

CHM 309

INDUSTRIAL RAW MATERIALS RESOURCE INVENTORY

PREPARED BY

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INDUSTRIAL RAW MATERIALS RESOURCE INVENTORY

Content: Survey of Nigeria's industries and their raw material requirement, mineral chemistry, fossils and their use, plant and animal products. Nuclear, solar and hydrodynamic sources of energy. Potential application of locally available raw materials as industrial feedstock. The principal chemical conversions in industries in Nigeria are Acylation, Alcoholysis, Alkalation, Amination, Diazotisation and coupling, fermentation, combustion, Pyrolysis or cracking, Reduction, Oxidation, Esterification, Dehydration, Condensation, Calcination, Halogenation, Hydrolysis, Nitration etc.

Factors Affecting Location of Industries

1. Raw materials
2. Infrastructural facility
3. Communication
4. Labour
5. Transportation
6. Market etc.

GLASS INDUSTRIES

1. Oluwa Glass Industries located in Ondo State at Okitipupa.
2. Toyo Metal Box Glass Industry in Ota.

Glass may be defined physically, as a rigid, undercooled liquid having no definite melting point and a sufficient high viscosity to prevent crystallization.

Glass may be defined chemically, as the union of the non volatile inorganic oxides resulting from the decomposition and fusing of alkali and alkaline earth compounds and other glass constituents..

Classes of Commercial Glass

1. Fused silica – Sometimes referred to as quartz glass. It is characterized with low expansion and high softening points, is also extraordinarily transparent to UV radiation.

2. Alkali silicates – Are the only two-component glasses of commercial importance. They are water soluble. Sand and soda ash are simply melted together and the products designated sodium silicates. Silicates of soda solution, also known as water glass is widely consumed as an adhesive for paper in the manufacture of corrugated paper boxes.

Soda Lime Glass – Represent by far the largest tonnage of glass made today and serves for the manufacture of containers of all kinds, flat glass, windows, plates, tumblers and table wares.

Lead Glasses – Are of great importance in optical works because of their high index of refraction and dispersion.

Boron silicates – Usually contain about 13 to 28% B_2O_3 and 80% silicates and have low expansion coefficients, excellent chemical stability. Among the diversified application of these glasses are laboratory glass ware.

Special Glasses – These includes the (1) colour of glass (2) Opal or translucent glass. Colours are produced by the absorption of certain high frequencies by agents in solution in the glass. The colouring agents of this group are the oxides of the transition elements e.g. T, V, Cr, Mn, Fe, Co and Cu.

The last four classes of glasses are made in Nigeria. Here is the major raw materials used.

RAW MATERIAL

Silica being the major raw material needs to be flux with soda ash, salt cake, limestone or lime. In addition, there is heavy consumption of lead oxide, potassium carbonate, borax, boric acid, metallic oxides, carbonates and the other salts required for coloured glass.

SAND

A glass-sand deposit has in many cases determined the location of a glass factory. Its iron contents should not exceed 0.45% for tableware or 0.015% for optical glass, as iron affects the colour of most glass adversely.

SODA

(Na_2O) is principally supplied by dense soda ash (Na_2CO_3). Other sources are sodium bicarbonate, salt cake, and sodium nitrate. The latter is useful in oxidizing iron important sources of lime (CaO) are limestone burnt lime from dolomite ($CaCO_3 \cdot MgCO_3$), the latter introducing MgO into the batch.

BORAX

As a minor ingredient, supplies glass with Na_2O and boric oxide. Borax is now in use in certain types of container glass. It also increases the chemical durability. Boric acid used in batches where only a small amount of alkal is wanted.

SALT CAKE

Long accepted as a minor ingredient of glass, and also other sulphates such as ammonium and barium sulphates are encountered frequently in all types of glass.

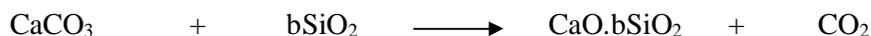
CULLET

Is crushed glass and other waste glass. It facilities melting and utilizes waste material.

Typical manufacturing sequences can be broken down into the following unit operations and chemical conversions.

- i. Transportation of raw materials to the plant
- ii. Sizing of some raw materials
- iii. Storage of raw materials
- iv. Conveying, weighing and mixing raw materials and feeding them into the glass furnace
- v. Reactions in the furnace to form glass
- vi. Shaping of glass product
- vii. Annealing of glass product (to reduce strain)
- viii. Finishing of glass product.

Chemical reactions involved can be summarized



It should be note that the ratio $\text{Na}_2\text{O}/\text{SiO}_2$ and CaO/SiO_2 are not molar ratio the ratio may be of the type $\text{Na}_2\text{O}/1.8\text{SiO}_2$ for example.

In an ordinary window glass the molar ratio are approximately 2mol Na_2O , 1mol CaO and 5mol SiO_2 .

CEMENT AND SOME BUILDING MATERIAL INDUSTRIES

Located at Ewekoro, Sagamu {Elephant brand}

Lion cement {Benue State}

Asaka cement {Gombe}

Lime {Lime Mortal}

Raw material

Limestone (CaCO_3) containing varying amount of magnesium carbonate (MgCO_3) is used as raw material for the manufacture of lime. Lime is manufacture by calcinng (heating) the crushed limestone to the temperature of 900 – 1100.



Limestone Quick lime



Magnesite Magnesia

To have limestone mortal, slacked lime Ca(OH)_2 is reacted with CO_2 from air.



Hence the crystals of CaCO_3 thus formed interlock sand particles, converting the plastic mass into a hard solid.

Portland Cement

Portland cement is by far the most important of the inorganic material which serve an essential ingredient of concrete.

Portland cement are mainly calcium silicates and calcium aluminates. It has this composition, 65% CaO , 20% SiO_2 , 5% Al_2O_3 .

The major raw materials are calcium materials such as marine shell, limestone and argillaceous materials such as clay, slate and gypsum.

CERAMIC INDUSTRIES

The traditional ceramic industries, sometimes referred to as the clay product or silicate industries. We should also know that pottery making is one of the most ancient of human industries. Ceramics generally are materials which can withstand higher temperature, resist greater pressures, have superior mechanical properties, posses special electric characteristic or can protest against corrosive chemicals. These are the major ceramic products.

- Whitewares e.g. (whiteware tiles, pottery, porcelain, storeware etc.)
- Structural clay product (building brick, face brick, terra cotta, tiles)
- Refractories (firebricks, chromite, magnesite, magnesise, chromite brick etc.)
- Specialised ceramic products
- Enamel and enamelted metal

Soda ash (Na_2CO_3)

Sodium nitrate

Pearl ash (K_2CO_3)

Cryolite (Na_3AlF_6)

Refractory ingredients which also serve as fluxing agents are:

Alumina (Al_2O_3)

Titania (TiO_2)

Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$)

Lime and limestone

Dolomite ($\text{CaMg}(\text{CO}_3)_2$)

The major chemical conversions are:

1. Dehydration at 150 to 650⁰C
2. Calcination e.g. of CaCO_3 at 600⁰C to 900⁰C
3. Silicate formation at 900⁰C and higher.

THE PERFUME INDUSTRY e.g. Avon (Ota)

A perfume may be defined as any mixture of odorous substance incorporated in a suitable vehicle.

Perfume, cologne and toilet water, deodorant are all collectively known as the fragrances.

Fragrance (perfume) are used industrially in masking, neutralizing and altering as in creating a distinctive aroma for normally odorless substances.

Raw Material

Formerly, practically all the products are used in perfumery use of natural origin. The finest modern perfumes are neither wholly or synthetic nor completely natural. The best product of the art is a judicious blend of the two in order to enhance the natural perfume. The constituents of perfumes are three folds:

1. The vehicle
2. The fixatives
3. The odoriferous elements.

The Vehicle

The modern solvent for blending and holding perfume materials is highly refined ethanol mixed with more or less water according to the solubilities of the oil employed. This solvent,

with its volatile nature, helps to project the scent it carries, is fairly inert to the solutes, and is not too irritating to the human skin. The slight natural odour of the alcohol is removed by deodorizing of the alcohol. This is accomplished by adding small amount of gum benzoin or other resinous fixatives to the alcohol and allowing it to mature for a week or two. The result is an almost odourless alcohol, the natural rawness having been neutralized by the resin.

The Fixative

In an ordinary solution of perfume substance in alcohol, the more volatile material EVAPORATES first, and the odour of the perfume consist of a series of impressions rather than the desired ensembles. A fixative is therefore needed to put off this difficulty. Fixatives may be defined as substances of lower volatility than the perfume oils, which retard and even up the rate of evaporation of the various odorous constituents.

Fixatives can be (i) Animal secretion e.g. Ambergris (ii) Resinous e.g. myrrh and oleoresins products (iii) Essential oil e.g. sandal wood (iv) Synthetic chemical.

Synthetic fixative commonly used today are odourless esters e.g. glyceryl diacetate, ethyl phthalate, benzyl benzoate. Other synthetic used as fixatives, although they have a definite odour of their own that contributes to the ensemble in which they are used. A few of these are vanillin, coumarin, acetophenone, cinnamic alcohol esters etc.

Odorous Substances

Most odorous substances used in perfumery came under three headings (1) essential oils (2) isolates (3) synthetic or semi synthetic chemicals.

Essential Oils – May be defined as volatiles, odoriferous oils of vegetable origin. Oil extracted by solvent extraction retain the component of the oil better than the one extracted by distillation.

The compounds occurring in essential oils may be classified as follows:

- (i) Esters of benzoic, acetic and cinnamic acids.
- (ii) Alcohols: Geraniol, citronellol, menthol.
- (iii) Aldehyde: Citral, citronella, vanillin, benzaldehyde.
- (iv) Acids e.g. benzoic, cinnamic.
- (v) Phenols: Eugenols, thymol.
- (vi) Ketones: Carvone, methone, camphor.
- (vii) Ethers: Anethole, Safrole.
- (viii) Lactones: Coumarin
- (ix) Terpenes: Camphene, pinene
- (x) Hydrocarbon: Styrene.

Volatile oils may be recovered by (1) Distillation (2) Extraction with volatile solvents.

Isolates

Pure chemical compounds whose source is an essential oil or other natural perfume material e.g. eugenol from clove oil, pinene from turpentine, anethole from anise oil.

Synthetic and Semi-synthetic

More and more important constituents of perfumes and flavours are being made by chemical synthetic procedures. Some constituents are chemically synthesized from an isolates or other starting material are classified as semi-synthetic e.g. vanillin, prepared from eugenol from clove oil. Linalone, from citral from lemon grass oil.

Some Synthetic and Semi Synthetics used in Perfumes and Flavours

Preparation involves some important chemical conversion.

Coumarin

Produced by condensation process. Coumarin occurs in Tonka beans and a lot of other plants. It was formerly used to amplify the flavour of vanillin, as a fixative and as a masking agent for disagreeable odours in products.

Using Perkin reaction

Phenyl ethyl alcohol

It has a rose – like odour and occurs in the volatile oils of rose, orange flower etc. It is an oil liquid and is much used in perfume formulation

SURFACE COATING INDUSTRY

Surface coatings include:

Paints – Relatively opaque solid coatings applied as thin layers, where films are usually produced to protect or hide the surface. The film produced may be as a result of the polymerization of a poly-unsaturated oil.

