

Introduction:

22.1

Industrial chemistry

Industrial chemistry is concerned with chemical processing of raw materials to useable and profitable products. Certain of these marketable products will be consumer goods and enter directly into economic life of the country. Others will be intermediates chemicals for the manufacture of consumer's items. Manufacturers of chemicals utilize some twenty percent of the total chemical output. In as much as the products of one become raw materials for further fabrication in another. Thus, the industry as a whole is its own best customer.

The chemical industry today is a very diverse sector of manufacturing industry with in which it plays a central role. It makes thousand of different chemicals which the general public only usually encounter as end or consumer products. These products are purchased because they have the required properties which make them suitable for particular applications e.g non stick coating for pans or weed killer. Thus chemicals are ultimately sold for the effect they produce.

Chemical processing may be defined as the industrial processing of the chemical raw materials leading to the products of enhanced industrial value. Generally this involve the chemical conversion, as in manufacture of sulphuric Acid from sulphur by oxidation and hydration, but the production of fibers from chemicals is also included such as nylon from hexamethylene diamine and adipic acid by more complicated chemical reactions. In all these chemical changes physical operations are intimately involved such as heat transfer and temperature control which are necessary to secure good yield required by competitive industry as for example the oxidation of SO_2 to SO_3 .

Economy of Pakistan

Chemical sector plays a fundamental role in economic development of any nation. The globalization forms the structure of the modern world. It converts the essential raw materials into more than seventy thousand variety products for industry as well as the goods of consumers, that people depend upon their daily lives.

Pakistan trades in chemicals with other countries to earn foreign exchange in the field of chemical industry such as a fertilizers, plastics, rubber, medicine, dyes and pigments, soaps and detergents.

The increase in imports is from 760 million US \$ in 2002-2003 to 5160 million US \$ in 2008-2009. The increment in export was shown from 118 million US \$ in 2002-2003 to 411 million US \$ in 2008-2009.

Chemical industry supply the farmers the fertilizers and pesticides which are essential for the crop growing and other agriculture products. Chemical industry also produces fibers and dyes which are used in textile industry and supply synthetic sweeteners and synthetic flavours which are used by food manufacturing companies.

The provision of essential chemicals to the pharmaceutical industry and health care industry is also a major role of chemical industry.

Artificial rubber requirement of Pakistan industry are also met by the very same chemical industry.

Chemical industry contributes indirectly to almost every sector of economy.

22.2 SAFETY CONSIDERATION IN THE PROCESS OF INDUSTRY

The following safety consideration in the process of industry must be kept in view before launching any industrial activity.

- To keep away the factory itself from corroding away, proper material of construction should be selected by the designing chemical engineers.
- To avoid harmful impurities in raw materials, to follow the course of chemical reactions and to secure the requisite yield and purity of products, careful process control by periodic analysis is required as well as modern instrumentation and automatic control.
- To transmit goods in a clean and economical manner from the manufacturer to the customer, suitable containers must be provided.
- To affect the safety of workmen and the plant all procedures, must be carried on in a non-hazardous manner.

- To secure the processes from excessive competition and to ensure an adequate return for a large sums spent on the research and plant.
- To guarantee progress to continue profits and to replace obsolescent processes and equipments much attention and money must be spent upon continuing research and development.
- To prevent the contamination of water and air, factories must avoid discharge of toxic material into the air and water of their localities.

22.3

Dyes

A dye is a substance which adds value to products for their cost. In most of the cases the colour of a product is the reason for its sale. The purpose of a dye is usually to help the purchaser sell his product to his customer. A dye must be coloured, but it must also be able to impart colour to something else on a reasonably permanent base before it can be considered as a dye.

Chemical Composition of a dye:

A dye consists of a colour producing structure called "The chromogen" (electron acceptor) and a part to regulate the solubility and dying properties called the auxochrome (electron donor). Without both parts, the material is simply a coloured body.

The chromogen is an aromatic body containing a colour giving group, commonly called the "chromophore". Chromophores groups cause colour by altering absorption bands in the visible spectrum. Some common chromospheres are given in the table 22.1 Dyes are usually classified on the basis of chromophore groups.

Table 22.1 Some common chromophore groups.

S. No	Chromophore	Structure
1.	Nitrosogroup	$-\text{NO}(\text{or } =\text{N}-\text{OH})$
2.	Nitro group	$-\text{NO}_2(\text{or NOOH})$
3.	Azo group	$-\text{N}=\text{N}-$
4.	Ethylene group	$-\text{C}=\text{C}-$
5.	Carbonyl group	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$

6.	Carbon–nitrogen group	$-C \equiv N, -\overset{\overset{N}{\parallel}}{C}-$
7.	Carbon–sulphur groups	CH_3-SH

The auxochrome, the part of the dye which causes it to adhere to the material which it colours (usually textiles) are $-NH_2$, $-OH$, $-NR_2$, $-COOH$ and $-SO_3H$ of these groups. $-NH_2$ and $-NR_2$ cause solubility in acids while $-OH$, $-COOH$ and $-SO_3H$ cause solubility in basic solutions.

Classification of Dyes:

Dyes are of many types. They may be classified into the following classes. The basis of classification being the “use” or “application” of the dye.

1. Acid dyes:

They are used for dyeing protein fibers such as wool, silk, nylon; also leather and paper. They contain one or more sulfuric acid substituents or other acidic groups. An example of the class is acid yellow 36 (Metanil yellow).

