NANOTECHNOLOGY

Nanotechnology is a field of applied science focused on the design, synthesis, characterization and application of materials and devices on the Nano scale. Nano size or nano means one billionth of a meter i.e. 1 nm = 1/1,000,000,000 of a meter. When a bulk material is changed into nano sized particle, the properties also change. The properties that are changed at nano scale are

Physical properties	(eg. handiness, melting point)
Chemical properties	(eg: reactivity, reaction rates)
Electrical properties	(eg: conductivity)
Optical Properties	(eg : color, transparency)

One best example of optical property at nano scale is gold. Bulk gold looks yellow but 12 nm nano sized gold particles look red.

NANOPARTICLES:

In nanotechnology, a particle is defined as small object that behaves as a whole unit in terms of its properties. These are further classified basing on the size as

- Nanoclusters: have atleast one dimension between 1 to 10 nanometers & narrow size distribution.
- Nanopowers: these are agglomerates of ultra-fine particles.
- Nanocrystals: nanometer sized single crystals / single domain ultra-fine particles.
- Nanotubes: these are members of fullerene structural family, which include spherical bucky balls. The name is derived from the length they are produced. Ex. As of 2008 they are produced up to several millimetres.
- Nanocomposites: these are mixtures blended with other compounds at nano scales.

Production:

Nanomaterials are often produced by

- Top-down technique: production of small pieces from large pieces of materials (etching).
- Bottom-up technique: creating materials by construction atom by atom or molecule by molecule. This is mainly done by self-assembly i.e. atoms & molecules arrange by themselves. The other way is by using tool to move each atom or molecule individually.

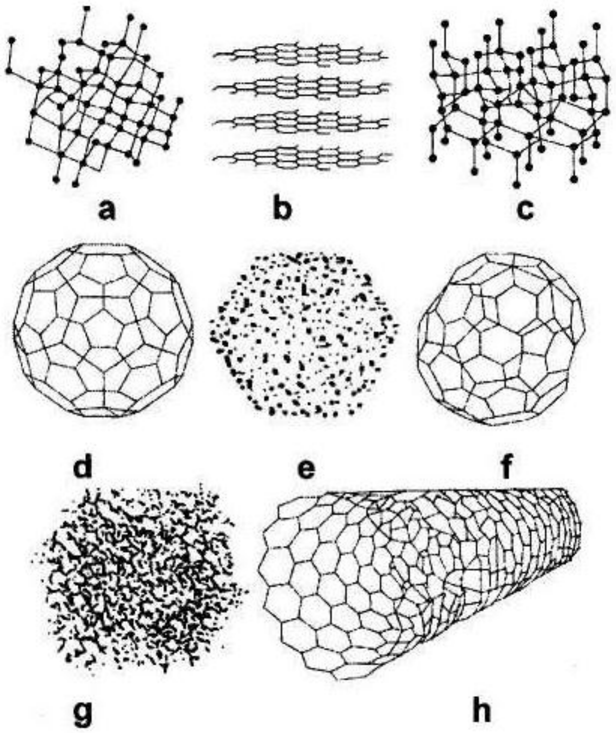
Applications:

The application of nanoparticles is currently in the area of intense scientific research, due to wide variety of potential applications in biomedical, optical and electronic field.

The other application can be studied from the products for ex: CNTs, bucky balls, Quantum dots.

Carbon nanotubes (CNTs)

Carbon nanotubes are an example of true nanotechnology. They are under 100 nm in diameter. They are allotropes of carbon with a cylindrical nanostructure. CNTs are sheets of graphite rolled up or twisted to make a tube of few nm in diameter and upto hundreds of micrometers long. Nanotubes have been constructed with length-to-diameter ratio of up to 28,000,000:1, which is significantly larger than any other material.



Some allotropes of carbon : a) diamond; b) graphite; c) lonsdaleite; d-f) fullerenes (C_{60}, C_{M0}, C_{70}); g) amorphous carbon; h) carbon nanotube.