Varnishes – They are clear coatings, non pigmented.

Enamels – They are pigmented varnishers.

Lacquers – Films formed by evaporation only.

Others are printing ink, polishes etc.

PAINTS

The major types of paints common in Nigeria are –

1. Emulsion paint – This is a water base paint. Here the solvent or vehicle is water.
2. Gloss – This is oil base or resinous or organic solvents e.g. ketone, toluene, kerosine.

However, a paint can be decorative or industrial in application.

Paint Constituents

Resins – Film former.

Synthetic resins – Alkyd, acrylics, winyls, esters, phenolic.

Natural – Shellac, rosin and ethers.

Solvents – Ketones, water, alcohol, glycol ethers etc.

Drying oil and fatty acids – Inseed oils, soybean oil, fatty acid, coconut oil etc.

Pigment and extender – Titanium dioxide, CaCO_3 , magnesium silicates, zinc oxide, red lead etc.

Driers – Cobalt, manganese, lead and zinc etc.

Plasticizers – esters of phthalic, sebasic, adipic acids.

Pigments and Extenders – It gives opacity to the paint. They are usually an inorganic substance. Pigment extenders or filler reduce the cost of paint and frequently increase its durability. In general, pigments should be opaque to ensure good covering power and chemically inert to secure stability. Without the film forming material, pigments would not be held on the surface.

Examples include:

White pigment: TiO_2 , ZnO , ZnS , AnO .

Black pigment: Carbon black, graphite, lamp black.

Blue pigment: iron blues, Ultramarine, copper phthalocyanine.

Red pigment: Red lead, iron oxides, cadmium reds.

Metallic: Aluminium, Zinc dust, Bronze powder.

Yellow pigment: Lead or zinc chromate, litharge etc.

Examples of extenders include: Gypsum, mica, barite, china clay, talc, silica etc.

The Binder – Is used as a suspension e.g. water, poly vinyl acrylates (PVA).

Solvent or Vehicle – The solvent or vehicle depends on the choice of binder used, the solvent provides the desired viscosity for smooth application and after it is applied, the solvent evaporates to leave the resin and the binder as the thick layer. The pigment or extender are usually suspended in a vehicle.

Additives – e.g. Plasticizers are being introduced into the formulas to reduce certain aspects of cracking in paints. Also additives can be anticorrosives, bactericides, anti-fungicides, corrosion agents.

Mixing Procedures for Emulsion Paints

The various operations needed to mix paints are wholly physical. Chemical conversions are involved in the drying of film only.

The film former usually resin e.g. poly vinyl acetate or acrylate are added to the pigment dispersion (which is obtained by adding some water dispersing pigment like TiO_2 , ZnS with extender). The pigment may be used also for tinting.

This is followed by preservative solution (usually chlorinated phenol) and an antifoam i.e. oil. The emulsion is stirred slowly and water is added. The emulsion paint formed is mixed, screened and mixed again before packaging.

A typical paint consists of 35% pigment and filler and about 21% film forming ingredients.

FLOWCHART FOR THE MIXING OF GLOSS PAINT e.g. gloss.

The manufacture of paint involves mixing, grinding, thinning, adjusting and finally filling.

VARNISHES

The term “varnishes” is applied to clear, transparent coating materials that dry by a process comprising evaporation of the solvents, followed by oxidation and polymerization of the drying oils and resins. Varnishes are a homogenous mixture of resin, drying oils, driers and solvents and they contain no pigment.

Varnishes fall into three general classes (1) Spar varnished (exterior) (2) Floor varnishes and (3) furniture finishes.

The types of oils and resins and the ratio of oil to resin are the principal factors which determine the properties of a varnish. The selection depends on the compatibility of different oil and resins and on the intended use of the varnishes. It is generally accepted that the oil in the finished coatings contribute to its elasticity.

SOAP AND DETERGENT

Soap is the sodium or potassium salt of stearic and other fatty acids, it is soluble in water and the solution has excellent cleansing properties.

Other metals such as calcium, aluminium and lead also form compounds with fatty acids but these compounds are insoluble and serves several other purposes e.g. lubricant, they are always designated “calcium soap”, “lead soap” etc.

Soap is made by the action of hot caustic solution on fatty oil with the simultaneous formation of glycerin.



Soaps are usually separated by the addition of salt (NaCl)

Coconut oil give a soap which is fairly hard but quite soluble.

Palm oil is usually coloured orange to brown and has 6% free fatty acids.

It is an important raw material and is used for toilet soap. Palm oil may be bleached by warming is and blown air through it.

Palm kernel oil is an oil of light colour.

Castor oil is used for transparent soap.

Olive oil of the lower grade, no longer edible is much favoured by the soap.

Grease can also be part of the raw material for soap making. (Grease = animal fat)

Methods of Manufacture

Ordinary toilet soaps and laundry soaps may be made by the boiled or hot process or cold process.

The cold process is more useful for special soaps.

Boiled Process

A solution of caustic soda testing 18 - 20° (12.6 – 14.4% NaOH) is run into a kettle tank and the melted fats, grease or oils are then pumped in. The amount of caustic is regulated so that there is just enough to combine with all the fatty acids liberated. Heat is supplied. There is no stirrer but agitation is supplied. The kettle is kept boiling until saponification is essentially complete; this requires about 4 hours.

Salt (NaCl) is then shoveled in and allowed to dissolve and the boiling is continued until the soap has separated forming the upper layer. The lower layer contains glycerin (4%) and salt and this is drawn off. The whole operation which was just described is termed the saponification change, and requires about 8 hours.

Cold Process

In order to make soap by the cold process. The fat is run in and heated to 54⁰C by the steam in the jacket, then the lyre (6.5% NaOH) and the mass is agitated. Since the reaction is exothermic. The heat may be turned off at this point.

After crutching for about an hour, the mixture stands for 3½ hours. Then it is agitated again and again rested. The liberated glycerin remains in the soap, which is run off at the base of the crutcher into frames and cooled and cut into smaller bars. Mixed sodium and potassium soaps are always made by the cold process.

Potassium soaps are soft and cannot be slated out by KCl.

Other Additives to Soap Making

Other additives such as sodium silicates, sodium bicarbonate and trisodium phosphate are other inorganic chemicals and are called builders.

Colouring and perfumes are also added.

DETERGENTS

Synthetic detergents were initially developed as soap substitute in an economy which was running short of fats and oil. These compounds were made resistant to insoluble hard water salt formation, and were a market improvement in wetting, cleansing and surfactancy in general.

The term “synthetic detergent” has been shortened to “Syndet” to describe the detergent ingredient along with other detergents additives.

“Surface active agent” has been shortened to “Surfactant” to describe the surface active principal or active ingredient.

Detergent Raw Material

A large volume of active organic compounds or surfactants, for both detergents and soaps are manufactured in final form by soap and detergent companies. Examples are linear alkylbenzene sulfonate (LAS) and fatty alcohol sulfonate. Most of the inorganic materials are purchased such as oleum, caustic soda, various sodium phosphates and a large number of additives.

Surfactants

These embrace any compound that affects (usually reduced surface tension when dissolved in water or water solution or which similarly affects interfacial tension between two liquids.

Soap is such a material, but the term is lost frequently applied to organic derivatives such as sodium salts of high molecular weight alkyl sulfonates or sulfates. Both soaps and detergents

act to reduce surface tension. The cleaning process consists (1) thoroughly wetting the dirt from the surface of the article being washed with soap or detergent solution (2) removing the dirt from the surface and (3) maintaining the dirt in a stable solution. In wash water, soaps or detergents increase the wetting ability of the water so that it can more easily penetrate the fabric and reach the soil.

Each molecule of the cleaning solution may be considered a long chain. One end of the chain is hydrophilic (water loving), the other is hydrophobic (water hating or soil loving). The soil – loving ends of some of these molecules are attracted to a soil particle and surround it. At the same time, the water loving end pulls the molecule and the soil particles away from the fabric and unto the wash water. This is the action which, when combined with the mechanical agitation of the washing machine or manual labour, enables a soap or detergent to remove soil suspend it and keep it from re-deposition on clothes.

Classification of Surfactants

In most cases, the hydrophobic portion is a hydrocarbon containing 8 to 18 carbon atoms in a straight or slightly branched chain. In certain cases, a benzene ring may replace some of the carbon atoms in the chain e.g. $C_{12}H_{25}$ -, $C_9H_{19}.C_6H_4$ -

The hydrophilic group may vary widely and may be

Anionic e.g. $-OSO_3^-$ or $-SO_3^-$

Cationic e.g. $-N(CH_3)_3^+$ or $C_5H_5N^+$

Zwitterionic e.g. $-N^+(CH_3)_3 (CH_2)_2 COO^-$

Semi – polar e.g. $-N(CH_3)_2O$

Non – ionic e.g. $-(OCH_2CH_2)_n OH$

In the anionic class, one finds the most used compounds, namely linear alkyl sulfonates from petroleum. Other examples are alkylbenzene – ether sulfonate, fatty alcohol – ethylene oxide sulfonate. Soap is also anionic in character.

Quaternary trimethylalkyl ammonium halide of which Cetyltrimethyl bromide is an example are the most common cationic surfactants.

Ingredients

Surfactant: Organic active

Builders: Sodium tripolyphosphate or
Tetrasodium pyrophosphate

Na_2SO_4

Soda ash

Function

Removal of oily, soil cleaning

Removal of inorganic soil
detergent – building

Filler

Filler with some building action

Additives:

Sodium silicate	Corrosion inhibitor with slight building action
Carboxymethyl cellulose	Anti – redeposition of soil
Perfume and sometimes dye	Improve products characteristics
Water	Filler, binder

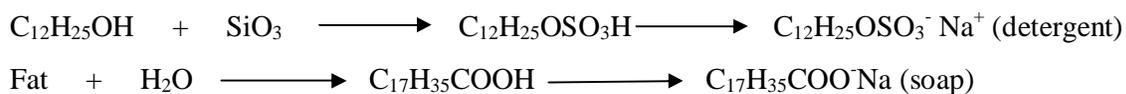
Anionic Surfactants

Alkylary sulfonates – The surfactant currently used in the largest volume is represented by alkyl benzene sulphonates. The alkyl benzene portion is synthesized from petroleum tetrapropylene and benzene using aluminium chloride (field crafts) as catalyst. These achieve the alkylation.

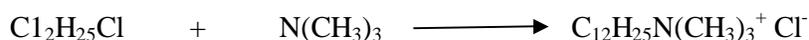
The usual means of sulphonation utilizes an excess of strong H_2SO_4 or oleum to approximate 100% sulphonation of the detergent alkylate. Alkyl benzene are mostly dodecyl and tri decylbenzene.

After sulfonation, it is neutralized, blended with chemical builder and flake dried.

Anionic, giving, in solution, surface active ions bearing a negative charge



Cationic, yielding, in solution, surface active ions positively charged



SOURCES AND RAW MATERIALS FOR POLYMERS

Polyamides and polyimides

Polyamides: They are defined as polymers which contain recurring amide groups (-CONH-) in the main polymer chain.