2. Basic Dyes:

These dyes can be used to dye wool or cotton with a mordant but are usually used for duplicator inks, carbon paper and typewriter ribbons. In solvents other than water, they form writing and printing inks. Basic dyes are mostly amino compounds soluble in acids and made insoluble by the solution being made basic.

Basic dyes were the first dye class made synthetically; “mauve” was a basic dye. Examples of the basic dyes are basic brown 1 (bismark brown), basic violet 3 (crystal violet) etc.

3. Azo dyes:

These are brilliant and long –lasting dyes and are used primarily for printing on cotton. These “ice colours” are made right on the fiber by coupling diazotized materials while in contact with the fibers.

4. Direct dyes:

These are used to dye cotton directly i.e. without the addition of a mordant. They are also used to dye union goods (mixed cotton and wool

or silk). These are generally azo dyes and their solubility in the dyes bath is often reduced by adding salt. Direct orange 26 and direct black 22 are typical direct dyes.

5. Disperse dyes:

Some fibers such as plastics, cellulose acetate, polyesters, nylon fibers, are difficult to dye. Disperse dyes are applied as very finely divided materials which are absorbed on to these fibers with which they then form a solid solution. The dye dissolves into the fiber at or near the glass transition temperature of the polymer. Some typical examples of the disperse dyes are disperse red 4, disperse red 77, disperse orange 25, disperse blue 27 etc.

6. Fiber –reactive dyes:

These dyes react with the substrate, usually cellulose to form a covalent link (bond) between the dye and the fiber. Cotton, rayon and some nylons are dyed by these dyes. Examples of this type include vinyl sulfone (sulfatoethyl sulfone)

7. Mordant dyes (and lakes):

Some dyes combine with metallic salts to form highly insoluble coloured materials, called lakes. Lakes are usually used as pigments. If a cloth made of cotton, wool or other protein fiber is impregnated with an Al, Cr or Fe salt and then contacted with a lake forming dye, the metallic precipitate forms in the fiber and the colours become far more resistant to light and washing. The azo and anthraquinone nuclei, having attached the groups like $-OH$ and $-COOH$, can act as mordant dyes.

8. Sulphur dyes (sulphide dyes):

These dyes have been used for a long time. They are large low costing group of dyes which produce dull shades on cotton. The chromophore is complex and not well defined. Sulphur dyes are usually colourless when in the reduced form in a sodium sulfide bath but gain colour on oxidation.

9. Solvent dyes:

Solvent dyes, sometimes called the spirit –soluble dyes are usually azo, triarylmethane or anthraquinones. They are used to colour oil, waxes, varnishes, shoe polishes and gasolines.

10. Vat -dyes:

Vat-dyes are water insoluble organic pigments that become water - soluble when mixed with powerful reducing agents in the dyeing process. The reducing operation formerly was carried in wooden vats and hence the name vat -dyes. These have highly complex chemical structures and mostly are derivatives of anthraquinone or indanthrone. Vat -dyes are quite expensive and are most often used on cotton fabrics that are to be subjected to severe conditions of washing and bleaching, such as men's shirts. Some vats are supplied as pastes for printing. The best known dyes of this class is indigo, which is one of the most popular colours in the world.

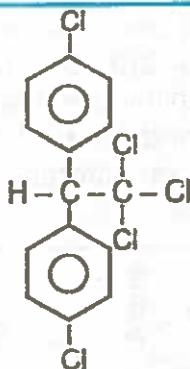
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Pesticides:

The use of chemical pesticides has been a major feature of modern agriculture. Our modern system of agriculture depends not only on our ability to stimulate plant growth, but also on our ability to control various insects or more generally, "pests" that would eat or destroy the crops in the fields or the harvest in the storage sheds.

It is not difficult to kill all the troublesome creatures that we include as pests. Poisons such as lead arsenate, $Pb_3(AsO_4)_2$ have been in use for a long time. Both lead and arsenic are damaging to a wide variety of living systems. Another traditional insecticide is nicotine sulphate, which is obtained from plants but is extremely poisonous to most pests and to man. Pesticides such as these general poisons are not really satisfactory. We would prefer a substance that destroys specific pests without injuring other insects, wild life, or man. Secondly a pesticide that breaks down in nature into harmless products is preferred.

Modern insecticides were ushered in by DDT in 1943. Its remarkable effectiveness against mosquitoes, which carry malaria and lice was immediately demonstrated in the world war II campaigns in Italy and the pacific. DDT has the formula.



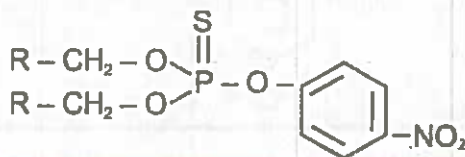
and the name "dichlorodiphenyl trichloroethane". It is good in specificity in that it acts directly on insects and not on mammals. But it does not distinguish between bad insects that destroy our crops and good insects, like bees, that assist them.

Unfortunately DDT fails to meet the second criterion i.e it, does not readily break down in nature to give harmless substances. DDT is a very stable chemical. Its half life is estimated to be 10 -15 years. It means that half of any DDT applied in any year still exists, somewhere, 10 or 15 years later. The persistence of DDT is more troublesome by its tendency to become concentrated in all forms of animal life. (The process is some times referred to as biological magnification). As is clear from its structure, DDT can not become involved in hydrogen bonding to water molecules, so it is water -insoluble. Further more the DDT molecule is non - polar. If a sample of DDT is shaken up with a two layer oil -and -water system, almost all the DDT will be found in the oil layer. In nature this distribution occurs and DDT accumulates in animals and in particular in their fatty tissues. Thus, although DDT can be used in very small quantities to control insects, it accumulates in the fatty tissues of each successive member of the food chain. An area may be sprayed with DDT so that the concentration of the DDT in the waters of the area might be much less than 1 ppm. But the food chain that proceeds from insects through fish to fish-eating birds can concentrate the DDT until it is at the 100 or 1000 ppm level. Even man is not immune from this DDT accumulation and our fatty tissues now contain something over 10 ppm of DDT more than would be tolerated in the foods we eat.