These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields. They conduct electricity and heat, amazingly well. Because of varying electrical properties they possess, they can be doped or modified with small amount of other elements giving them electrical properties that include fully insulating, semi conducting and fully conducting. They are extremely strong (stronger than steel and world's strongest material known), resilient and flexible. They are also hydrophobic (water repellent) and bind easily to proteins. Their final usage, however, may be limited by their potential toxicity. If the nanotube consists of one type of graphite it is called single walled nanotubes (SWNTs) or number of concentric tubes called multi walled nanotubes (MWNTs).

Composites of CNTs and polymers which have high electrical conductivity have applications in conventional cold cathode or a polymer LED. Incorporated into a polymer matrix CNTs can produce composites with a very high strength and high elastic modules which may lead to the development of ultra-resistant materials for use as reinforcement fibres.

Applications of carbon nanotubes

1) Energy: Because of large surface area main applications are for electrical energy storage particularly as hydrogen storage medium, as fuel component, in gas diffusion layers, charge storage devices in batteries etc.

2) Conductive or reinforced plastics: Electromagnetic interference/ Radio frequency interference shielding components, coatings for enclosures, gaskets and other uses such as electrostatic dissipation, antistatic materials, transparent conductive coatings and radar-absorbing materials. By loading insulation plastic with (CNTs), they have been added into side mirror plastics of automobiles.

3) Field emission property is used in field emission flat panel displays in flat screen televisions and computer monitors, others include low- voltage cold-cathode lighting sources, lightning arrestors and electron microscope sources.

4) Molecular electronics and in electronic circuits at nanoscale dimensions CNTs become ideal candidates for the connections in such molecular electronics. They have been demonstrated as switches themselves. Also CNT based non-volatile random access memory for PC's have been in use. CNT based transistors are being developed now.

5) Thermal materials: To move heat from one place to another anisotropic thermal conductivity of CNTs are used in chips, ribbons of CNTs and aligned structures. Composites with CNTs have been shown to dramatically increase their bulk thermal conductivity, even at very small loadings.

6) Structural composites: The mechanical properties such as stiffness, toughness and strength of CNTs are used in advanced composites requiring high valves.

7) Fibres and fabrics: CNT added super-strong fibres have been applied in body and vehicle armor, transmission line cables, woven fabrics and stain-resistant textiles.

8) Catalyst support: SWCNTs have enormously high surface area and are capable of attaching any chemical species to their sidewalls and therefore become unique catalyst supports. These include cerium oxide, platinum, gold, palladium, molybdenum, nickel and iridium nonoparticles.

9) Ceramics: A ceramic material reinforced with CNTs becomes far tougher than conventional ceramics, conducts electricity and heat and also acts as a thermal barrier, hence used in coating turbine blades. More stronger material can be made with CNTs mixed aluminum oxide and niobium metal which has more electrical conductivity and toughness which is used in thermal barrier coatings.

10) Air, water and gas filtration: CNT based air and water filtration devices are used to block smallest particles and to kill most bacteria, by making use of MWNTs.

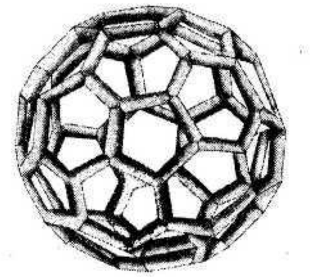
11) Biomedical applications: Research is just underway. Cells have been shown to grow on CNTs, so they have no toxic effects, and hence can be used as coatings for prosthetics and surgical implants and as vascular stents and neuron growth and regeneration. DNAcan be bonded to CNTs which can be inserted into a cell, which has potential application in gene therapy.

12) Consumer goods : CNT reinforced plastic packaging is used to keep food fresh for long periods, for making tennis rackets, baseball bats and bicycle components stronger. CNT reinforced plastic beer bottles keep it cool for longer periods of time.

13) Air crafts: Because of tensile strength, light weight and flexible nature CNTs are **used in ultra-**light structural materials for wings of advanced air craft and space problem to make them stronger and more energy efficient.

