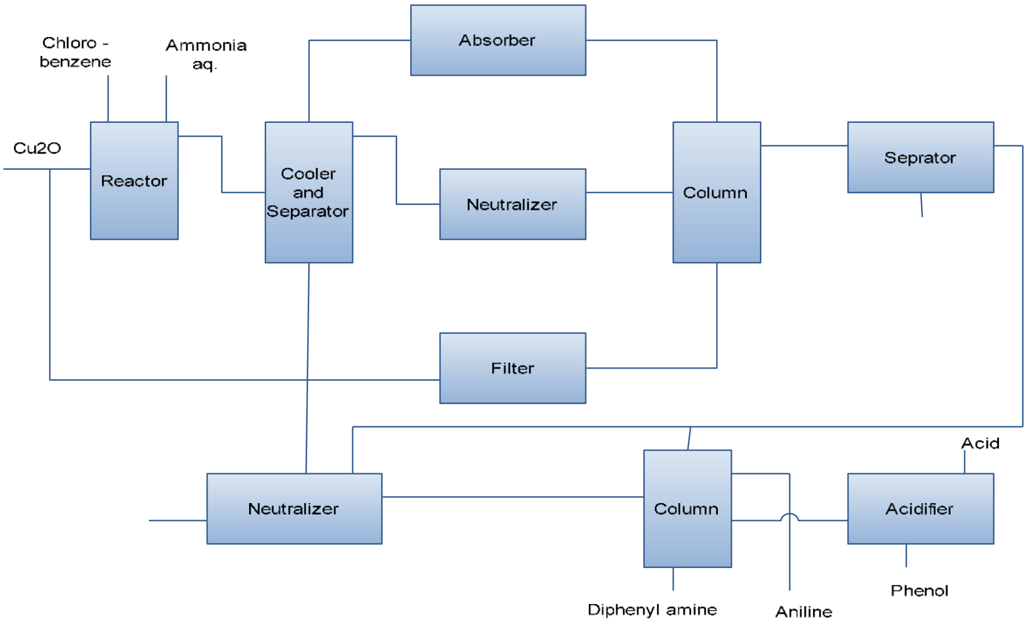


Figure: Flowchart for production of Aniline from chlorobenzene by Ammonolysis

Chlorobenzene is charged into a series of horizontal, rotating high - pressure rolled steel **autoclave**. Approximately 0.1 mole of **cuprous oxide** and 4 to 5moles of 28 to 30% aqueous **ammonia** per mole of **chlorobenzene** are added. The reaction is initiated at a temperature of **180°C** and is later maintained at **210 to 220°C** under constant agitation. The pressure rises to **750 to 850 psi**. The **active catalyst** is **cuprous chlorine** produced from cuprous oxide by the product ammonium chlorine as follows:

$$Cu_2O + 2NH_4Cl \longrightarrow Cu_2Cl_2 + 2NH_3 + H_2O$$

A **large excess** of **ammonia** solution is used to **suppress** the phenol producing **side reaction** ($C_6H_5Cl + NH_3 + H_2O \longrightarrow C_6H_5OH + NH_4Cl$).
If the indicated ratio of reactants is used, the rate of aniline formation is about 20 times greater than the rate of phenol formation.

The reaction **products** are **cooled** below 100°C and run to a **separator**. The free ammonia continues to absorption and condensing system for recovery. The settled **reaction mass** separates into **two layers**: **aniline rich** lower and an **aqueous** upper layer. The approximate distribution of reaction products not including unreacted chlorobenzene in the two layers is as follows: **aniline layer** 82% aniline, 5% phenol, and 1% diphenylamine; **water layer** 5 % aniline, 0.5% phenol, 9% chlorine ion (NH_4Cl), 3% cuprous oxide and 14% ammonia.

The **aqueous layer** is drawn from the top of the separator and is run to a **neutralizer**, where it is treated with **sodium hydroxide** or **lime**. A sufficient amount of alkali is used to react with the ammonium chloride and phenol. The solution is **fractionally distilled**, and the liberated ammonia expelled first is recovered in an **absorption system**. The **second fraction** consists of aniline and water, which are separated by decantation. The **residual solution** of sodium phenate and sodium chloride is filtered to remove the precipitated copper oxides, which are reused in subsequent runs.