Generally, it has been found, that almost all chlorinated pesticides including DDT appear to have a variety of undesirable effects. That is why pressure from environmentalists has lead to the nearly total ban of the

use of DDT in the U.S and all over the world. However, there are still some chlorinated pesticides that are used for more specific targets than was DDT. They include mirex, chlordane, heptachlor, aldrin and dieldrin.

The controversy over DDT and other chlorinated hydrocarbons spurs attempts to find pesticides of a different chemical type. One of the important alternatives is parathion.



This compound breaks down fairly readily to products that appear to cause no biological damage. It is, however, toxic to man and other animals as well as to insects. Thus it avoids long term damage but unless handled carefully it can make for that by short term effects.

In short, the ideal pesticide is clearly not yet available. In fact, chemical poisons will probably turn out to be only one route to the control of the pests that compete with us for our crops.

22.5 Petrochemicals:

Formerly, it was easy to define petrochemicals. They were relatively pure identifiable substances derived from petroleum and used in the chemical trade. But now the original products, separated from petroleum are converted into more desirable sometimes complex, products. That is the oil companies are entering the chemical business; chemical companies are entering the oil business, and the whole group is expanding greatly. So most organic chemical substances could be considered petrochemicals.

The first organic chemical made on large scale from a petroleum base was isopropyl alcohol (isopropanol), first produced by Standard Oil of New Jersey in 1920. By 1925 Standard Oil of New Jersey was making 75 tons per year of isopropyl alcohol and the emergence of petrochemical industry was established in many minds. Currently well over 80 per cent of all organic chemicals are petrochemicals.

While separating individual species from petroleum, the processes involve well refined engineering methods. The most important of these methods are (i) distillation and (ii) selective adsorption. Once separated,

however, most materials then undergo chemical conversion into more desirable products. Alkylations involving propenes and butenes yield C_6 to C_8 hydrocarbons for high octane gasoline. Propylene becomes polypropylene, polyamines or propylene glycol and others. Likewise 98 percent of the raw material, for aromatic compounds, is obtained from petroleum.

The most basic raw materials (table 22.2) supplied by petroleum refineries or natural gas companies are LPG, natural gas from cracking operations, liquid distillate (C_4 to C_6), distillate from special cracking processes and selected or isomerized cyclic fractions for aromatics. Most of these substance are of high value for fuel use.

Table 22.2: Primary Precursors petroleum –petrochemicals:

Raw materials by Distillation	Precursors (basic Chemicals) by conversion.	Intermediates by conversion	Finished Products By conversion
Paraffins And cyclics	Olefins, diolefins, Acetylene, aromatics	Various inorganics and organics,	Inorganic And organics
Natural gas			
Sulfides		S, H_2S synthesis gas	Carbon black
Hydrogen	H_2S		H_2SO_4 ,
Methane			NH_3
Refinery gases			Methanol
	Acetylene	Acetic acid	Formaldehyde
Ethane	Isobutene	Acetic anhydride	Acetates
Propane	Ethylene	Isoprene	Fibers
N –butane	Propylene	Ethylene – oxide	Rubber
Hexane	n –butanes	etc	Rubber & fiber
Heptanes		Butadiene	Rubber
Refinery naphtha's		Adipic acid	Fibers
		Ethyl benzene	Styrene
		Styrene	Rubber

Naphthalene		Cumene	Phenol, acetone
Benzene	Cyclohexadiene	Alkyl benzene	Nylons
Toluene	Toluene	Phenol	Plastics
Xylems	Toluene	Benzoic acid	Phenol
Methyl naphthalene's	O -, m -, p -, xylene, toluene naphthalene	Pthalic anhydride	Plastics

The lower members of the paraffine and olefin series have been the preferred and most economical sources of organic raw materials for conversion. So tables are shown concerning the derivations from methane (Table 22.3) and ethylene (table 22.4)

Table 22.3 Petrochemicals from Methane	
Basic	Uses, (Percent)
Ammonia	Fertilizers (80%) plastics and fibers (10 %) explosives (5%)
Carbon black	Tyres (65%) other rubber (25%) colorant and fillers (10%).
Methanol	Polymers (50%), solvents (10%), derivatives ($HCHO, CH_3COOH$)(40%)
Chloromethane	
Methyl chloride (CH_3Cl)	Silicones (57%), tetramethyl lead (19%)
Methylene chloride (CH_2Cl_2)	Paint remover (30%) aerosol propellant (20%) degreaser (10%)
Chloroform ($CHCl_3$)	Fluorocarbons (90%)
Carbon tetrachloride (CCl_4)	Fluorocarbons (95%) degreasing, fumigant etc (5%)
Acetylene	VCM (37%), 1,4 - butanediol (25%) v . acetate (14%), v. fluoride and acetylene black (5%)
Hydrogen Cyanide	MMA (58%), cyanuric chloride (17%), chelating agents (13%), NaCN (9%).