Carbon bucky balls or fullerenes, C_{60}

The fullerenes are a class of allotropes of carbon which conceptually are graphene sheets rolled into tubes or spheres. These include the carbon nanotubes which are of interest both because of their mechanical strength and also because of their electrical properties. Fullerenes are the classic three-dimensional carbon nanomaterials. This is made of 60 carbon atoms arranged in a soccer ball-like shape and is less than 1 nm in diameter. It has a hollow interior. There are now thirty or more forms of fullerenes up to and beyond C_{120}. The important fact for nanotechnology is that atoms can be placed inside the fullerene. Systems with appropriate material inside the fullerene ball are conducting and are of particular interest. eg., The hollow structure can fit a molecule of a particular drug inside, while outside buckyball is resistant to interaction with other molecules in the body. So, they can be safe functional drug *'Containers'* that can enter cancer cells, without reacting with them. Bulk or thin films of pure C_{60} are only semiconducting and have a room temperature resistivity of 108 Wcm. Buckminsterfullerene C_{60}, also known as the buckyball, is the smallest member of the fullerene family.



Fullerene

A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated.

The potential applications have been limited and include catalysts, drug delivery systems, optical devices, chemical sensors and chemical separation devices.The molecule can absorb hydrogen with enhanced absorption when transition metals are bound to the fullerenes, leading to potential use in hydrogen storage. Fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure of resistant bacteria and even target certain types of cancer cells such as melanoma.

Combination of nanotubes and fullerenes are used in molecular pumps and pistons.

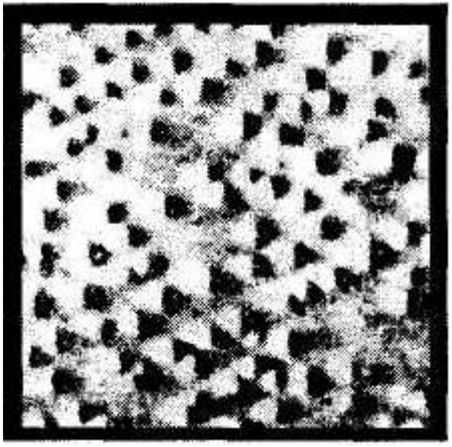
Other applications:

- To replace steel in suspension bridges, ultra high speed fly wheels.
- To produce nanowires of gold and zinc oxide.
- To replace indium-tin oxide in LCDs, touch screens and photovoltaic devices, for displays for cell phones, PDAs (personal digital assitant also known as palmtop computers) and ATMs.
- For economical electrical motor brushes.In light bulb filament - as an alternative to tungsten filament in incandescent lamps.

- As magnets by coating MWCNTs with magnetite.For optical ignition - 29% iron enriched with SWNT placed on top of a layer of explosive material such as Pentaerythritol tetranitrate (PETN) which can be ignited with angular camera flash.
- As artificial muscles.to increase tensile strength and halt crack propagation of concrete.
- To be used in cancer therapy in medical health sector to bring active agents into living cells. Thus, there is intense interest in finding a way to produce nanotubes in large quantities.

Quantum dots (QD)

They are often referred to as artificial atoms. Quantum dot is a semiconductor that exhibits quantum confinement properties in all three dimensions. The size is in the range of 1-10 nm. They may be metallic, for example gold, or chalcogenide based eg. cadmium selenide, lead selenide or cadmium sulfide. They display any chosen colour in UV region. Because of this property multi colour lasers are developed.



Quantum Dots

Micrograph of pyramid-shaped quantum dots grown from indium, gallium, and arsenic. Each dot is about 20 nanometers wide and 8 nanometers in height.

Present applications :

1. Q.Ds have high potential for photovoltaic applications. They can absorb photons from solar radiation and release electrons to generate electricity.
2. Used to manufacture extremely efficient thin-film PVs (Photovoltaic cells).
3. Used in transistors, LEDs and diode layers as agents for medical imaging.
4. Optical encoding and multiplexing applications in all trafficking, tumor targeting and diagnostics.