The **aniline layer** is withdrawn from the bottom of the separator and treated with 50% **sodium hydroxide** solution. Approximately 0.2 percent of the volume of the aniline layer is used. The solution is fractionally distilled, yielding first aniline -water mixture, which is further treated as described previously. The **second fraction** is technically pure (97 to 90%) **aniline**, the residue is steam distilled, yielding diphenylamine. The phenol is recovered by acidifying the residue mostly sodium phenate and distilling. The **yield** of aniline is 96% based on chlorobenzene.

1.27 m-NITROANILINE

100 parts of **dinitrobenzene** is added to 1000 parts of **water** at **90^{0}C** contained in a reducer fitted with reflux condenser and a propeller type stirrer. **Upon emulsification**, 245 parts of **sodium sulfide** ($9H_2O$), dissolved in a minimum of water, is gradually run in. The **dinitro** compound is gradually **reduced** to **m-nitro aniline**, the **end point** being determined by the formation of a definite black streak when ferrous sulfate solution is added to filter paper spotted with some of the reducer liquor.

A **modification** in the preceding process involves the **use** of an **organic solvent**, which is immiscible with water, for the m-dinitrobenzene. Accordingly, 100 parts of technical **dinitrobenzene**, 90% purity and 160 parts of either solvent **naphtha** or **toluene** are put into reducer, and the mixture is warmed to **60^{0}C** to effect solution. Then, 4000 parts of **hot water** is added, and the m-dinitrobenzene solution is stirred and heated to **95^{0}C**. A hot **polysulfide** (Na_2S_3) solution – made by heating 720 parts of 7% Na_2S with 40 parts of flowers of sulfur – is then added rather rapidly. The reaction of polysulfide is distinctly exothermic, and the charge boils vigorously, but overheating is avoided because of vaporization of solvent. Reduction of the dinitrobenzene to m-nitro aniline is found to take place quickly under such conditions.

To hot **reduction mass** is first **filtered** to remove any free sulfur, and the solvent naphtha in the filtrate is distilled with steam. The dissolved **m-nitro aniline crystallizes out** in the form of bright **yellow crystals** when the residual liquor is cooled. After washing, the product has a **melting point** of about **113^{0}C** and can be **used** directly in the manufacture of **azo dyes**. A **yield** of approximately **90–92%** of theory is attainable, and the process is applicable to other m-dinitro compounds, e.g., m- dinitro derivatives of toluene and xylene.

SULFONATION AND SULFATION

2.0 INTRODUCTION

Sulfonation may be defined as any chemical process by which the **sulfonic acid group (SO_2OH)** or the corresponding salt or sulfonyl halide group (e.g. **$–SO_2Cl$**) is **introduced** into an **organic compound**. These **groups** may be situated **on** either a **carbon or** a **nitrogen** atom. **Sulfonates** of the **second type** (e.g. $RNHSO_2ONa$) are termed **N-sulfonates** or **sulfamates**.

Particular types of sulfonation include **sulfo-chlorination** (introduction of an $-SO_2Cl$ group into an alkane using sulfur dioxide and chlorine), **halo-sulfonation** (reaction of halosulfonic acid $—ClSO_3H$ or $—FSO_3H$ with an aromatic or heterocyclic compound to introduce an $—SO_2Cl$ or an $—SO_2F$ group), **sulfoxidation** (use of sulfur dioxide and oxygen to sulfonate an alkane), **sulfo-alkylation**, **sulfo-acylation** and **sulfo-arylation** (introduction of sulfalkyl, sulfoacyl or sulfoaryl groups).

Sulfation involves placement of **$—OSO_2OH$ group** on **carbon** yielding an acid sulfate ($ROSO_2OH$) or of the **$-SO_4-$** group **between two carbons**, forming the sulfate $ROSO_2OR$

Sulfato-alkylation designate introduction of a sulfated alkyl group into an organic compound.

2.1 CLASSIFICATION OF SULFONATES

¾ Aliphatic and alicyclic
¾ Aromatic
¾ Heterocyclic and
¾ N-sulfonates or sulfamates.