Polyimides: Are polymers in which the chains contain recurring imide groups.



The most important examples include Nylon, Proteins.

Raw Materials

1. Adipic acid: The principal commercial route to adipic acid is from Benzene as follows

2. Hexamethylene diamine: The standard commercial route to hexamethylene diamine is from dipic acids as follows:



We still have Nylon 6:6, Nylon 11, Nylon 6 etc.

PROTEINS

Proteins are naturally occurring polyamides. They contain recurring amide groups and are polymers of amino acids.

Hydrolysis of protein yield the free amino acids upon which the polymer is based

A few proteins have found technological use as adhesives, fibres and plastics.

POLYESTERS

For examples: Unsaturated polyesters, Alkydes (resins), Polyesters thermoplastic elastomers, polyesters plasticizers, polyarylate, poly (ethylene terephthalate)

Unsaturated Polyesters

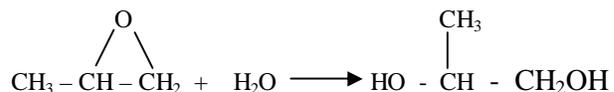
The polymers making up this group of polyesters are linear polyesters containing aliphatic unsaturation which provides sites subsequent cross – linking.

Raw Material

Linear, unsaturated polyesters are prepared commercially by the reaction of a saturated diol with a mixture of an unsaturated basic acid (or corresponding anhydride).

a. Diol e.g. ethylene glycol, propylene glycol.

Propylene glycol is the diol most widely used for the manufacture of linear unsaturated polyesters. It is prepared by the hydration of propylene oxide



b. Unsaturated acids and anhydrides

Phthalic anhydride: The most important modifying components used in the manufacture of linear unsaturated polyesters is phthalic anhydride. The anhydride is generally obtained by the oxidation of o-xylene

ALKYDS

They are network polymers which find extensive use as surface coating. The most important polyesters of this type are derived from phthalic anhydride and glycerol. The esterification of glycerol with phthalic anhydride gives a glassy, brittle material which is of commercial interest.

Raw Materials

The principal raw material involved in the preparation of alkyd resins are polyhydric alcohols (polyols) and dibasic acid (or corresponding anhydrides) together with the modifying oils (or corresponding acids).

Example of a (1) Polyhydric alcohol used is



Example of (2) Dibasic acids and anhydrides used is Phthalic anhydride.

(3) Modifying oil and acids

Oils are commonly designated as drying, non-drying and semi-drying according to the effect of O₂ on thin films of the oils.

Film of drying oil – dry and insoluble between 2 – 6 days.

Film of non-drying oil – Fluid after 20 days.

Semi-drying oil – Becomes tacky after about 7 days.

Since alkyd resin cannot be classified according to the type of oil they contain. Therefore, we have drying oil resins e.g. also used in furniture for hard ware or metal furniture and house hold paints.

Semi – drying oil resin – Used to improve adhesion and also used among plasticizers.

Polyester Plasticizers

Are linear saturated polyesters of low molecular weight i.e. less than 10,000 (oligomer). It may be noted that low molecular weight saturated polyester of a different kind are also of commercial importance.

Polyester plasticizers are prepared by a diol – dicarboxylic acid condensation . in a typical process, a mixture of the reactant is heated at 200 – 250⁰C in an inert atmosphere for several hours with continous removal of water. By such process, polyesters with molecular weights up to about 1000 may be prepared. If higher molecular weight material is required, an excess of diol is used in the reaction.

Diols e.g. ethylene glycol

Diacid e.g. Adipic, sebacic acid

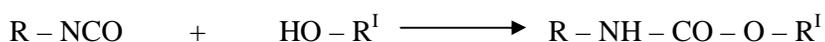
Poly Urethanes

Poly urethanes are defined as polymers which contains urethane groups (- NH – CO -) in the main polymer chain. In technologically useful polymers urethane group is not usually the principal group present; other groups such as esters, ether, amide and urea groups are generally contained in the polymer chain in appreciable number.

Several kinds of polyurethane are of commercial significance and are conveniently classified into the following major types: flexible foam; rigid foam; integral foams; elastomers; surface coatings and adhesives. At present, about 50% of polyurethane output is in the form of flexible foam and 25% is as rigid foam. The remainder finds use in such application as elastomers, surface coatings, adhesives and binders.

Raw Materials

The urethane group results from the interaction of an isocyanate and a hydroxyl compound.



It will be apparent that this reaction leads to polyurethane when multifunctional reactants are used.

When diisocyanate and diol react together, a linear polyurethane is obtained whilst a diisocyanate and a polyhydric compound (polyol) lead to a cross-linked polymer.

Thus, diisocyanate and diols and polyols are the principal raw materials used in the manufacture of polyurethanes.

Diisocyanates are prepared by phosgenation of 1^o amines.



a. Toluene Diisocyanates

Toluene is the starting material for the production of toluene diisocyanate (TDI)

And thus, hydroxyl groups are available to participate in the urethane reaction. These polyesters are prepared by the rx (e.g. adipic acid + glycols)

FOAMS

Polyurethane foams are produced by forming a polyurethane polymer concurrently with a gas evolution process. Provided these two processes are balanced, bubbles of gas are trapped in the polymer matrix as it is formed and a cellular product results. The matching of the two reactions is essential for the formation of satisfactory foams. If the evolution of the gas is too rapid, the foam initially rises well but then collapses because polymerization has not proceeded sufficiently to give a matrix strong enough to retain the gas. If polymerization is too fast, the foam does not rise adequately.

By selection of appropriate reactants, it is possible to prepare foams of varying degrees of cross-linking. Slightly cross-linked products are flexible foams whilst cross-linked products are rigid foams.

Flexible Foams: Mainly used for furniture cushioning, mattresses etc.

b. Diol and Polyols

The earliest polyurethanes were based on asphaltic diol (glycols). Today, production of polyurethanes has mainly involved polymeric hydroxyl compounds. The use of these materials permits the manufacture of a much wider range of products at relatively low cost. The polymeric hydroxyl compounds which have received most attention are polyesters and polyethers.

(i) Polyethers for polyurethanes

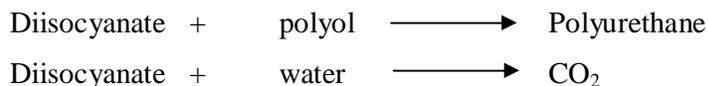
The polyethers most widely used for the production of polyurethanes are hydroxyl – terminated derivatives of propylene oxide. Polyether triol of relatively high molecular weight (about 3,000) are extensively used for the production of flexible foams whilst polyols of low molecular weight (about 5,000) are used for rigid foams and surface coatings.

(ii) Polyesters used for Polyurethanes

The polyesters used in the preparation of polyurethanes generally have molecular weight in the range 1,000 – 2,000 and are liquids or low melting solids. They are usually saturated. These polyesters are hydroxyl – terminated.

General Preparation of Flexible Foam

The gas used in the production of flexible foam is usually CO₂, formed by the interaction of isocyanate and water. In a system containing a diisocyanate, a polyol and water two principal reactions proceed simultaneously namely;



As indicated above, a satisfactory foam is obtained only if these two reactions are in step. Catalyst play a crucial role in commercial operation.

Toluene diisocyanate is usually the preferred isocyanate for the production of flexible polyurethane foams. We need to know that flexible foams are based on either polyesters or polyethers. Either can serve as the source of –ol. Therefore, we have polyether flexible foam and polyester flexible foam.

A typical formulation for flexible polyether foam would be as follows

- Polyether triol = 100 parts by weight
- 80: 20 Toluene diisocyanate = 40 part by weight
- Water = 3.0
- Triethylenediamine = 0.5
- Stannous octoate = 0.3
- Silicone block copolymer = 1.0

Flexible polyurethane foams are open-cell structures which are usually produced with densities in the range 24 – 48 kgm³. It is majorly in upholstery application.

Rigid Foams

Are used for the insulation of appliances such as freezer, refrigerators, in cars.

The principle underlying the production of rigid polyurethane foam is fundamentally the same as that used for flexible foams, namely a reacting isocyanate/ polyol mixture is simultaneously expanded by gas generation. The essential difference between the two products lies in their degree of cross- linking; whereas flexible foams are highly cross – linked. This high degree of cross – linking is achieved by using isocyanate. Rigid foams, unlike flexible foams are now mainly based on polyether rather than polyesters.

A difference between manufacture of rigid and flexible foam is in the blowing agent generally used. Flexible foam are invariably blown by CO₂. Rigid foams are also blown by CO₂ generated by isocyanate – water reaction but usually low boiling halogenated alkenes are employed (trichlorofluoro methane 24⁰C).

A typical formulation of rigid polyester foams might be as follows

- Polyester polyol = 100 parts by weight
- Polymeric diphenyl methane diisocyanate = Stoichiometric + 5%
- Trichlorofluoro methane = 50
- Triethylene diamine = 0.5
- Silicone block copolymer = 1.0
- Glycerol = 10 (cross –linking agents)

Others include integral foam.

Polyurethane are also used in surface coating, and adhesives.

POLYDIENES

Polydienes constitute an external group of polymer. These groups are called Rubbers.

Types of rubbers are (1) Natural rubber (2) Polyisoprene (3) Polybutadiene, Styrene – butadiene etc.

The most useful of these commercially is Styrene – butadiene which is used in the production of automobile tyres etc.

SILICONES

Silicones are products which can be fluids, elastomers or resins. They are used as hydraulic fluids, lubricants. They are also majorly used for the production of laminates.

Silicones are defined as polymers comprising alternate silicon and oxygen atoms in which the silicon atoms are joined to organic groups.

According to the above structure, it can be (1) linear and (2) network, both of which fluid technologies use.

Raw Materials

The basis of commercial production of silicones is that chlorosilanes readily react with water to give silanols which are unstable and condense to form siloxanes.

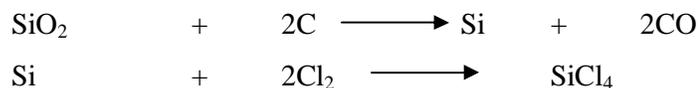
Dichlorosilanes lead to linear silicones

Polymer of the above form the basis of silicone fluids and elastomers.

Trichlorosilanes gives branched and cross – linked silicones.

Structure of this types form the basis of silicones resin

Commercial process for the preparation of chlorosilanes start either from silicon or silicon tetrachloride both obtained from silica.



Abeokuta commercial and industrial company, Asero Housing Estate

This company produces urethane foams. The main uses of these foams includes mattresses, carpets, underlay, automotive sealing, furniture, textile padding etc.

Chemistry of foam productions

The reaction of an isocyanate with an hydroxyl compound gives an urethane group according to the reaction.



Therefore, the diisocyanate and diols or polyols are the principal raw material.

Raw materials for foams production

Polyol (Poly G – 53OSA)

Dimethylethylamine (DMEA)

Toluene diisocyanate (TDI)

CH₂Cl₂

Stannous octoate

Silicon oil

Water

Pigment

Most of these raw materials could be obtained commercially from Dow chemical company in USA or DU Pont.