Table 22.4 Petrochemicals from Ethylene:

Basic Derivatives	Uses, (Percent)
Ethyl Benzene	Styrene (99%) , solvent (1%)
Ethyl chloride	TEL (90%), ethyl cellulose of pharmaceuticals (5%)
Ethylene dichloride	VCM (84%) solvent (7%)
Ethylene glycol	Antifreez (38%), polyester fibers and films (49%)
Ethylene oxide	Glycol (60%) Rthoxylates (10%) glycol ethers (10%)
Perchloro ethylene	Textile cleaning (40%) metal cleaning (21%) chemical intermediates (6%).
Polyethylene	
Low	Film, sheet, molding and extrusion plastics.
High density	Film sheet molding and extrusion plastics
Styrene	Polystyrene (52%) ABS (9%), SBR (7%) polyester resins (6%) SB latex (6%)
1,1,1 trichloroethane	Cold cleaning (40%) Vapour degreasing (22%) Adhesives (12%), aerosols (10x), electronics (6%)

Fractional Distillation of Petroleum:

Petroleum in the unrefined form is called crude oil. It is a naturally occurring thick viscous brown or greenish black liquid which is obtained from earth crust. It consists of mostly hydrocarbons along with some other elements, mainly sulphur, nitrogen and oxygen. Crude oil is first treated to remove sulphur or sulphur compounds that may be present. The cleaned hydrocarbon material is then distilled, and fractions with various boiling ranges are collected. (figure 22.1). The principal goal of refinery operations is the production of gasoline.

The principal fractions and some of the principal routes in the treatment of crude oil in an oil refinery during fractional distillation are :

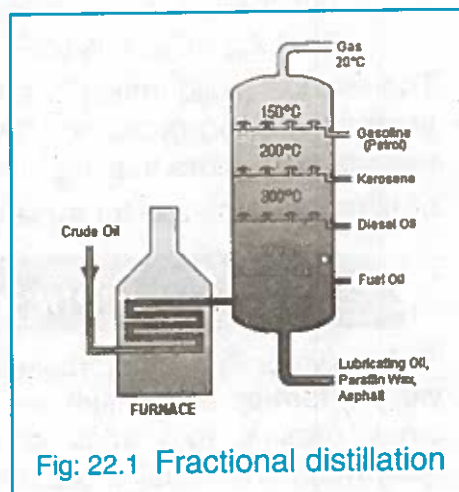


Fig: 22.1 Fractional distillation

1. **Refinery gas:** It is a mixture of hydrocarbons containing methane, ethane, propane, and butane, i.e., C_1 to C_4 atoms per molecule. It is obtained at a temperature below 20°C , and is used as "fuel" and for making other organic compounds.
2. **Petroleum ether:** It is obtained in the boiling range $20^\circ - 60^\circ\text{C}$, contains pentane and hexane ($C_5 - C_6$) and is used as solvent.
3. **Light naphtha:** It is obtained in the boiling range $60 - 100^\circ\text{C}$, contains hexane and heptane ($C_6 - C_7$) and is used as solvent.
4. **Gasoline:** This is the most important fraction containing hydrocarbons from C_7 to C_{10} . It is obtained in the boiling range $80^\circ - 180^\circ\text{C}$ and is used as motor fuel.
5. **Kerosine (Paraffin oil):** It is obtained in the boiling range $160^\circ - 300^\circ\text{C}$ and contains hydrocarbons from C_{11} to C_{15} . It is used as jet fuel, and for oil-fired domestic heating. It can also be used for cracking to produce gasoline (motor fuel).
6. **Heavy oil (Diesel oil, fuel, oil, gas oil):** This fraction is obtained in the boiling range 300° to 400°C and contains hydrocarbon from C_{15} to C_{18} . It is used as industrial fuel and as fuel for diesel engines.
7. **Lubricating oil:** It is a mixture of non-volatile liquids which is obtained at a temperature above 400°C . It contains hydrocarbons from $C_{18} - C_{20}$. It is used for lubricating heavy machinery.

The residue (solid mass) is still a mixture of higher hydrocarbons which is used for making greases, Vaseline, waxed paper and candles. The final residue (with more than C_{30}) is a black coal tar and is called asphalt, pitch or bitumen. It is used for metalling roads.

22.6 Synthetic polymers (PVC and Nylon):

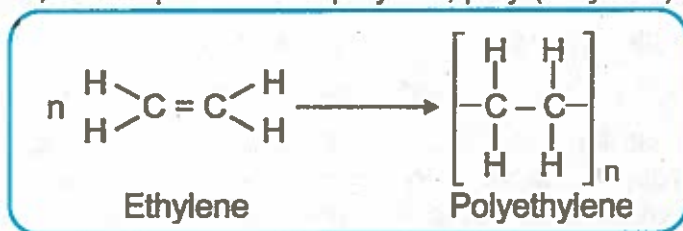
A polymer is a macromolecule (sometimes with a very high molecular weight) formed as a result of a process known as polymerization whereby small organic molecules combine together to form large molecules (polymers). The small molecules which undergo polymerization are called "the monomers." Thus a polymer is a large molecule built up from many

hundreds or thousands of monomer units joined together. The well known plastic polyethylene or polythene is composed of large molecules formed by the repeated combination of ethene molecules.