The first three types have the - SO_2OH group on carbon, the chemical nature of which determines the classification. Thus, $C_6H_5OCH_2SO_2ONa$ (sodium-phenoxymethanesulfonate) would be considered an aliphatic sulfonate.

For **practical reasons**, it is also useful to refer to **three other types of sulfonates**, namely those **derived from petroleum fractions**, from **lignin**, and from **fatty oils**. These materials are mixtures of indeterminate or variable composition, probably comprising one or more of the main chemical types of sulfonates together with sulfates and other sulfur compounds, and are made largely by empirical procedures. All three types are commercially important.

2.2 CLASSIFICATION OF SULFATES

Sulfates may be classified as sulfated alkenes, alcohol sulfates, cyclic sulfates, sulfated carbohydrates and sulfated nitrogenous polysaccharides.

2.3 GENERAL PROCEDURES FOR PREPARING SULFONATES

¾ Treatment of an organic compound with SO_3 or a compound thereof
¾ Treatment with a compound of SO_2

¾ Condensation and polymerization methods
¾ Oxidation of organic compound which already containing sulfur in a lower state of oxidation such as RSH.

Condensation procedures refer to the reaction of organic sulfonates building blocks (such as $HOCH_2CH_2SO_3Na$) with other organic compounds (such as long-chain acid chlorides) to form new sulfonates with altered properties; these methods include sulfoalkylation, sulfoacylation and sulfoarylation.

For the **preparation of sulfates**, the **first** and **third** (i.e. sulfatoalkylation) methods only are of interest.

2.4 SULFONATING AND SULFATING AGENTS AND THEIR PRINCIPAL APPLICATION

Sulfonating and sulfating agents are of two types (1) inorganic and (2) organic. The latter type is employed in the condensation procedures.

2.4.1 Principal sulfonating and sulfating agents

Sulfur trioxide and compounds thereof

¾ Sulfur trioxide, oleum, concentrated sulfuric acid (SO_3 plus water)
¾ Chlorosulfonic acid (SO_3 plus HCl)
¾ Sulfur trioxide adducts with organic compounds
¾ Sulfamic acid

The sulfur dioxide group

¾ Sulfurous acid, metallic sulfites
¾ Sulfur dioxides with chlorine
¾ Sulfur dioxide with oxygen

Sulfoalkylating agents

¾ Sulfo-methylating agents (hydroxy and aminomethanesulfonates)
¾ Sulfo-ethylating agents (hydroxy-chloro and methylaminoethanesulfonates, ethylenesulfonic acid)
¾ Miscellaneous sulfo-alkylating agents, sulfo-acylation, sulfo-arylation, sulfato-alkylation

2.4.2 Uses and application of sulfonate and sulfates

Millions of tons of **sulfonates** are manufactured annually **lignin sulfonates** obtains as a **by-product** of **paper manufacture** constitutes the major single product. These compounds have achieved a wide variety of interesting and important uses. Most of them are employed as such in acid or salt form for application where the strongly polar hydrophilic - SO_2OH group confers needed properties on a comparatively hydrophobic non-polar organic molecule. A **few sulfonates** are both marketed and used in acid form, including methane and toluenesulfonic acids as catalysts and phenolsufonic acid as an **electroplating additive**. A considerably larger group is marked in salt form and used in acid form; such compounds include **mothproofing agents**, and synthetic tanning agents. In these cases, the salts are applied in acid medium, thereby liberating the free -SO_2OH group, which firmly attaches the organic molecule to the textile fiber or leather. The major quantity of **sulfonates and sulfates** is both marketed and used in **salt form**. This **category includes** detergents, emulsifying, deemulsifying, penetrating, wetting and solubilising agents, lubricant additives, and rust inhibitors. Polymeric sulfonates include dispersing agents, elastomers, water-soluble synthetic gums and thickening agents and ion exchange resins which function as strong acids with complete water insolubility and unusual combination of properties leading to many important applications.

Aromatic sulfonyl chlorides -RSO_2Cl are useful for preparing sulfonamides (including sulfa drugs, dyes, tanning agents, plasticizers and the sweetening agents (saccharin) and sulfonate ester (insecticides).