Properties and functions of the raw materials

Polyols or Diol:- It is a non-poisonous oily chemical. It gives strength to the foam.

Preferably, 1,4 - butanediol are used for flexible foams while polyhydroxyl compounds (e.g. ethane 1,2, diol (ethylene glycol) {HO (CH₂)₂ OH}, 1,4 – butanediol is used for rigid foam.

Dimethylethylamine (DMEA)

It is a very strong catalyst for water reaction, dangerous, poisonous. It serves as a heating agent in foam production. Absence of it will cause peel-off at the sides of the foam and even make drying very slow

Diisocyanates



(Phosgenation of primary amines)

There are different types of diisocyanate

(a) Toluene diisocyanate

(b) Hexamethylene diisocyanate

(c) Diphenylmethane diisocyanate

(d) Naphthlene 1,5 - diisocyanate

Among these diisocyanate, TDI is mostly used.

Toluene diisocyanate (TDI)

TDI is a poisonous chemical. It reacts vigorously with other chemicals to form foam.

It is usually the last raw material to be added during mixing because its addition to the mixture instantaneously generates CO₂ which affects rising of the foam.

Synthesis of TDI

CH₂CL₂

Very poisonous and flammable. It serves as blowing agents and has a cooling property.

Stannous octoate

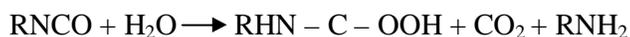
It is a catalyst mainly for polyol reaction. It controls the texture of the foam and give support as the foam rises.

Silicon oil

This acts as a surfactant in foam production. It controls liquid mixing, cell structure, stability.

Water

Water is a reactant blowing agent. Water in conditions with the other blowing agent makes the foam to rise quickly by hydrolyzing TDI to generate CO₂ which is trapped within the cells of the foam.



Fertilizers

Fertilizers place back in the soil the ingredient removed by plants or add materials needed by native soils to make them productive or more productive. Fertilizer represents the largest single item among agricultural chemicals. Most fertilizers in use are mineral fertilizers.

Classification of mineral Fertilizers

Mineral fertilizers are classified according to their agrochemical significance, the amount and kinds of nutrients.

As regards the content of the elements i.e nitrogen, phosphorus and potassium, fertilizers can also be divided into ordinary (single) and combined (composite) fertilizer.

Ordinary fertilizer includes one of the main nutrient substances. Fertilizers containing two or three elements (combined fertilizer) are called double and triple respectively. The latter are also called complete because they contain all the three main nutrient element. As regards the solubility in soil waters, fertilizers can be divided into water – soluble and soluble in soil acids. All nitrogen & potassium fertilizers are soluble in water. These fertilizers are easily assimilated by plants, but on the other hand are washed out of the soil more rapidly by soil waters. The fertilizers soluble in soil acids include most phosphates. They dissolve much more slowly, but are preserved longer in the soil.

With respect to their physiological effect on the soil being fertilizer, all fertilizers are divided into acid, alkaline and neutral ones.

Finally, let us conditionally divide all the fertilizers manufactured by the chemical industry as regards the content of the main nutrient substances into:

Nitrogen fertilizer – contain nitrogen

Phosphorous fertilizer – contain phosphorous

Potassium fertilizer – contain potassium

Phosphorous fertilizers

Phosphorous fertilizers include simple and double super-phosphate belonging to the class of water – soluble fertilizers.

Raw material used for phosphorous fertilizers

The raw materials are natural phosphates, namely apatite and phosphorites. Phosphorous is in an insoluble form in these compounds chiefly in the form of fluoroapatite $\text{Ca}_5\text{f}(\text{PO}_4)_3$ or tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$. Apatite is a mineral contained in volcanic rock.

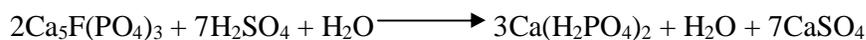
Phosphorites are minerals of sedimentary origin, and are extracted in addition to apatite. To produce fertilizers assimilated by plants and used in any soil, the insoluble natural phosphates have to be transferred into water – soluble or easily assimilated salts.

Production of super-phosphate

The chemical industry produces simple super-phosphate, which is chiefly a mixture of monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and gypsum CaSO_4 , and double super-phosphate which is hydrated calcium monophosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

The production of simple super-phosphate consists in the decomposition of fluorapatite with sulphuric acid.

The overall reaction equation is



The reaction begins immediately after the phosphate is mixed with the conc. H_2SO_4 and terminates in 20 – 40 minutes. The temperature in the reaction rises to 120°C . The formed monocalcium phosphate is first in solution and begins to crystallize.

The principal shortcoming of simple superphosphate is the relatively low content of P_2O_5 in the fertilizer. To produce a more concentrated phosphorous fertilizer, natural phosphorous are decomposed with 70% phosphorous acid.

Nitrogen Fertilizers

Nitrogen fertilizers are divided into ammonia (containing nitrogen in the form of the cation NH_4^+), nitrate (containing nitrogen in the form of NO_3^-), ammonium nitrate (containing both ions) and the amide fertilizers (containing nitrogen in the form of NH_2).

Production of Ammonium Nitrate Fertilizer

Ammonium nitrate may be used as fertilizers for any crop and any soil. But this fertilizer has poor physical properties.

The process of producing ammonium nitrate consists of neutralization of weak nitric acid with gaseous ammonia.



LUBRICANTS

Lubrication is a phenomenon which takes place when a third substance is introduced between the two moving bodies thereby reducing friction between them.

Whenever two bodies are moving together with their surfaces in contact, certain amount of friction takes place. Friction is known as thief power and destroyer of bearings. The chief cause of friction is chemical bonding of elements or Van der Waal's attraction.

Friction

While studying about lubricant, it is worthwhile to have elementary knowledge of friction and wear. Purpose of lubrication is to minimize both friction and wear in any system of moving surface. It has been experimentally established with the help of electron microscope that even the best polished metal surface is not smooth but consists of ASPERITIES and VALLEYS.

When two such surfaces come into contact simple laws of friction are allowed.

- (1) Frictional force is proportional to the normal load applied
- (2) Frictional force is independent of apparent area of contact.

The force required to start sliding is to overcome the barrier of static friction and the force required to keep the surface in motion is to overcome the barrier of kinetic friction; and it is well established that former force is greater than the latter ones.

Wear

Wear is the process of shearing due to movement of surface; the peaks of the softer metals are picked up by asperities or peaks of harder metal. Through softer metal may lose more pick-up, in practice both the metals may lose pick-up even in presence of lubricants in course of life. This material loss or deformation of moving parts is known as WEAR.

Types of Lubricants

Lubricants can be broadly divided into various categories starting from liquid through semi-solid e.g.

- (1) Lubricating oil
- (2) Lubricating emulsion
- (3) Lubricating grease
- (4) Lubricating solids.

Lubricating Oils

Lubricating Oil are classified into 3 categories (i) animal & vegetable oil (ii) mineral oils (iii) synthetic oil.

(1) Animal and Vegetable oil :- Animal and vegetable oil was the sole source of lubricants before the lubricants originated from mineral source.

Vegetable oil are found in

(a) Olive oils, higher grade of this are edible while lower grade are for lubricants. Others are pal oil, castor oil, whale oil etc.

2. Mineral oils – This is known as petroleum oils, and is obtained from petroleum crude. Distillations of various properties basically depend on their boiling points which are separated. These distillates are further treated or refined to form suitable oils. Shorter chain oils possess lower viscosity as compared to long chain. Mineral oils are used mostly because they are abundant and cheap.

A scientific illustration of industrial lubricants (mineral oils) is shown below:

Emulsion Lubricants

Emulsion is a system which occurs between two immiscible liquids preferably oil and water in such a way that one phase gets dispersed into another in the form of minute droplets. The dispersed phase is known as internal phase whereas the other one is known as external phase. To keep emulsion intact, a third agent called emulsion or stabilizing agent is added. Emulsifiers are compounds having both polar and non – polar characteristics. Molecules of an emulsifier

consist of one end HYDROPHILIC and the other molecule is wetted with oil, whereas hydrophilic end is wetted by water.

Example of emulsifier is sodium pulmitate.

Emulsion of water and oil can be termed as oil in water or water in oil. Emulsion of 50% lubricating oil and water is used for lubricating of steam cylinders to keep the wall cool with less oil consumption.

Semi-Solids Lubricants (gels and Greases)

Greases are semi-solid lubricants prepared with special quality of “stay put” and are used to prevent bearing from dirt and water. To be more specific by behaviour and structure, they are typical colloidal system called Gels.

When many colloids solutions are coagulated, a semi – rigid gel is formed. Examples of grease are:

- i. Lime soap grease: This grease covers the major share of market and are most suitable for lubricating water pump and tractors since they are cheap and resist displacement of water. The lime soap grease oil is made of slaked lime, fats and lubricating oil. Temperature above 65⁰C however destroys lime soap grease due to less of combined water. Lime soap made from fats and slaked lime is further mixed mechanically with desired amount of lubricating oil.

Others are (ii) Aluminium base grease (iii) Lithium base grease

MANUFACTURE OF LUBRICATING OILS

Manufacture of Mineral Oils

Main source of lubricating oil are fractions of crude petroleum. The boiling parts of these crudes is quite high and not suitable to distillation under atmospheric pressure. So the fraction and distillation is carried out under reduced pressure. The reduced pressure of vacuum distillation produces mainly three lubricating fractions i.e. light, medium and heavy stocks.

These individual fractions are further treated with refining operations consisting of (a) Solvent extraction (b) Dewaxing and (c) Finishing for desired quality of lubricant.

- (a) Solvent Extraction - This process removes asphaltic compounds from the stocks. These asphaltic compounds are mainly responsible for formation of acid sludges having low viscosity index numbers. This process of solvent extraction improves the flow properties and stability of lubricants.

Phenols are the common solvents used for this purpose, other include furfural, benzene and chlorinated solvents such as dichloroethylether.

- (b) Dewaxing – Particularly non – asphaltic types of crudes consist of waxes. These waxes have the range of melting point below 32°C – 71°C if they are paraffin groups. These waxing at lower temperature crystallize within lubricating oil thereby lowering the fluidity of oil. Pour point is the temperature at which an oil will no longer flow from a standard test tubes. These waxes increase the pour point which detrimental to the quality of a lubricant. Since lubricants with lower pour point are considered superior, dewaxing is done to lower the pour point. Dewaxing is also carried out by solvent extraction technique. These waxes are soluble in number of solvents such as methyl – ethylene ketone, benzene etc.
- (c) Finishing: After the above two treatments, oil still contains some undesirable colour bodies, micro crystalline wax etc. This purification is normally carried out by filtration through active clay or bauxite. The hydrogen is flushed in under pressure and high temperature. This hydrogen treatment converts disulphides and other sulphur compounds present in the oil to H_2S gas which is removed.

SYNTHETIC LUBRICATING OILS

In good number of modern machines, vegetable as wells as mineral oil may fail to serve as lubricants due to extreme condition of pressure, speed and temperature. Special kinds of lubricants may be required for many systems such as furnance equipment, bearing of jet planes etc. Therefore, lubricants which will not only work under extreme condition but also will bear a wide range of variable conditions have been synthesized by the help of organic and inorganic chemicals. Synthesis oil are usually silicon phosphates and esters e.g.