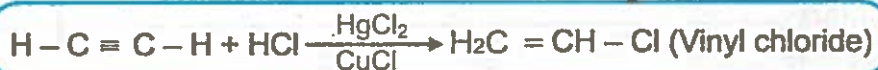
Polymers are classified as either "addition polymers" or "condensation polymers" depending on their method of formation.

a. Addition Polymers:

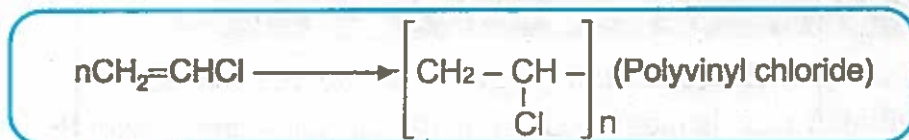
In these polymers, the repeating unit (monomer) keeps on adding to itself or to the growing polymer so that a long chain polymer is produced. That is to say addition polymer results from the self-combination of many monomer units into a substance with a molecular weight which is a multiple of the monomer. The empirical formula of the addition polymer is the same as that of the monomer. For example, when ethylene is heated under pressure, a transparent solid polymer, poly (ethylene) is obtained.



An endless chain is built up by successive addition of the C_2H_4 units. The product has an average molecular weight of 2000–20,000, depending on the temperature and pressure. Acetylene forms an addition product with HCl called vinyl chloride in the presence of HgCl_2 or CuCl .



Vinyl chloride molecules combine with themselves to produce molecules of very high molecular weight, called poly (vinyl chloride) or PVC.



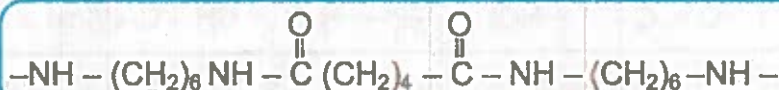
Industrial Preparation of PVC:

The largest branch of the vinyl family is polyvinyl chloride (PVC). The popularity of PVC is due to its excellent physical properties, its ability to be compounded for a wide range of applications, its ease of processing and

its relatively low cost. The liquid monomer is formed into tiny globules by vigorous stirring in water containing a suspending agent. A typical recipe lists 100 parts of water, 100 parts of liquid vinyl chloride, 1 part of a persulphate catalyst and 1.5 parts of an emulsifier such as sodium lauryl sulphate. The autoclave operates at approximately 50°C for 72 hours to give a yield of 90 percent of polymer with a particle size of 0.1 to $1.0\ \mu\text{m}$. Recovery of these particles may be accompanied by spraying or by coagulation by acid addition. A PVC compound can be tailor-made to achieve whatever balance of properties is desired by using plasticizers, stabilizers, lubricants and fillers.

b. Condensation Polymers:

In the chemistry of carbon there are many reactions where the combination of two or more substances is accompanied by the elimination of small simple molecules such as water (H_2O), hydrogen chloride (HCl), ammonia (NH_3) or methanol (CH_3OH). Such reactions are often called condensation reactions. If the carbon-chain back bone has two functional groups attached to it, a condensation reaction can occur involving polymerization. And the polymer produced in such a case is called condensation polymer. For example, Nylon is a condensation polymer, produced by the reaction between a diamine and a dibasic organic carboxylic acid. If the diamine is hexamethylene diamine (1,6-diaminohexane) and the dibasic acid is adipic acid (hexanedioic acid) then the condensation polymer is nylon (6, 6) (six carbon atom in each monomer).



Preparation of Nylon (6, 10) (the nylon rope trick)

$50\ \text{cm}^3$ of a 2% (by volume) solution of decanedioyl dichloride (sebacoyl chloride) in CCl_4 is measured into a $100\ \text{cm}^3$ tall-form beaker $25\ \text{cm}^3$ of an aqueous solution containing 2.2g of 1,6-diamino hexane (hexamethylene diamine) is added carefully to the beaker so that the aqueous solution floats on top of the CCl_4 solution, without mixing. A thread of the nylon is drawn from the interface between the two liquids, using a pair of forceps and wound around thick glass rod. (Figure 22.2)

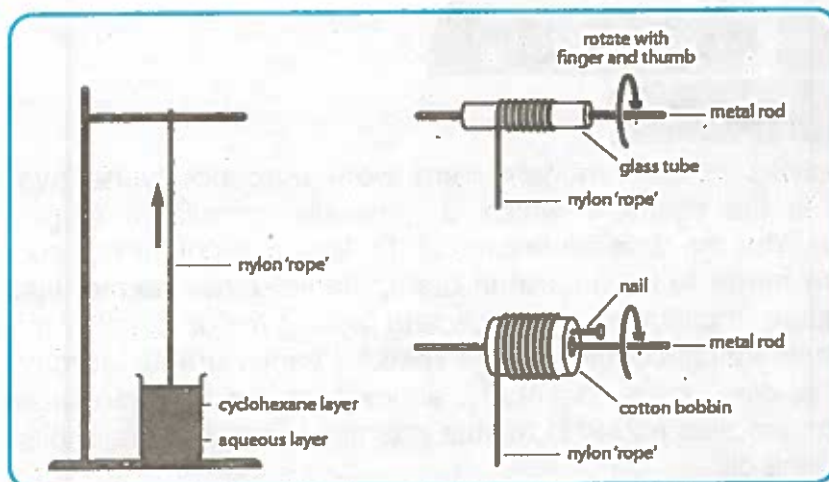


Fig: 22.2

Uses of PVC and Nylon

1. PVC or poly vinyl chloride is widely used in imitation leathers, floor coverings, corrugated roofing material, drainage pipes, electrical pipes, gramophone records etc.
2. Nylon is well known as synthetic fiber in carpets, fabrics, rope, stockings and other clothings. Because of its mechanical strength, nylon is also used in moulded machine parts such as gears and bearings.