Sulfamates include herbicide, sweetening agent and blood anticoagulant. Sulfonates and sulfates find use **as intermediates** for preparing organic **compounds not containing sulfur**, notably phenols (prepared by caustic fusion of various sulfonates) and alcohols (made by hydrolysis of sulfated alkenes). Phenol, resorcinol, the naphthols, hydroxy-anthraquinones and 8-hydroxyquinoline are phenols so produced while ethanol and isopropanol are examples of alcohols made from the sulfates.

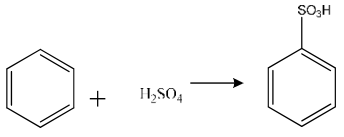
2.5 BENZENE SULFONIC ACID OR MONOSULFONATION OF BENZENE

2.5.1 Raw materials

Under **optimum condition**, the **reaction time** for this process has been calculated at **1.5hr. at 180°C** using a seven-stage reactor, continuous process10 moles of benzene per mole of sulfuric acid required. In contrast, the same process operated in batches at 160-

180°C would require 14 hr. and 6-8 moles of benzene per mole sulfuric acid. Thus the continuous method increases by nearly ten times the capacity of the batch method. It is further estimated that the ratio of benzene used, to benzene reacted could be reduced as low as 3 :1 by doubling the time of reaction. The efficiency of the process can be further increased by using 10% oleum instead of sulfuric acid, thereby reducing the required water removal without substantially raising by product sulfone formation.

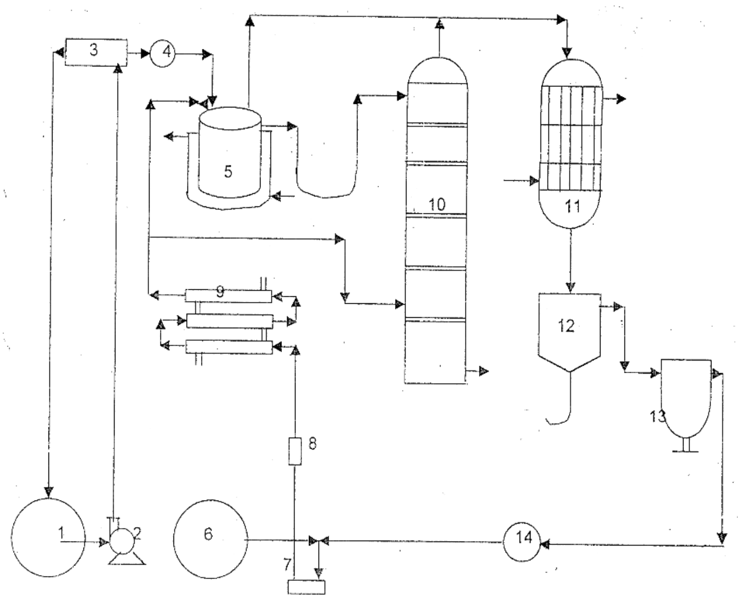
2.5.2 Reaction



2.5.3 Manufacture

Benzene can be monosulfonated efficiently and on a continuous basic by the partial pressure distillation method. A typical operating procedure based on the flow diagram shown in figure is as follow.

Sulfuric acid is continuously pumped from storage tank (1) by means of pump (2) through pressure regulator (3) and meter (4) to the sulfonator (5) **Liquid benzene** from storage tank (6 or 14) is continuously fed by pump (7) through meter (8) to the direct vaporizer super heater (9) and hence to the sulfonator (5) and the Sulfonation tower (10) In the Sulfonation,



1. H_2SO_4 storage tank
2. Pump
3. Pressure regulator
4. Flow-meter
5. Sulfonator
6. Liquid benzene storage tank
7. Pump
8. Meter
9. Vaporizer
10. Sulfonation tower
11. Condensor
12. Separator
13. Neutralizing drier
14. Liquid benzene storage tank

Sulfuric acid reacts with **benzene**, and the **reaction mass** containing **30%** un-reacted sulfuric acid flows out continuously to the top of the Sulfonation tower (10) which is arranged like a plate column, the reaction mass flows downward through the tower while further reacting with a **countercurrent stream** of benzene vapour.