Future applications :

1) For new generation of quantum computers that will render today's computers and credit card encryptions technology obsolete.
2) For cellular imaging
3) As light emitting diodes - Q D - EED (electronic emitting diode) & Q D - U LED (light

emitting diode) displays.

EXPLOSIVES AND PROPELLANTS:

An explosive is defined as “a substance or mixture when subjected to thermal or mechanical shock, it gets very rapidly oxidized exothermically into products of potentially increased volume with a sudden release of potential energy”.

The amount of power able to produced from a given weight volume of explosive is called “power to weight/volume ration”. The power to volume ratio is small for gases while liquids and solids have better power ratio.

Characteristics of Explosives:

1. It should be cheap and stable under natural conditions.
2. It must have at least one chemical bond which can be easily broken or the molecules should have low dissociation energy.
3. The rate of decomposition should be fast to produce large volume of gaseous products exothermically.
4. It should have positive oxygen balance. The oxygen balance indicates oxygen, available in the molecule, which can be utilized to oxidise the carbon and hydrogen into CO2 and water respectively.

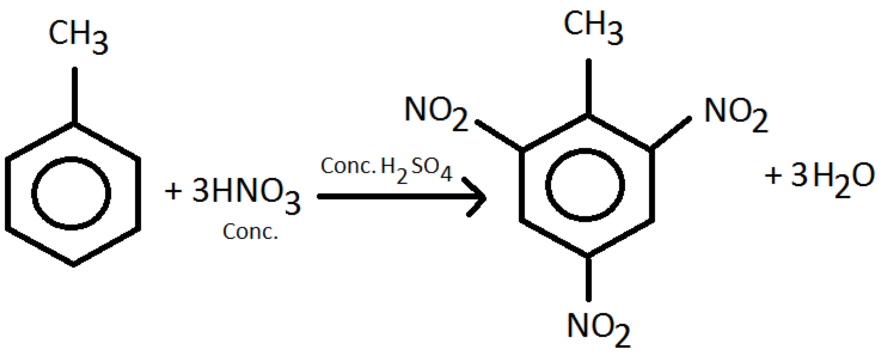
Uses:

Explosives can be used for constructive as well as destructive purpose. Some of the uses are:

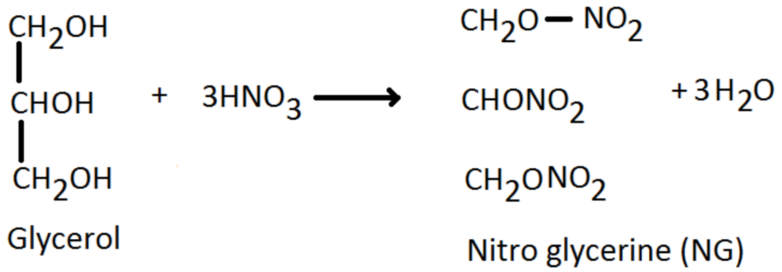
- For breaking coal, quarrying limestone, bauxite, granite. Etc.
- In making of roads and tunnels particularly in the hilly regions.
- For blasting ores of iron and other metal ores.
- To manufacture bombs, grenades, etc.
- As an ammunition in water.
- For launching of satellite with the help of rocket.

Important Explosives:

a. TNT (Trinitrotollune): It is prepared by the reaction between toluene and nitration mixture. It is crystalised after washing with ammonical solution of Na2SO3 followed by cold water.



b. Nitro Glycerine: It is prepared with the addition of glycerol to the cold mixture of 60% conc. H2SO4 and 40% Conc. HNO3 at 10^{o}C by constant stirring. It is separated and washed with water then with dil. Na_2CO_3(6%) to remove traces of acids. It is dangerous to handle and safety transport. It is mixed with inert absorbent (Wood pulp, Saw Dust etc.).