Silicon lubricants; examples is

Silicon atoms are attached to each other through oxygen atom which imparts stability to structure at high temperature and gives oxidation resistance properties. Various organic groups can replace R in the silicon structure, the nature and size of group replace R controls physical and chemical properties of lubricants such as viscosity volatility, flash and fire paints. Silicon oils are especially known for high viscosity index and very low volatility.

However, there are two main drawboards in such lubricant

1. Under extreme condition, sometimes the chain breaks forming SiO₂ which works as an abrasive and
2. They are suitable for boundary lubrication.

Mechanism of boundary lubrication can be defined as between two moving/ sliding surfaces. Silicon oil can be used as Hydrodynamic lubrication which is a complete fluid lubrication. In such system, lubricants is placed between two sliding surfaces, mechanically exacts parts, sliding surfaces, bearing etc.

Lubricating Oils Additive or Blending

To improve quality of oil, the following are added

1. Viscosity Index Improver: These additives prevent the oils from thinning at higher temperatures and from solidifying at lower temperatures. Such additives are usually hydrocarbon polymers like

They can either be polyisobutane or polystyrene or lay chain akyly acrylates and polyesters. Hexanol also work as viscosity index improver.

2. Pour Point Depressant: This type of additives helps the oil to maintain fluid characteristics even at low temperatures. Pour point depressants are paraflow and other polymeric materials.
3. Anti – oxidants: This anti-oxidant reduces affinity of oxygen toward oil e.g. phenols, organic phosphorus compounds. These anti-oxidant also reduces engine deposit showing an improvement on octane requirement.
4. Corrosion Inhibitor: these substances are added to reduce or prevent any kind of corrosion to bearings of other metal surfaces. These additives are effective by not allowing a contact of metal surfaces to corrosive substances e.g. metallic salts of complex organic thiophospheric acids.
5. Foam Depressant: Certain additives are added to depress the foam formation in the process of lubrication. This additives are usually silicon derivatives or oil insoluble liquids such as glycols or glycerol.
6. Emulsifiers: These additives promotes emulsion formation between water and lubricant. Such compounds are alkali metal solids of carboxylic acid and sulphuric acid and ethanol etc.

ORIGIN OF PETROLEUM

Petroleum oil is usually considered to be formed from organic matter like animals, fishes and vegetable debris accumulating in sea basins and buried there by sand and silt. The debris may have been decayed and decomposed under anaerobic (reducing) conditions, resulting in removal of most oxygen. The oil may also have been distilled from partially decomposed debris due to increased pressure and temperature generated by earth movement.

Due to temperature changes, earth movements and differences in density between oil and salt water, the oil migrates from the source rock to accumulates in favourable geological formations. The favourable location means a porous sedimentary rock (reservoir rock) capped by an impermeable rock which prevents escape of oil and gas. The reservoir rocks are generally coarse grained sandstone, limestone.

To bring the oil to the surface, wells are drilled. Initially, the gas pressure may be considered to force some oil to the surface, but later it has to be extracted with the help of pumps. The oils directly obtained from these wells are known as crude oil.

CLASSIFICATIONS OF PETROLEUM CRUDES

Most crudes consist of mixture of various hydrocarbons, ranging from the simplest hydrocarbon gas (methane) to the most complex solid paraffin wax or bitumen. Small amounts of nitrogen and sulphur are also invariably present in petroleum.

Depending on the type of the hydrocarbons predominating in the oil, petroleum oils can be classified into the following three main groups:

- i. Paraffinic: It consist of hydrocarbons of paraffin wax. Paraffinic hydrocarbons contains four aliphatic, one naphthalene and one aromatic groups. An oil may be called paraffinic, if aliphatic groupings are more than 75% of the whole.
- ii. Naphthenic: Consist mainly of hydrocarbons of naphthenic series and distillation yields some wax in the distillates and the residue mainly consists of asphalt. Naphthenic hydrocarbons contains three naphthenic, two aliphatic and one aromatic groups. An oil may be called naphthenic, if naphthenic rings are more than 70% of the whole.
- iii. Ashphatic: The oil of this group is rich in non – paraffinic hydrocarbon (aromatic and naphthenic) groups and distillation yield asphalt or bitumen in residue. Asphaltic hydrocarbons contains three aromatic, two aliphatic and one naphthenic groups. An oil containing more than 60% aromatic rings of the whole, may be called asphaltic oil.

PRODUCTS OF REFINING

Precursors of Petrochemicals: Are converted from gas, natural or cracked, LPG. To distinguish the increasing importance of acetylene, olefins and aromatics for petrochemicals, these compounds have been designated “Precursors” leading to the finished products. The principal precursors are acetylene, propylene, benzene, xylene, ethylene, toluene and naphthalene.

Inter-relationship of precursors from natural gas, petroleum and coal.

MANUFACTURE OR PETROLEUM REFINING

The refining or manufacturing of petroleum products and of petroleum chemicals involves two major branches, physical change or separation operations.

Physical change (separation operation)

Chemical change (conversion processes)

The separation branch of refining can be broken down into the ordinary unit operation as follows:

1. Heat transfer: Equipment should be clean to maintain satisfactory heat transfer and to remove fouling, which frequently greatly reduces transfer rates.
2. Distillation: This ranks among the more important unit operations. The crude oil is pumped in the form of water – in – oil emulsion which is broken by adding de – emulsifying agents or by electrical treatment. Chloride should be removed completely, since these corrode and damage the refining equipment. In this operation, separation is based upon volatility and the process stream may be separated by distillation into a more volatile “lighter” component and a less volatile “heavier” component.

In many applications of distillation in separation of petroleum products, the volatility difference is too low to be practical, and it must be enhanced by the addition of a solvent or an entrainer. The variation of distillation which a solvent of low volatility is used to enhance separation is called “extractive distillation” e.g. separation of butenes from butanes with furfural. When solvent of high volatility is added “azeotropic distillation” e.g. production of high purity toluene using methyl ethyl ketone as the entrainer, and also distillation to produce alcohol (aldehyde).

The crude petroleum after removal of dirt and water, the crude petroleum is processed by “fractional distillation” to obtain the following fractions

- a. Natural gas: It boils below 30°C .
 - b. Gasoline: Its boiling range is $30 - 200^{\circ}\text{C}$. This is also known as petrol and can be further divided into aviation spirit ($30 - 150^{\circ}\text{C}$), motor spirit ($40 - 180^{\circ}\text{C}$) and vaporizing oil ($110 - 200^{\circ}\text{C}$) for tractors.
 - c. Solvent spirit: It boils in the range $120^{\circ}\text{C} - 250^{\circ}\text{C}$. This is white spirit and is used as substitute of turpentine solvent.
 - d. Kerosine or light oil: It boils at the range $140 - 290^{\circ}\text{C}$. It is used as burning oil and tractor fuel.
 - e. Gas oil or diesel oil: its boiling range is $200 - 370^{\circ}\text{C}$. It is mainly used as fuel for diesel engine.
 - f. Heavy fuel oil: Its boiling range is above 250°C . This is used in metallurgical furnances.
 - g. Other products: Residue left after the above separation is thick and on further treatment yields paraffin wax, mineral jelly (vaseline), lubricating oils and grease and bitumen.
3. Absorption is another unit operation to separate a higher boiling constituent from other components of a system of vapour and gases. Absorption is widely employed in the recovery of natural gasoline from well gas and of vapours given off by storage.
 4. Adsorption: Is employed for about the same purpose as absorption; in the process just mentioned natural gasoline may be separated from natural gas by adsorption on charcoal. Adsorption is also used to remove undesirable colours from lubricating oil, usually employing active clay.
 5. Filtration after chilling is the usual method for the removal of wax from wax distillates.

Conversion Process

Petroleum offers such a fertile field for chemical synthesis both for gasoline or for petrochemicals for example:

1. **Cracking:** Distillation of an average grade crude petroleum oil yields 20 – 30% petrol, 30 – 40% intermediate oils and 25 – 50% residual fuel oils. The requirements of high quality gasoline available by distillation process. At the same time, the heavier fractions will be in surplus. Therefore, greater yields of gasoline at the expense of gas and heavy fuel oil fractions are obtained by the process known as **Cracking**.

Cracking is a process by which the larger molecules are broken down to smaller molecules giving more useful lighter fractions. Important cracking processes developed so far are (a) Thermal cracking (b) Thermal reforming (c) Catalytic cracking

Thermal cracking: When heavy petroleum oil is heated above the decomposition temperature, the molecules are broken and rearranged to give smaller molecules of the paraffin and olefin series and some hydrogen. However, polymerization also occurs to some extent to give some molecules larger than those originally present. Thus, this increases the yield of gasoline and proportion of ring compounds present. The gas formed contains high proportion of alkenes and the residue is called petroleum coke. The characteristic reaction of thermal cracking is



Thermal cracking can be carried out in liquid phase or vapour phase. In the liquid phase, low temperature (450⁰C) and high pressure are employed, whereas in the vapour phase higher temperature (600⁰C) and low pressure 20 – 23kg/cm³ are employed.

Thermal Reforming: This involves both cracking and isomerization. It is identical to thermal cracking except that the feed stock has roughly the same boiling range as the product and the temperature and pressure are usually higher.

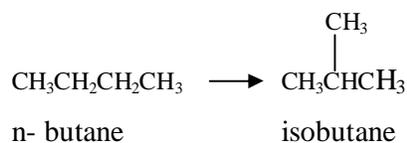
Catalytic Cracking: This is the major process for converting a heavy fraction into high – octane gasoline. The process splits larger molecules into smaller ones at much lower temperature and pressure in the presence of certain catalyst such as natural or artificial clays (e.g. bentonite activated by H₂SO₄ or synthetic aluminosilicates. The advantages of this over thermal cracking are (I) better yield of gasoline and (ii) better control of process. The main effect of the catalyst is to direct the cracking of alkanes towards the centre of the molecules and to convert alkenes into the corresponding alkanes.

2. **Reforming:** After the primary distillation of petroleum and the secondary cracking of heavy fractions, a large quantity of saturated and unsaturated hydrocarbons are present in gases or naphtha, or kerosine fraction. Reforming process change the nature of hydrocarbons in

distillate oil and are used for the improvement of gasoline and for the conversion of naphtha into gasoline. The various process for reforming include (a) Polymerization (poly-reforming), alkylation, isomerization, hydroforming and platforming.

Poly-forming (polymerization) is the method of converting C₃ and C₄ alkenes produced in thermal and catalytic cracking into high – octane gasoline. The gases are first washed with water to remove H₂S and then passed over the catalyst (60% H₂SO₄). The following equations is typical of polymerization reactions. Propene, butene and isobutene are the olefins usually polymerized.

Isomerization has been developed mainly to convert straight chain butane into methyl propane and also to convert straight chain hexane and pentane into branched chain alkanes. More importantly, isomerization conversion process has become of the utmost important in furnishing the isobutane needed for making alkylate as a basis aviation gasoline.