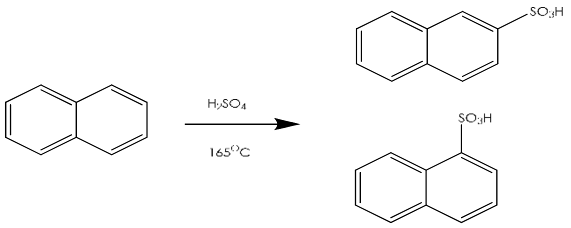
The exit benzene-water vapour are continuously discharged from top of tower (10) to condenser (11) and stratified in separator (12) and the benzene storage (14) while the benzenesulfonic acid, containing **2.5-3.5%** of sulfone and **3-4%** of sulfuric acid is continuously drawn off at the bottom of the tower.

2.6 NAPHTHALINE β - SULFONIC ACID

2.6.1 Raw materials

Naphthalene, sulfuric acid, water, steam etc

2.6.2 Reaction



2.7.3 Manufacture

The hydrocarbon is reacted with sulfuric acid; in addition to the desired isomer, about 15% of the alpha isomer is also formed.

Naphthalene (3,350 1b - 26.2 1b moles) is charged to a **cast iron sulfonation kettle**, 500 gal capacity, equipped with propeller or anchor agitator and heated either directly with generator gas or by **high-pressure** (100 1b) jacket steam. It is melted by heating to **90-110 °C**. **Sulfuric acid** (3,350 lb of 96% strength - 32.8 lb moles) is then added with agitation, the temperature being allowed to rise to about **160 °C**. The batch is held at **160 -165°C** for about **2hrs** to complete reaction, during which time **water** (approx. 400 lb-22.2 lb moles) and **naphthalene** (approx. 350 lb -2.7 lb moles) distill off and are collected by condensation. The reaction **products contains** mainly monosulfonic acids (85 % beta and 15% alphas) plus some **sulfone**,free sulfuric acid, disulfonic acids and tar. The **undesired a- sulfonate** is now removed by blowing **dry steam** into the charge to effect **hydrolytic desulfonation**, the liberated naphthalene being distilled and recovered. It is essential to employ dry steam to avoid foaming and to maintain a temperature in the range **160-165°C** to ensure rapid reaction. About **16% or 540 lb** of the original naphthalene employed is recovered, leaving the **β-sulfonate** contaminated with only about 0.1% alpha isomer.

The **hydrolyzed** sulfonation mixture is discharged into the water with good agitation and the resulting solution is run into the brine to form the sodium sulfonate salt. The **slurry** so obtained is **agitated** for **10 hr** as it **cooled to 30 °C** this yields an easily **filterable precipitate**. The filtration is accomplished by pumping or blowing the sodium sulfonate suspension into a pressure filter containing wooden plate filters and rubber-coated frames. The shell of the filter is coated with tar to minimize corrosion. The filtrate is permit to stand and more salt added if necessary and then it is refiltered to collect any additional sulfonate that has crystallized out.

The **second crop** of sodium sulfonate is not as pure as the first. The filter cakes are washed with a minimum of water and these washings are employed to advantage as part of the liquor in the sulfonation dilution tank. The filter cake of sodium sulfonate containing about 70 % water is pressed hydraulically to a water content of about 30%. The press cakes are dried to moisture content of about 5%, disintegrated and delivered to the **caustic fusion kettles** for conversion to **β -naphthol**. The **yield** is about **90%** of theory on the basis of naphthalene consumed.

Factors ensure rapid and complete sulfonation

¾ use of about **25% excess acid**, corresponding to about 40% excess over that actually converted to sulfonate

¾ Distillation of a **quantity of water** (22.2 moles) only **slightly less** than the amount of naphthalene (23.5 moles) sulfonated

¾ Use of an **elevated reaction temperature**. At this temperature, water will distill from dilute acid until it has increased to 68% in concentration, which is above the concentration (64%) required to sulfonate naphthalene at this temperature.

¾ As in every important sulfonation, **several modified procedures** have been suggested to reduce the acid factor more closely to theoretical, including the use of excess naphthalene or operation under vacuum. Continuous operation has also been studied. None of these expedients has been adopted commercially. Variations in the working up procedure have however sometimes proved advantageous.