Society, Technology and Science

Nylon was the first truly synthetic fiber, resulting from the brilliant research of the late Wallace H-Carothers of the Du Pont company. The introduction of synthetic fibers changed the textile industry because their properties differ from natural fibers. Nylon creates draperies, flame-resistant product and clothes. Other uses include, carpets, tyres of vehicles, stockings and tights etc. Kevlar is used in ropes, tyres, sports equipment and bullet-proof vests. Polyester is used in outer wears because of its tenacity and durability. Its hydrophobic property makes it ideal for garments and jackets. It is also used for making sails of sailboat, water hoses for fire fighting.

a) Lipstick

Lipsticks in their modern form were introduced after world war I. Lipstick is the cosmetic which is generally formulated to provide both protection (for the delicate tissues of the lips) and colour (for appearance). They are made to be neutral in taste, stable under normal fluctuation of temperature, moisture and air flow and lacking major toxicity and irritancy.

The chemical composition of lipsticks varies greatly. It may include a mixture of oils, waxes, pigments, antioxidants and preservatives. Usually perfumes are also added in minute quantity to combat the unpleasant fatty odour of the oil.

Lipstick is mainly composed of a mixture of non-volatile oil (e.g. castor, vegetable, mineral or wool fat, lanolin oil) and solid wax (e.g; bees wax or carnauba). The addition of oil makes the wax-based product to be softened and easily applied. To reduce the "stickiness", usually, esters of fatty acids (like 2-propyl myristate) is also added.

The most important characteristic of a lipstick is considered to be its colouration. The colours and dyes of lipsticks include many water-soluble (also fat soluble) products, such as erythrosine (redish pink synthetic dye), amaranth (dark red to purple azodyes), brilliant blue eosin or tetrabromo fluorescein.

The dyes must be water-insoluble, otherwise, the colour would quickly fade or be removed in a short time by the consumer through the movement of the saliva-soaked tongue across the lips. Water-soluble dyes such as green or blue food dyes can be used to provide lipstick colouration, but they are, usually, first combined with metal oxides such as aluminum hydroxide $[Al(OH)_3]$ to form an insoluble precipitate that is then suspended in the oil base of the lipstick.

b) Nail Varnish and Remover**i. Nail Varnish**

Nail varnish or Nail Polish is a lacquer applied to human finger nails or toe nails to decorate or protect the nail plate.

Nail polish started traditionally in clear red, pink and brown colour. Since that time, many new colours and techniques have been developed, resulting in nail polish that is found in an extremely diverse variety of

colours. Beyond solid colours, nail polish has also developed an array of other designs and colours. Such as nail polish stamps, crackled, magnetic, nail polish strips and stickers. Some nail polishes are used to cause nail growth, make nails stronger, prevent nails from breaking, cracking and splitting and to stop nail biting. Nail polish may be applied as one of several components in manicure.

Most of nail polishes are made up of nitrocellulose dissolved in a solvent (e.g; butyl acetate or ethyl acetate) and either left clear or coloured with various pigments. Basic components included are: film forming agents, resins and plasticizers, solvents and colouring agents. Adhesive polymers (e.g; tosylamide-formaldehyde resin) are added to make sure that the nitrocellulose adheres to the nail surface. Plasticizers (e.g. camphor) or chemicals that link between polymer chains, spacing them to make the film sufficiently flexible after drying. Pigments and sparkling particles (e.g; mica) add desired colour and reflecting properties. Thickening agents (e.g; stearalkonium hectorite) are added to maintain the sparkling particles in suspension within the bottle. Ultraviolet stabilizers (e.g; benzophenone-I) resist colour changes when the dry film is exposed to direct sunlight.

Nail polish ingredients often include toluene, formalin etc. Solvents such as toluene and xylene and petroleum based products have been linked to cancer. Formaldehyde (formalin) may cause allergic reactions and is unsafe for use by asthmatic people. It is a carcinogen. However, the nail polish industries (makers) are under pressure and are now trying to reduce or eliminate toxic ingredients, including phthalates, toluene and formaldehyde.

Water based nail polish is based on acrylic polymer emulsion (e.g; styrene-acrylate copolymer) and pigments similar to those used in water colour paints. This is marketed as environmentally conscious products, since nail polish is considered a hazardous waste by some regulatory authorities. When applied, the solvent (water) does not completely evaporate as in the case of the traditional nail polish; part of water is absorbed through the fingernail.

ii. Nail Polish Remover

Nail polish is removed with nail polish remover or nail pads which is an organic solvent, but may also include oils, scents and colouring. The most

common type of nail polish remover contains acetone $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$. It is powerful and effective but is harsh on skin and nails which can even make them more brittle. Acetone is a volatile organic compound which can also be used to remove artificial nails, that are usually made of acrylic. There are many different types of nail polish removers in the market and different brands may have different chemical compositions. However, the principal ingredients in most of them are acetone, ethyl acetate or butyl acetate and alcohol. The "non-acetone nail polish remover" usually contains ethyl acetate which is less aggressive solvent and can therefore, be used to remove nail polish from artificial nails. These chemicals used are known to dehydrate the skin, cause irritation to eyes and make nails dry and brittle. They also have a distinct chemical smell and are highly inflammable. To counter the dehydration and brittleness effects, many removers also contain conditioning ingredients like castor oil, ethyl palmitate or lanolin.

Application:

With liquid removers, the remover is taken on a cotton ball or tissue and wiped over the nail to strip away the finger nail polish on it. Depending upon the type of finger nail polish, the number of applied coats and the type of remover, one application may suffice for removal or several application may be necessary.