Hydro-reforming is the process for reforming low-octane gasoline or naphtha by reaction with hydrogen in the presence of catalyst (alumina). In this process, desulphurisation also take place by the reaction of hydrogen with sulphur to form H₂S.

Platforming involves the use of platonic chloride catalyst (coating on alumina) in the process of reforming with hydrogen.

CHEMICAL TREATMENT

Some types of chemical treatment to remove or alter the impurities in petroleum products is usually necessary to produce marketable materials. Depending upon the particular treatment used, one or more of the following purposes are achieved:

- (1) Improvement of colour
- (2) Improvement of odor
- (3) Removal of sulphur compounds
- (4) Removal of gums, resins and asphaltic materials
- (5) Improvement of stability to light and air.

Of these, removal of sulphur and improvement of stability are the factors usually governing the treatment employed.

Sulphur may be reduced by (1) Hydrogenation (which also removes metal -and nitrogen) (2) Treatment with caustic soda (3) Treatment with caustic soda plus a catalyst.

Several processes are available for the alteration of objectionable sulphur and the consequent improvement in colour. A method that reduced the odour and still remain a method of testing for the oil quality. This process consists in agitating the oil with an alkaline solution of sodium plumbite and a small amount of sulphur. The sulphur compounds usually found in oil are mercaptans. These give the material a disagreeable odour and cause corrosion. This treatment would convert mercaptans to comparatively harmless disulphides according to the equation;



The oxidation of mercaptans to less objectionable disulphides can be accomplished with a variety of mild oxidizing agents e.g. oxygen plus a catalyst such as copper chloride. The presence of sulphur in gasoline, even in the less objectionable disulphides form is undesirable. Not only does it increase corrosion and air pollution, but it decreases the effectiveness of lead antiknock agent.

It is now a common practice to add antioxidant to prevent the formation of gums, rather than to remove them chemically. Among the anti-gumming materials used are α -naphthol, cresol, wood tars.

OIL PRODUCTS DERIVED FROM COAL

Some liquid fuels can be obtained either by mixing pulverised coals with fuel oil (colloidal fuels) or by carbonisation of coals. The important liquid fuels are colloid fuels, coal tar and benzole.

Colloidal Fuels: These are the suspension of pulverised coal in fuel oils stabilized by the addition of an emulsifier such as sodium stearate.

Coal Tar Fuels: These are liquid fuels obtained by blending coal tar distillation products obtainable by coal carbonisation. Their calorific value is high and sulphur contents are low which makes them suitable for metallurgical furnaces. (Sulphur is harmful since it is absorbed in metals)

Benzole: Crude benzole is recovered from coke oven gas and from other gases produced at high temperatures. Benzole having an octane number of 90 can be mixed with petrol and used as a fuel for internal combustion of engines.

LIQUID FUELS DERIVED FROM COAL HYDROGENATION

Coal is not only the country's fuel, but share with petrochemicals, the furnishing of the basic raw materials for many essential industries. When coal is thermally pyrolysed or distilled by heating without contact with air, it is converted to a variety of solid, liquids and gaseous products. The nature and amount of each product depend on temperature used in the pyrolysis and the variety of coal.

Coal can be converted into oils by reaction with hydrogen under pressure in the presence of catalyst. This process is known as hydrogenation and can yield liquid fuels up to 65% by weight of the coal processed.

Further capital and maintenance costs are quite high, making the process uneconomical when natural petroleum oil is available cheaply. Several coal hydrogenation plants were built in Germany, Korea, U.S.A. but were closed down as economic grounds.

MANUFACTURE OF PETROCHEMICALS

Raw materials and Feedstock

The basic raw materials supplied by petroleum refineries or natural gas companies are LPG, natural gas, gas from cracking processes, liquid distillate (C₄ to C₉), distillates from cracking processes and cyclic fractions for aromatics.

Such mixtures are usually separated into their constituents at the petroleum refineries and chemically converted into their reactive precursors before being subjected for manufacturing the various petrochemicals actively used by the manifold industries.

FLAVOURS

There are only four basic flavours which the nerve endings in the taste buds, of the tongue can detect; sweet, sour, salt and bitter. The popular conception of flavour, however, includes the combination of these four basic stimuli with concurrent odour sensation. Apple, grapes and lemon for instances, tastes merely sour, with a trace of bitterness from the tannins present. The main conception of the apple taste is due to the odour of acetaldehyde, amyl formate, amyl acetate and other esters present in the volatile portion.. The principle of perfume blending is also applicable to flavour manufacture. The best flavouring essences are natural products altered and reinforced where necessary by synthesis.

It is noteworthy that many essential oils find application in the flavour industry e.g. citrus oils, peppermint and spices.

Natural Fruit Concentrates

- Distillation and extraction of the fruit – The ripe fruit is mashed before subjected to steam distillation until all the aroma is concentrated in a small portion of the aqueous distillate. The portion is then extracted with petroleum and ether removed under vacuum to let an essence of the fruit used.
- Concentration of the juice – The expressed and filtered juice is concentrated in vacuum evaporators until a low degree of heat until the water is largely driven off, and the sugar is high enough to inhibit bacterial growth.

VANILLA

They are found in *Vanilla planifol*. Substances identified in the Vanilla bean are alcohol, aldehyde, Vanillic acid, Vanilylethyl vanillin etc.

Vanillin – Is one of the most widely used flavours which can be isolated from the Vanilla bean. However, Vanillin can be synthesized from eugenol obtained from oils of cloves, and then followed by oxidation to Vanilline using Nitrobenene as oxidizing agent.

CHOCOLATE AND COCOA

It occurs in the seed of *Theobroma cacao*. The pods are split open and the seed is allowed to ferment from 2 – 7 (hours/days) during which the embryo is killed and tannin content reduced. The fermented beans are dried and shipped to manufacturing centre and then heated in a rotary roasters, which eventually develop the true chocolate flavours and aroma, removes unpleasant tannins and volatile matter.

MONOSODIUM GLUTAMATE



The compound is an important flavouring agent, yet has no flavour of its own. It accentuates the hidden and little known flavours of food in which it are used.

ADHESIVES

The materials which can surface together are known as adhesives. Gum and glues are very common adhesives.

Mechanisms of joining the surfaces by adhesives may be one of the following:

1. Specific Adhesion: In this, the surfaces are held together by valence or intermolecular forces of attraction.
2. Mechanical Adhesion: In this case, the surfaces may fill the voids of porous surfaces and the surfaces are held together by interlocking action.
3. Fusion Adhesion: In this case, the surfaces are partially dissolved in true adhesive or solvent.

In general, adhesives can be classified as Starch adhesives, Protein adhesives and Synthetic adhesives.

Starch Adhesives

These are prepared by heating starch suspension in water with dilute alkali until the starch granules burst. These can also be made by the treatment of starch in dilute acids, enzymes and peroxides. These possess a lower strength and are not resistant to water.

Protein Adhesives

A major amount of protein is prepared from animal skin or animal tissues available from the leather industry or hides and blood from the slaughter houses, or from bones. Another source of glue is casein (protein of milk) which is obtained by coagulating the skimmed milk by the treatment of dilute acids. Casein formed is then separated and mixed with lime and preservatives. For its use as an adhesive, the glue is mixed with water to form a paste which is applied to the surfaces by specific as well as mechanical adhesion. A cheaper protein glue can be obtained by mixing soya bean cake with hydroxides of Calcium and Sodium.

Synthetic Adhesives

Synthetic adhesives are polymer resin used in the plastic industry. Similar to plastic, these are also either thermosetting or thermoplastic. The most important thermosetting adhesives are uncured phenol formaldehyde which is sold as a solution, a solid or a thin film. The resin is applied between the surfaces and cured by pressing and heating the surfaces to 110 – 170⁰C. Curing results in the formation of cross link having good strength and is resistant to water.

Commonly used thermoplastic adhesives are cellulose derivatives and raw rubber dissolved in suitable solvents. Cellulose acetate can be dissolved in solvents and applied as adhesives. Raw rubber dissolved in solvent can be used as water proof adhesives.

Curing of raw rubber can be accomplished by chemicals or by application of heat and pressure.

EXPLOSIVES

An explosive is a material which under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of great deal of heat and much gas.

Explosives differ widely in their sensitivity and power. The most primitive explosive known to mankind is gunpowder. The earliest synthetic explosives consisted of charcoal, sulphur and nitrate of either Na or K. When this mixture is ignited by outside means or source, a large volume of hot gases is produced.



Characteristics of Explosives

1. Explosives must be stable for storage under ordinary conditions of temperature and pressure. For this reason, an explosive which decomposes at 100°C is taken as unstable or unsafe, whereas if it does not decompose till 200°C it is taken as stable or safe. Explosives should also be chemically stable.
2. For obvious reasons, the reaction taking place must be exothermic. In general, the energy released should be in the range of 1000 cal/g and more. Although, some explosives like Ammonium nitrate give 346 cal/g.
3. The rate of reaction should be quite high so that heat/energy of reaction should be accumulated faster than it is released further. This will cause an abrupt rise in temperature and explosion will occur.
4. The end products of explosive reactions must be gases preferably having low molecular weight which will give a volume change. Under a sudden rise in temperature, these gases expand with a blast.

Properties of explosives must have to do with (1) Sensitivity (2) Stability (3) Brisance and (4) Strength (5) Oxygen balance.

1. It must be sensitive enough and sensitivity of an explosive is determined by finding the height from which a standard weight must be allowed to fall in order to detonate the explosive. Sensitivity to impact, friction, electric spark, heat.
2. Stability – See characteristics above.
3. Brisance – This means shattering action of explosives. It must scatter on explosion. The shattering may be measured by exploding a small quantity of it in a sand bomb, i.e. a heavy walled vessel filled with standard coarse sand which is crushed by the explosion. The amount of sand crushed is a measure of the explosive force and shattering action.
4. Actually, brisance is probably a combination of strength, velocity and shattering action

5. Oxygen balance – Oxygen present in the molecules of explosives compounds is quite common. It relates to the power or brisance of the explosives. Power and brisance increase simultaneously from – ve to zero. – ve \longrightarrow 0 \longrightarrow + ve (-...0...+)
oxygen measurement for the explosives.

Measurement of oxygen balance is not peculiar to all explosives because nature of oxygen linkage is different in different molecular structures and they matter a lot for energy output. It is noteworthy that in some cases, it is not always that CO₂ is formed, reaction may end up at CO formation and in many cases only CO is formed. For this reason, oxygen balance is calculated on the basis of C \longrightarrow CO instead of CO₂. It is expressed as % surplus or deficiency of oxygen by weight, thus for a compound C_aH_bM_cO_d oxygen balance will be

Since power and brisance is a measure of oxygen balance. Oxygen balance for Nitrobenzene is – ve and therefore the power and brisance of Nitrobenzene is small.

There are three fundamental types of explosives (1) Mechanical (2) Atomic and (3) Chemical.

We are interated in chemical aspects.

Chemical explosives are classified as:

(A) Detonating or High Explosives

This may either be (1) Primary or initializing explosives (detonators) e.g. lead azide, mercury fulminate, or lead trinitroresorcinate and (2) Secondary explosive e.g. TNT, Cyclonite (RDX), Pentaerythritoltetranitrate (PAT), Picric acid, Dinitrotoluene (DNT).