Classification of Explosives:

Normally explosives are classified into three types as followed:

1. Primary or initiating explosives.
2. Low explosives or propellants.
3. High explosives.

Primary or Initial Explosives or Detonators:

These are sensitive materials. These explode on receiving even a slight shock or fire. Hence, they should be handled with utmost care. Detonators are used in small quantities in cartridges and shells to start or initiate the explosion of the main explosive which is relatively less sensitive. The explosion of a detonator is initiated by spark, flame or sharp blow and normally happens in two stages of deflagration and detonation. Deflagration is the actual process of burning with a flame, which further changes result into detonation on the basis of burning conditions.

Some of the examples of detonators and their uses including Lead azide (PbN_6), mercury fulminate ($Hg(CNO)_2$) and diazido dinitrophenol (DDNP). Lead azide has excellent initiating actioned storage stability and low cost. It is used for military purpose. DDNP is used mostly in commercial blasting caps as it can initiate explosion even in less sensitive high explosive.

Low Explosives or Propellants:

These are basically explosives which normally burn and do not explode suddenly. The combination reaction is relatively slow compared with detonators. The evolved gases in the combustion readily disperse without building high pressure, ultimately they can be controlled easily.

Examples of low explosives are

1. Gun powder or black powder.
2. Cordilite
3. Nitrocellulose or Smokeless powder.

Gunpowder is a mixture of Potassium Nitrate (75%), Charcoal(15%) and sulphur(10%). These are not explosives but on sparking, the mixture explodes due to redox reaction as follows.

$$10KNO_3 + 3S + 8C \rightarrow K_2SO_4 + 3K_2S_2 + 4CO_2\uparrow$$

$$4K_2CO_3 + 7S \rightarrow K_2SO_4 + 3K_2S_2 + 4CO_2\uparrow$$

(excess sulfur slow the reaction)

$$4K2SO4 + 7C \rightarrow 2K_2CO_3 + 2K_2S_2 + 5CO_2\uparrow$$

(excess carbon, more CO_2 slow the reaction)

The excess of carbon and sulphur leads to generation of more CO_2 gas by volume by using K_2CO_3 and K_2SO_4.

Nitrocellulose is a smokeless explosive called cordite giving off CO, CO_2, N_2 and water vapour.

High Explosives:

These are more energetic than detonators and insensitive to mechanical shock and fire. High explosives are further sub classified into four groups

1. Single compound explosives which contain only one chemical entity.
2. Binary explosives.
3. Plastic explosives and
4. Dynamites.

Single Compound Explosives: They contain only one chemical compound. For example, ammonium nitrate, 2,4,6-trinitrotolune(TNT), pentaethythritol tetranitrate (PETN), RDX or Cyclonite, chemically known as cyclotrimethylenetrinitramines picric acid (Trinitrophenol), tetryl (nitroayl nitroamine).

Binary Explosives: Basically they are a mixture of TNT with other explosives. TNT is an important ingredient.

For example: Amotol (A mixture of TNT + ammonium Nitrate (50-80%))
Pentolite (A mixture of 50% TNT + 50% PETN)
Tetrytol (A mixture of 70% Tetryl + 30% TNT)
Tropex (A mixture of 40% RDX + 40% TNT + 20% Al Powder)
Titronol (A mixture of 80% TNT + 20% Al Flakes)

Plastic Explosives: These are combination of explosives which in plastic state can be hand moulded to varous shapes without much risk. They are mainly used for industrial applications and military uses. For example, PETN or RDX mixed with oil/wax, moulded into desired shape such as flexible sheet or putty like mass without any rests.

Dynamites: Explosives containing nitroglycerene as the main ingredient are called dynamites.

$$4C_3H_5(NO_3)_3 \rightarrow 10H_2O\uparrow + 6N_2\uparrow + 12CO_2\uparrow + CO_2\uparrow$$

It is an oily liquid and detonates at 50°C or by shock. With the above reaction, one volume of dynamite will be converted into 10,000 volumes. Hence, it is alsways mixed with an inert absorbent such as starch, sawdust or wood pulp.