To understand how nail polish remover works, it is necessary to know that a finger nail polish remover and a finger nail polish both contain similar organic solvents; the nail polish also contains drying agents, thickeners, hardening agents and colouring agents. The organic solvent in a nail polish keeps them in a liquid state, while the solvent present in remover, dissolve the hardened polish and transforms it back into its original liquid form. When the nail polish remover is applied to the nail polish that is to be removed, the solvent molecules of the remover interrupt, loosen and break the polymer chains of the polish. This dissolves the hardened polish and transforms it back into its original liquid form. It can then be wiped off from the nail.

c) Hair Dyes

Hair dyes are the dyes, used for hair colouring. The purpose of this practice is to change the hair colour to a colour regarded as more fashionable or desirable and or to restore the original hair colour after it has been discoloured by hair dressing processes or sun bleaching.

Types of Hair Dyes:

Hair dyes, also called hair colouring are commonly classified into four groups.

1. Permanent hair dyes.
2. Semi-permanent hair dyes.
3. Demi-permanent hair dyes.
4. Temporary hair dyes.

These are briefly discussed here.

1. Permanent Hair Dyes:

Permanent hair colouring is usually carried out with oxidation dyes. The ingredients of these products include an oxidizing agent (usually hydrogen peroxide), coupling agents or couples (which are meta-substituted derivatives of aniline) and the primary intermediate (which are aromatic para-compounds such 1,4-diaminobenzene or 4-aminophenol or 2,5-diaminotoluene). The process is essentially performed under basic conditions, for which ammonia is usually used.

The combination of H_2O_2 and the primary intermediate causes the natural hair to be lightened which provides a blank canvas for the dye. Ammonia opens the hair shaft so that the dye can actually bond with the hair and ammonia speeds up the reaction of the dye with the hair.

The couplers (meta-substituted derivatives of aniline) are the chemical compounds that define the colour of the hair dye. Various combinations of primary intermediates and couplers provide different shades of hair colours.

2. Semi-permanent hair dyes:

These dyes have smaller molecules than temporary and are therefore, able to partially penetrate the hair shaft. That is why these colours can survive washing with typically 4-5 shampoos. Semi-permanent hair dyes contain no or very low levels of developers, peroxide or ammonia and are thus, safer for damaged or fragile hair. However, they may still contain the toxic compound p-phenylenediamine or other such ingredients.

The final colour of each strand of hair depends on its original colour and porosity, so there will be a large variations in shade across the whole head. This gives a more natural result than that of a solid permanent colour. Semi-permanent colour can lighten the hair.

3. Demi-permanent hair dyes:

These are in fact, permanent hair colours that contain an alkaline agent other than ammonia (e.g; ethanolamine, sodium carbonate) and the concentration of H_2O_2 in the developer may be lower than used in a permanent hair colour. Since the alkaline agents employed in these colours are less effective in removing the natural pigment of hair than ammonia, these products provide no lightening of hair colour during dyeing.

As a result, they can not colour hair to a lighter shade than it was before dyeing and are less damaging to hair than permanent counterpart.

4. Temporary hair dyes:

Temporary hair dyes are most oftenly used to colour hairs for special occasions such as weddings, costume parties etc. They are available in various forms, such as resins, shampoos, gels, sprays and foams. A temporary hair colour is typically brighter and more vibrant than semi-permanent and permanent hair colour. The dye molecules in temporary hair colour are large and can not penetrate the cuticle layer. The colour particles remain absorbed (closely adherent) to the hair shaft and are easily removed with a single shampooing.

22.8

ADHESIVES

Adhesives are the materials, usually in liquid or semi-liquid states, that adhere or bond items together. They come from either natural or synthetic sources. Although a large number of materials can be bonded by means of adhesives, they are specially useful for bonding thin materials.

Adhesives cure (harden) by either evaporating a solvent or by chemical reactions that occur between two or more constituents.

Importance

With the passage of time and during their development, adhesives have gained an important position in an increasing number of production processes. There is hardly any product in our surroundings that does not contain at least one adhesive in it. For example the label on a beverage bottle, protective coating on automobiles, profiles on window frames, bonding formica to wooden counters or attaching out soles to uppers in foot wear.

TYPES OF ADHESIVES

Adhesives are mainly classified into two classes.

1. Non-reactive adhesives.
2. Reactive adhesives.

The basis of classification is their method of adhesion.

1. NON-REACTIVE ADHESIVES:

These adhesives may be either of natural or synthetic origin. Drying adhesives, pressure sensitive adhesives, contact adhesives and hot adhesives are some examples of this class.

Drying Adhesives:

There are two types of adhesives that harden by drying;

(i) Solvent based adhesives:

Which are a mixture of ingredients (typically polymers) dissolved in a solvent. White glue, contact adhesives and rubber cements are the members of the drying adhesive family.

(ii) Polymer dispersion adhesives:

These are also known as emulsion adhesives and are milky white dispersions often based on polyvinyl acetate (PVAc). They are extensively used in the wood working and packing industries; also used in fabrics and fabric based components and in the engineered products such as loudspeaker cones.

Pressure Sensitive Adhesive (PSA):

These adhesives form a bond by the application of light pressure to adhere the adhesive with the adherent. Once the adhesive and the adherent are in close proximity, molecular interactions, such as "Van der Waals forces" become involved in the bond, contributing significantly to its ultimate strength. Major raw materials for PSA's are acrylate based polymers.