Initializing or Primary High Explosives – are quite sensitive material which can be used to explode by the application of fire or by means of a blow. They are very dangerous to handle and are used in comparatively small quantities to start the explosion of larger quantities of less sensitive explosives.

Secondary High Explosives – Are materials which are quite insensitive to both mechanical shock and flame but which explode with great violence when set off by an explosive shock such as that obtained by detonating a small amount of an initializing explosive in contact with the high explosive. Decomposition precedes by means of detonation, which is the rapid chemical destruction progressing directly through the mass of the explosive. Detonating many proceed at rates as high as 6000m/s.

(B) Deflagrating or Low Explosives (e.g. colloided cellulose nitrate, nitrocotton)

Low explosives or propellants differ from high explosives in their mode of decomposition; they only burn. Burning is a phenomenon that proceeds not through the body of the material but through the layers parallel to the surface. It is quite slow in action, it rarely exceeds 0.25m/s. The action of low explosives is therefore less shattering.

Some Important Explosives

There are number of explosives available in market related to specific purposes either industrial, social or defense.

Detonators, primer or initiators are equally important.

1. **Nitroglycerine:** Was the first high explosive to be employed on a large scale. It is a colourless oil liquid formed by the nitration of glycerin with mixed acid. It is sensitive to shock and friction and seldom used alone as explosive, but used largely in the manufacture of dynamites.

The product is called glycerol trinitrate.

2. **Cellulose Nitrate:** This is an explosive which is a nitrated cotton. The cellulose molecules is a highly complicated one with a molecular weight as high as 300,000. Any given sample of cellulose contains a wide distribution of molecules, all having the empirical formula

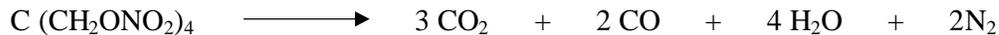
[C₆H₇O₂(OH)₃]. There are thus three hydroxyl groups per fundamental (glucose) unit that may be esterified with nitric acid/ H₂SO₄.



It is a white solid used in propelling powders and also in making dynamites.

3. **Dynamites:** Dynamite is made from glycerol trinitrate. Modern dynamite generally use wood flour, ammonium nitrate as the agent employed to absorb the glyceryl trinitrate to which an oxidizer is added. If cellulose nitrate is used, then gelatin dynamite is produced. Due to its high VOD (velocity of detonation), they are preferred for detonation of building or digging into rocks, submarine blasting. It is used also as a primer/ initiator or other less sensitive explosive.
4. **Pentaerythritol tetranitrate (PETN) [C(CH₂ONO₂)₄]:** PETN is one of the most brisant and sensitive of the military high explosives. Similar to glycerol and cellulose, PETN is another poly(OL) with 4 – OH group.

PETN may be made as represented above by the nitration of pentaerythritol with strong nitric acid at about 50⁰C. the reaction decomposition when exploded is



5. **RDX – Cyclonite:** Chemically known as sym – trimethyla trinitramine [(CH₂)₃ N₃ (NO₂)₃], is one of the most powerful explosives known at the present time. RDX – cyclonite is used in a mixture with TNT and Aluminium, known as Torpex, for mines, torpedo warheads. It is also employed as an ingredient in explosives for shells and bombs and desensitized by wax on only materials.

It is a colourless crystal made by destructive nitration of hexamethylene tetramine with conc. HNO₃ as represented above.

6. **TNT (Trinitrotoluene) :** In spite of other new explosives developed symmetric TNT remains an important military explosive, particularly in mixtures with ammonium nitrate (amatol). Its low melting point (80⁰C).permits loading unto bombs and shells in the molten state. TNT is made by multi stage nitration of toluene with a mixture of H₂SO₄ and HNO₃.

TNT is not sensitive to impact or friction and its ignition temperature is 250⁰C. it is a yellow crystal, which is an explosive on its own. However, it forms a part of many military explosives.

7. **Blasting agents:** Has become the principal industrial explosive because they may be handled in simple machinery without danger and their cost is very low. The term “blasting agent” is usually applied to ammonium nitrate mixtures sensitized with non – explosive fuels such as oil or wax. Such mixtures are not explosive, even with conventional blasting caps, and requires a powerful booster to start detonation.

Other explosives include (8) Lead azide, (9) Tetryl, (10) Picric acid etc.

SOLAR ENERGY

Direct use of solar energy means using light which is a form of electromagnetic radiation.

Electromagnetic radiation is a wavelike phenomenon that moves energy across distances. Not only light but Radiowaves, Microwaves, X-rays and Gamma rays are all forms of electromagnetic radiation. One thing that distinguishes each of these types of radiation from the other is its wavelengths.

Both Ultraviolet and Infrared lights are visible to the human eye. UV light has wavelengths shorter than Violet light and IR light has wavelengths longer than Red light.

Infrared light is sometimes called radiant heat, but is not really heat energy until it is absorbed by the skin or some other surfaces. Hot objects radiate Infrared. The Sun mostly radiates visible light but also a substantial amount of UV and IR light.

It is obvious that Sunlight is stronger than candle light. Irradiance describes how much energy is striking a surface.

Instruments for measuring Solar radiation are called Pyranometer.

Most Solar radiation comes from a relatively thin, relatively cool (5000⁰C) layer near the Sun surface known as the Photosphere. When the Sun’s energy reaches the Earth’s orbit, it contains a harmful % of UV light and even a few Gamma and X-rays. However, when passing through the Earth’s atmosphere, these harmful rays are largely filtered out along with some wavelengths of visible light. The Sunlight that strikes a solar collecting surface can be direct (or beam), diffuse or reflected. Direct Sunlight comes directly from the Sun, Diffuse Sunlight does not come directly from the Sun but is first reflected from dust particle, air, clouds and water vapour. But reflected Sunlight bounces from trees, snow, landscapes, mirrors and other Earthbound surfaces.

HEAT TRANSFER

Adding heat, removing heat, heat gain and heat loss are the subjects of the theory of heat transfer. Heat transfer theory is used in the study, design and testing of Solar heat collectors, heat storage, units, heat exchangers, heating systems, industrial process heaters, solar air conditioning and power generating equipment and all other solar application that involve the use of heat.

There are three ways by which heat can be gained, lost or transferred;

1. Conduction
2. Convection
3. Radiation

CONDUCTION

Thermal conduction is simply the flow of heat through an object or material and it occurs as energized molecules transfer energy to their less – energized neighbours.

The thermal conductivity, K, of a material determines how fast heat flows through the material. The larger K is the faster heat flows e.g. heat flows faster through Aluminium than through wood, so aluminium has a higher thermal conductivity.

$$q = \frac{KA}{d} (T_1 - T_2) \quad \text{or} \quad q = \frac{A}{R} (T_1 - T_2)$$

Where, K = Thermal conductivity in W/m⁰C

d = Distance heat must flow

A = Cross sectional area

T₁ = Temperature of hot side

T₂ = Temperature of cool side

R = ^d/K = Conduction resistance in m²⁰C/W

q = Rate of heat flow in watts

Example –

1. One end of a 10cm copper wire is 4mm in diameter is maintained at 0⁰C while the other end is maintained at 100⁰C. If the thermal conductivity is 386 W/m⁰C, how much heat is conducted through the wire. (Answer = 4.9W)
2. One side of a sample of glass wool insulated is maintained at –20⁰C while the other is maintained at 20⁰C. If the thermal resistance of the insulation sample is 2.1m²⁰C/W, how much heat per unit is transferred through the sample?

Since, $q = \frac{KA}{d} (T_1 - T_2) \quad \text{or} \quad q = \frac{A}{R} (T_1 - T_2)$

Since the area is not given, the heat flow per unit area.

$$\frac{q}{A} = \frac{1}{R} (T_1 - T_2)$$

Can be calculated as

$$q/A = 1/2.1 [20 - (-20)]$$

$$q/A = 19 \text{ W/m}^2$$

CONVECTION

Convection refers to the transfer of heat by a moving fluid.

The heat transfer rate, q , in watts for convection is

$$q = h A (T_s - T_f) \quad \text{or} \quad q = \frac{A}{R} (T_s - T_f)$$

Where, h = Convective heat transfer coefficient

A = Area of flow surface

T_s = Temperature of surface

T_f = temperature of fluid

$R = 1/h =$ Convective resistance in $\text{m}^2\text{C/W}$

RADIATION

Radiative heat transfers is the transfer of heat in different bodies of heat energy by Infrared or visible light due to differences in temperature e.g. radiation of heat by a hot stove to a cooler objects in a room. Any hot surface tends to lose heat by giving off Infrared light energy. The Infrared cannot be seen, but can be felt as it is absorbed by the skin.

Heat is easily transmitted as Infrared light by warm surfaces and Infrared light is easily accepted by many surfaces and transformed into heat. Note that a very high temperature surface (over about 3500°C) emits mostly visible light, while a lower temperature surface emits mostly Infrared light.

Of course, there are many different kinds of faces: A painted metal surface at 100°C radiates several times faster than a polished surface at same temperature.

The painted heat radiator is called a blackbody. The rate at which a blackbody radiates energy depends only on its temperature and its surface area.

$$q (\text{blackbody}) = \epsilon \sigma A T^4$$

Where, T = Temperature of object, K or R

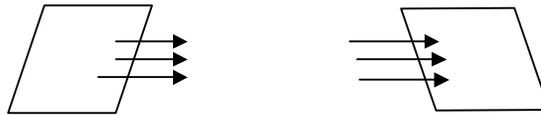
$A = \text{Area of radiating surface m}^2$

$r = \text{Stephan –Boltzin constant} = 5.67 \times 10^{-8} \text{ Wm}^2 \text{ K}^4$

What is a blackbody?

- A blackbody absorbs 100% of the radiation.
- A blackbody are perfect absorber and perfect emitter of radiation
- A blackbody radiate energy faster than any other surface can.

Heat Transfer by Radiation between Two surfaces



SOLAR HEATING SYSTEMS

Solar heating involves more than heat collectors. It also involves distribution of heat to the rooms of a building and the storage of unneeded heat for later use at night or during cloudy periods.

Any dark surface that faces the Sun is a solar heat collector; it is dark precisely because it has absorbed some light energy and converted it to heat instead of reflecting the light away. Collector glazings or transparent covers can be made of glass, plastics or fibreglass. Calass is chosen most often because of its long life, high solar transmittance (the fraction of Sunlight it allows to pass through) and low transmittance for Infrared radiation from the collectors.