The strength of dynamites vary with % of absorbent. They are as follow:

1. Straight Dynamites: 50%-60% nitroglycerene in wood + Na_2NO_3.
2. Blasting gelatin dynamites: 91.5% nitroglycerine + 8% nitrocotton + 0.5 $CaCO_3$.
3. Gun Cotton: Nitrating the cotton with Conc. H_2SO_4 + Conc. HNO_3.
$$C_6H_7O_2(OH)_3 + 3HNO_3 \rightarrow C_6H_7O_2(NO_3)_2 + 3H_2O$$
4. Cordite: Gun Cotton (65%) + notro glycerine (30%) and petroleum jelly (5%) in acetone.

Precautions during the storage of explosives:

Explosives produce enormous amount of energy and hence, utmost care must be taken while storing. Some important precautions:

1. Different explosives should be stored in separate boxes.
2. Detonators and explosives should be stored in separate containers.
3. During power failure, any flammable source should not be used in any case.
4. In the storage place, electric fittings and wiring should be properly insulated and checked time to time.
5. The explosive stores must be strictly prohibited from smoking/firing within a radius of 50m.
6. Necessary caution on explosive related activities should be given on notice boards and watch men should guard round the clock.

Blasting Fuses:

A fuse is defined as ‘a thin water-proof canvas length of tube containing gun powder arrangement to burn at a given speed for setting off charges of explosive’. They are of two kinds:

- Safety fuse: it is used in initiating caps where electrical firing is not used. For example, Black powder when wrapper of water proof fabrics (speed: 30 – 40 sec/ft).
- Detonating fuse: It has a speed of over 6,000m per second and consists of a charge of high velocity explosive such as TNT in a small bent tube.

ROCKET PROPELLANTS:

Rocket propellants are the mixture of fuel and oxidant whose combustion takes place in a definite time and controlled manner with production of huge volume of gas.

A propellant reacts quickly and produces a large volume of hot gases at a temperature of 3000°C and a pressure of 300 kg/cm2. The evolved hot gases exit through a nozzle at highest velocities, i.e., 2-3 km/sec facilitating upward movement of the rocket, according to Newton's third law of motion.

Characteristics of a Good Propellant:

The important characteristic of rocket propellants includes:

1. They should produce low molecular weight products (H2, CO, CO2, N2, etc.) during combustion.
2. They should burn at slow and steady rate producing high temperature.
3. They should possess high density.
4. They should be non-hygroscopic and non-corrosive.
5. The time taken by the propellant to catch fire in the presence of oxidizing agent called 'ignition delay'. A good propellant should possess a low ignition delay.

Classification of rocket propellants:

These are generally classified into

a. Solid and
b. Liquid propellants.

Solid propellants:

The solid propellants can be homogenous or composite. The homogeneous solid propellant is a solid propellant or mixture of propellants thoroughly mixed in a colloidal state. They are:

a. Single base propellant: ex. Nitrocellulose.
b. Double base propellants: containing a binary mixture of propellants in colloidal state. For example, Ballisite which is a mixture of nitrocellulose and nitroglycerine. Cordite (65% nitrocellulose + 30% nitroglycerine + 5% petroleum jelly).

Composite solid propellants are heterogeneous solids containing oxidising agents dispersed in the fuel mass. For example: Gun powder. Common oxidising agents are KNO_3, $KClO_4$ and NH_4ClO_4 incorporated in a PVC or Thiokol rubber.

Liquid propellants:

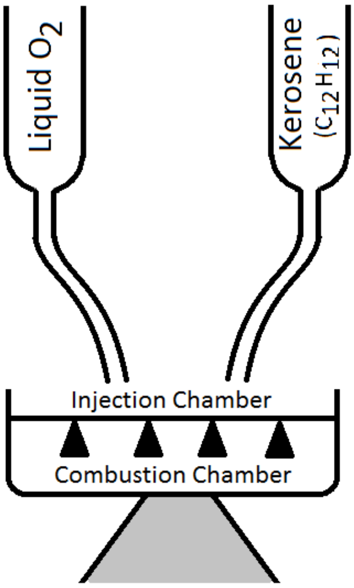
The liquid propellants (i.e. fuels and oxidizer) should exhibit:-

(a) Low freezing point (less than -400 deg Celsius)
(b) High Boiling Point/High decomposition temperature
(c) High specific gravity
(d) High specific heat and thermal conductivity
(e) Low vapour pressure and low viscosity
(f) Low temperature variation of viscosity and vapour pressure and low coefficient of thermal expansion
(g) Good physical and chemical stability
(h) Hypergolic combustion with ID less than 50 milliseconds
(i) Smooth and stable combustion
(j) No smoke at exhaust
(k) Less toxicity and safety in handling
(l) Easy availability
(m) High performance

Liquid propellants can be monopropellants or bipropellants.