Contact Adhesives:

These are used in strong bonds with high "shear-resistance" like laminates, such as bonding formica to a wooden counter and in footwear, as in attaching outsoles to uppers. Examples of contact adhesives are

natural rubber and polychloroprene (Neoprene). It must be remembered that contact adhesives must be applied to both surfaces and allowed for some time to dry before the two surfaces are pushed together. Once the surfaces are pushed together, the bond forms very quickly.

Hot Adhesives:

These are also known as hot melt adhesives or thermoplastics and are applied in molten form ($65^{\circ}\text{C} - 180^{\circ}\text{C}$ range) which solidify on cooling to form strong bonds between a wide range of materials. Hot adhesives containing "ethylene vinyl acetate", are particularly popular for crafts because of their ease of use and the wide range of common materials they can join. A glue-gun is one method of applying hot adhesive. The glue-gun melts the solid adhesive, then allows the liquid to pass through its barrel onto the material where it solidifies. Thermoplastic glue may have been invented around 1940 by "Proctor & Gamble" as a solution to water based adhesives commonly used in packing at that time failing in humid climates, causing packages to open.

2. Reactive Adhesives:

These adhesives chemically react with the material, when harden. They may be;

- (i) Multiparts Adhesives
- (ii) One Parts Adhesives

i. Multiparts Adhesives:

These adhesives harden by mixing two or more components which chemically react. This reaction causes polymers to cross link into acrylics, urethanes and epoxies. Commercially, there are several combinations of multi-component adhesives that are used in the industry. Some of these combinations are:

- a) Polyester resin-Polyurethane resin.
- b) Polyols-Polyurethane resins.
- c) Acrylic Polymers-Polyurethane resins.

The individual components of these adhesives do act as adhesive by nature. These components, however, react with each other after being mixed and show full adhesion only on curing.

ii. One Part Adhesives:

These adhesives harden via a chemical reaction with an external energy source such as radiation heat or moisture. Light curing adhesives are generally acrylic based, and due to their rapid action, they are significantly used in electronics, telecommunications, medical, aerospace, glass and in optics.

Heat curing adhesives include epoxies, urethanes and polyimides, while moisture curing adhesives cure when they react with moisture present on the substrate surface or in the air. This type of adhesives include cyanoacrylates and urethanes.

Key Points:

- Dye is a substances which adds value to product for their cost.
- Pesticides are chemical substances used for destroying insect and other organisms harmful to cultivated plants or to animals.
- Petrochemicals are relatively pure identifiable substances derived from petroleum and used in the chemical trade.
- A polymer is a macromolecule formed as a result of a process known as polymerization.
- Addition polymer are long chain giant organic compounds which are assembled from many smaller molecules.
- Condensation polymer formed through a condensation reaction, releasing small molecules as by-products.
- Industrial Chemistry is the study of fundamental chemical processes used in industry for transferring raw material to useful commercial products for society.
- Lipstick is mainly composed of a mixture of non-volatile oil and solid wax.
- Nail varnish or nail polishes is a lacquer applied to human finger nails or toe nails to decorate or protect the nail plate.
- The most common type of nail polish remover contains acetone.
- Permanent hair colouring is usually carried out with oxidation dyes.
- Adhesive are the material usually in liquid or semi-liquid state, that adhere or bond items together.
- Adhesives are of two types non-reactive adhesive and reactive adhesives.
- Non-reactive adhesives may be of natural or synthetic origin.
- Reactive adhesives chemically react with material, when harden.
- Cosmetic products apply to body, especially the face, to improve its appearance.
- Hair dye is usually soluble substance for staining or colouring.

Exercise

Q1. Choose the correct one.

(i) "Mauve" is an example of _____ dye.

- | | |
|-----------|----------|
| a) Acidic | b) Basic |
| c) Direct | d) Azo |

(ii) Which is true for DDT? It is

- | | |
|--------------------|-------------------------------|
| a) Not a pollutant | b) an antibiotic |
| c) an antiseptic | d) a non-degradable pollutant |

(iii) Which one of following is not petrochemicals?

- | | |
|----------------|-----------------|
| a) Naphthalene | b) Mineral oils |
| c) Wax | d) table salt |

(iv) What is called "black gold"?

- | | |
|--------------|----------------|
| a) Petroleum | b) Coal |
| c) Coal Tar | d) Natural gas |

(v) Petrochemicals are used in the manufacture of

- | | |
|--------------|-----------------|
| a) Polythene | b) Detergents |
| c) Fibers | d) All of these |

(vi) Which one of the following is synthetic polymer?

- | | |
|--------------|--------------|
| a) Cellulose | b) Protein |
| c) Rubber | d) Polythene |

(vii) Which one of the following is condensation polymer?

- | | |
|----------|------------------|
| a) PVC | b) Polythene |
| c) Nylon | d) None of these |

Q2. Short questions.

- (i) Differentiate between reactive and non-reactive adhesives.
- (ii) How nail-polish remover removes the nail-polish?
- (iii) Why temporary hair dyes are removed with single shampooing?

- (iv) What are the uses of PVC and nylon?
- (v) Write down the four applications of pesticides.
- (vi) How DDT reaches to animals fatty tissues?
- (vii) Differentiate between addition and condensation polymers.

Long question

- Q1. (a) Define Dyes. What is its chemical composition?
(b) How dyes are classified.
- Q2. Explain the fractional distillation of petroleum.
- Q3. What is meant by hair dyes. Classify it into different groups?
- Q4. What are adhesives. Discuss its importance in our daily life?
- Q5. Explain the types of adhesive.
- Q6. Write a note on following:
 - a) Petrochemicals
 - b) Synthetic polymers
 - c) Lipsticks
 - d) Nail polish and its removers