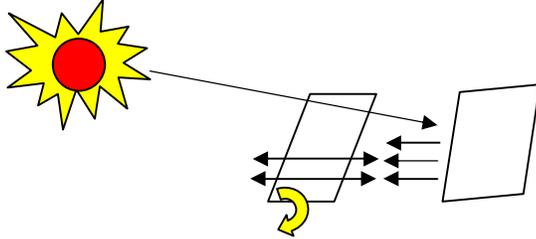
A plane glass is a hard, solid object and yet visible light can pass through it almost as if it were nothing. In addition, glass prevents the transmittance of most radiant heat infrared light. Thus, if we take a dark surface and over it with a sheet of glass, we have a fairly effective solar collector i.e. that really let light in, converts the light to heat and then slows down any radiant heat. One disadvantage of glass cover is that if it is placed within an inch or two on the dark collecting surface, it creates a dead – air space or zone of fairly still air that acts as insulator. The combination of a dark surface with a glass cover results in an “energy trap”. It lets light enter but allows neither light nor heat to escape in large amount. This energy trapping process is known as the **green house effect**.

We have an active solar heating system and passive solar heating system.

An active solar heating system actively distributes the heat throughout the building when pumps, fans or other equipment physically move the heat around.

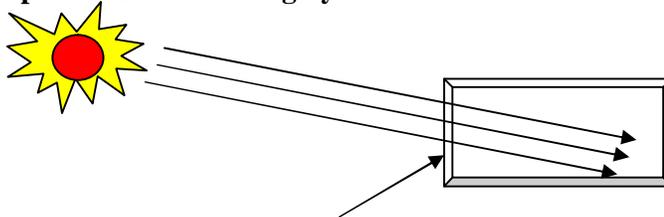
A passive system depends on natural forces to distribute heat e.g. natural convection rather than fans move heated air in a passive system.

How glazing improves the performance of solar collectors



1. Glass stops wind
2. Glass lets sunlight through
3. Dead air space insulates
4. Dark surface absorbs Sunlight and radiates Infrared
5. Glass absorbs most Infrared from the absorber and radiates less Infrared
6. Part of hot surfaces loses are made up for since the warm glass radiates some Infrared back to absorber.

A simple passive Solar Heating System



Heat collection is accomplished via the green house effect; the glass admits Sunlight, dark coloured walls and floors absorb the Solar energy transforming it to internal energy which may subsequently be given up as heat.

The heat is distributes throughout the room by natural convection; as air near the floor and walls are heated, it rises and is replaced by cool falling air. Heat is stored in the massive concrete walls and floors since heat collected at the surface slowly moves inside. During the night, this absorbed heat energy is slowly released, heating the cool room air.

Active Solar Heating System

In an active system, solar energy is generally collected by a group of several flat plate solar collector panels, box like devices that are mounted on a south – facing wall or roof. Each solar collector as it is often called has tubes or channels that a heat transfer fluid passes through.

The heat transfer fluid is the air, water or other substances that removes the collected heat and carries it to the inside of the building. The basic part of any flat – plate collector are the absorber, the cover, the insulation and the box or frame that holds it.

The important part of a typical flat plate solar collector are: ‘black’ solar energy – absorbing surface with means for transferring the absorbed energy to a fluid; the envelop transparent cover which also reduces convection and radiation losses to the atmosphere and back insulation to reduce conduction losses.

ENERGY STORAGE IN SOLAR PROCESS SYSTEM

Energy storage may be in the form of sensible heat of a solid or liquid medium, as heat of fusion in chemical systems, or as chemical energy of products in a reversible chemical reaction.

Products of solar processes other than energy may be stored e.g. distilled water from a solar still may be stored in tanks until needed. The choice of media for energy storage depends on the nature of the process. For water heating, energy storage as sensible heat of stored water is logical. If air heating collectors are used, storage in sensible latent heat effects in particular storage unit are indicated such as sensible heat in pebble heat exchanger. If photochemical processes are used, storage is probably most logically in the form of chemical energy.

Thermal energy is the goal of the nuclear industry. To achieve this goal it was necessary to develop a unique family of materials to meet nuclear specifications along with physical and chemical ones.

THE NUCLEAR REACTION

The reactions on which the nuclear industry is based involve the nucleus of the atom. These nuclear reactions result in the conversion of mass, m , to energy, E , as defined by Einstein’s equation;

$$E = m c^2$$

Where, c is the velocity of light

There are two types of nuclear reactions that lead to the production of energy, fission of heavy nuclei and fusion of light nuclei. In addition, nuclear reactions involving the capture of neutrons are important in the production of additional fission and fusion fuels. The energy evolved from grams of nuclear fuels is equivalent to that evolved from tons of chemical fuels.

Fission Reaction

Nuclear fission is the splitting of heavy nuclei into smaller one with the release of energy. The fission reaction depends mostly on Uranium – 235, the only naturally occurring nuclide that is fissionable with thermal neutrons. However, other fissionable nuclides are readily produced in the nuclear reactor, the most important being Plutonium –239 and Uranium – 233.

A typical fission reaction is as follows



Neutrons are produced in the fission and the nuclear reaction can be made self-sustaining.

Similarly, ${}^{238}\text{U}$ undergoes thermal neutron (n) capture with subsequent Beta decay to ${}^{239}\text{Np}$ and then to ${}^{239}\text{Pu}$.



${}^{235}\text{U}$ or Plutonium used for atomic bombing in the World War II, which exerted initially to destructive force of 20,000 tons of TNT by converting only small fraction of the mass of ${}^{235}\text{U}$ or Plutonium into energy.

Fusion Reaction

Lead to production of energy by the conversion of Hydrogen to Helium. Indeed maintenance of heat of the Sun and the Stars depends on energy released during the fusion of light atoms.



The fuels for the fusion reactions are Hydrogen – 2 and Hydrogen – 3, more commonly called deuterium and tritium. Deuterium is a naturally occurring isotope of Hydrogen. Tritium is the neutron – capture product of Lithium – 6.

A third possible fuel for fusion is Helium – 3, the decay product of radioactive Tritium.

The fusion reaction practical interest are

Reaction

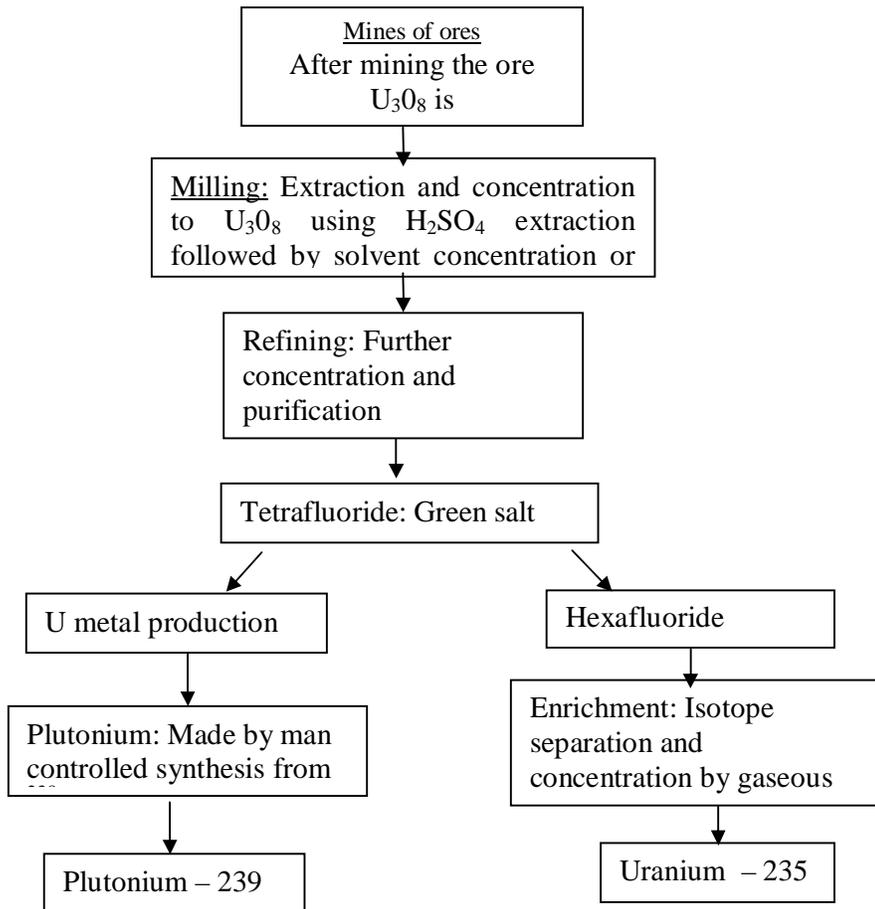
1. ${}^2_1\text{H} + {}^2_1\text{H} \longrightarrow {}^3_1\text{H} + {}^1_1\text{H} + 4\text{MeV}$
 $\qquad\qquad\qquad \qquad\qquad \qquad \longrightarrow {}^3_2\text{He} + {}^1_0\text{n} + 3.25\text{MeV}$
2. ${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0\text{n} + 17.6\text{MeV}$

NUCLEAR FUELS

They are fissionable isotopes used as sources of energy in nuclear reactors. Three isotopes that have a higher probability of fission than capture are ^{233}U , ^{235}U and ^{239}Pu . These sustain the fission reactions and therefore called nuclear fuels. Of these isotopes, only ^{235}U occurs in nature. The other two are produced artificially. UO_2 enriched to varying percentages is widely preferred because of its melting point, thermal conductivity, high density and resistance to the effects of irradiation. The starting material is UF_6 enriched to the desired percentage.

Feed Material Production or nuclear Fuel Cycle

Flow chart representing the main steps from ore to usable nuclear materials.



STEPS:

1. Mining of Ore: Involves extraction and concentration to improve U_3O_8 , yellow cake. Mined ores carry only low % of uranium. These are generally leached with H_2SO_4 or HNO_3 , the leached solution are concentrated by solvent extraction or by ion exchange and finally precipitated by caustic soda to form yellow cake.

2. Refining for Feed Material: It involves the extraction of pure Uranium from nitrate or sulphate solutions by an organic solvent, at first diethyl ether and later tributyl phosphate, diluted with kerosine or hexane.
3. Enrichment: The only procedure used to separate significant quantities of ^{235}U from ^{238}U is the gaseous diffusion method. UF_6 is a gas and $^{235}\text{UF}_6$ can be separated from $^{238}\text{UF}_6$ by a method based on the difference in the diffusion rate through porous barriers. It means fluorination of UO_3 will give isotopes $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ which are then separated using gaseous diffusion.
4. Nuclear Fuels: Nuclear fuels are produced specially for reactor use.
5. Mechanical Fabrication: Mechanical fabrication of Uranium and Plutonium fuel elements with or without enrichment. This involves mechanical shaping into plates, rods or tubes.

Equation

A summary of the overall reaction industrialized to obtain Uranium is

NUCLEAR REACTORS

It is defined as devices containing fissionable material in sufficient quantity and so arranged as to be capable of maintaining a controlled, self – sustaining nuclear fission chain reaction.

NUCLEAR HAZARD

The hazards involved in nuclear industries are by far greater than those in other industries. Radiation is greatly feared because it cannot be sensed with the ordinary human senses. The contamination of gases, solids and liquids by substances emitting alpha, beta and gamma radiation are all possible and must be guarded against.

NUCLEAR WASTE DISPOSAL

The disposal of nuclear waste is a difficult problem. The radioactive materials must be stored for many years until they decay to harmless materials. Disposal by burning in deep wells, the ocean or in underground tanks has been considered. One of the difficulties is that such wastes are often liquid that could be easily stored in underground tanks.