Monopropellants: they have the fuel and oxidizer available in the same molecule or as a solution of both. For example, Nitro methane, hydrogen peroxide, hydrazine, ethylene oxide and a mixture of 21.4% methanol and 78.6% hydrogen peroxide.

Bipropellant contains the liquid fuel and oxidizer is kept separately and injected into the combustion chamber. For example, liquid hydrogen, hydrazine, kerosene, aniline, ethyl alcohol and a ammonia etc. the common oxides are liquid oxygen, ozone and hydrogen peroxide.



Bipropellant in rocket

Comparison of Solid and liquid Propellants:

SNO	Solid Propellant	Liquid Propellant
1	Simple Propulsion system, with greater reliability	Complex propulsion system, which reduces reliability.
2	Greater propellant density and density impulse.	Lower propellant density.
3	Propellant easy to handle, store and transport.	Propellant is difficult to store and transport and often dangerous to handle.
4	Can e loaded stored in rockets in ready to fire condition for long periods.	Can not be loaded and stored in rockets in ready to fire condition.
5	Rapid employment of rockets in quick succession possible.	Long check-out procedure before launch.
6	Overall development of propulsion system is less expensive.	Overall deployment of propulsion system is more expensive.
7	Due to above reasons more commonly used with tactical or short-range missiles.	Less commonly used with tactical or short range missile.
8	Lower performance capability	Higher performance capability.
9	Less commonly used with very large, long range missile.	More commonly used with very large long range missile and spaces booster. Long burning times.
10	Difficult to control and cut off thrust accurately. Intermittent operation of rocket is difficult.	Easy to control and cut off thrust and to restart engine. Intermittent operation is possible.
11	Propellant cost usually higher.	Propellant cost usually lower.

LUBRICANTS:

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. This mutual rubbing of one part over the other leads to resistance of movement, which is termed as friction. Friction usually causes the wear and tear of the machinery, and since heat is generated in this process, it also reduces the efficiency of the machinery. Therefore to overcome the problems created due to friction we employ a substance coined as lubricant. Thus a lubricant may be defined as “a substance which reduces the friction when introduced between two surfaces”. And the phenomenon is known as lubrication.

Criteria of a good lubricant

Any substance which shows the process of lubrication must satisfy certain key functions. They are:

1) The foremost function of a lubricant is to reduce friction.
2) The lubricant should keep moving parts apart.
3) It should transfer heat and act as a coolant.
4) It should reduce the wear and tear as well as surface deformation, caused due to rubbing action of a two sliding surfaces.
5) It prevents rust and corrosion and thereby reduces the maintenance and running cost of the machines.
6) It carries away contaminants and debris which would otherwise damage the surfaces of the machinery.
7) It acts as a seal.
8) It should also reduce the loss of energy in the form of heat.
9) As the use of lubricant minimizes the liberation of frictional heat, the expansion of the metals can be reduced.

CLASSIFICATION OF LUBRICANTS

On the basis of their physical state, lubricants can be classified as :

a) lubricating oils (or liquid lubricants)
b) greases (or semi-solid lubricants) and
c) solid lubricants

Lubricating oils

These lubricating oils provide a continuous fluid film over the moving or sliding surfaces. They also act as cooling and sealing agents, and prevent corrosion. For eg : animal and vegetable oils, mineral or petroleum oils, and blended oils. These oils possess good oiliness, they are costly and undergo oxidation easily in the presence of moist air or aqueous medium. They are also useful in the preperation of greases and used us additives to improve lubricating characteristics of petroleum oils. However these are now less preferred.

Examples of vegetable oils: Olive oil, palm oil, castor oil, rape seed oil and hazel nut oil.

Examples of animal oils: Whale oil, lard oil and tallow oil.

Mineral oils obtained by fractional distillation of petroleum are cheap, quite stable under operating conditions and abundantly available and these replaced the utility of animal and vegetable oils. Further, since a single oil does not possess all the good qualities of lubrication, certain specific substances (i.e. additives) have to be added to achieve the desirable characteristics. This resulted in blended oils.

Examples :

1) to improve the oiliness of a lubricant, vegetable oils like coconut oil or castor oil, fatty acids like palmitic, stearic or oleic acid are used as additives.
2) to improve viscosity index of lubricants, hexanol is added.
3) organic compounds of phosphorus or antimony are added as corrosion protectives.
4) tri-cresylphosphate is added as an abrasive inhibitor.

Since under the conditions of high speed machinery, wide variations in temperature conditions, fire risk and heavy load the petroleum oils cannot be effectively used as lubricants. This led to the development of synthetic oils or lubricants which operate even below -26 °C and above 121 °C.

Ex: di-basic acid esters, polyglycol ethers, fluoro and chloro hydrocarbons, organophosphates, silicones and silicate esters function as synthetic lubricants.

Greases or semi-solid lubricants

A semi-solid lubricant obtained by combining lubricating oil with thickening agent is termed as grease. Unlike lubricating oils that flow of their own accord, most greases flow only under pressure. Greases are classified on the basis of the soap used in their manufacture as soda-based greases, lithium based greases, calcium based greases and axle greases. Compared to lubricating oils, greases cannot effectively dissipate heat from the bearing. That's why the grease lubricates, bearing works at relatively lower temperatures as compared to the oil-lubricated bearings.

Solid lubricants

These are used either as a dry powder form or mixed with oil or water. The commonly used solid lubricants are graphite and molybdenum disulphide. Graphite is used either as a powder or as a colloidal dispersion in water (i.e. aquadag) or in oil (i.e. oildag) or as a grease. Colloidal dispersion of graphite is called as dag (deflocculated acheson graphite). Graphite as oil dag is used for lubricating the internal combustion engines, air compressors and lathes. Graphite grease which is soapy to touch, is used at high temperatures.

Molybdenum disulphide has a sandwitch like structure in which layer of molybdenum atoms lie between two layers of sulphur atoms. This is effective upto 800 °C where as graphite is effective upto 370 °C. Molybedenum disulphide also can be used in powder form or as a dispersion in petroleum oils, 2-propanol, water and synthetic oil. It is largely used in air-frame lubrication and wire drawing dyes. Mixture of graphite (7%) and Molybdenum disulphide (70%) bonded with silicates (23%) are capable of withstanding high temperatures, low pressures and nuclear radiations and hence used in space vehicles.

PROPERTIES OF LUBRICANTS

Viscosity

Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of a lubricating oil, i.e., the lower the viscosity, greater the flow ability. Viscosity is also coined with 2 other terms i.e.,

a) Absolute viscosity : This is defined as "the tangential force per unit area which is required to maintain a unit velocity gradient between two parallel layers. It is denoted by T] and its units in C.G.S. system is *poise.*

b) Absolute kinematic viscosity: It is the ratio of absolute viscosity to density for any fluid. It is denoted by 7 and its units in C.G.S. system is *stokes.*

Viscosity helps in the selection of good lubricating oil. For instance, light oils have low densities and easy flow abilities and are used on parts moving at high speed. Heavy oils are used on parts moving at slow speed under heavy loads. Further the variation of viscosity of a liquid with temperature is called viscosity index. Generally for every 1 °C rise in temperature the viscosity index decreases by 2%. However, the viscosity of good lubricating oil should not change much with a change in temperature.

The mathematical expression for viscosity index (VI) is $= \frac{L-U}{L-H} \times 100$

where, U = viscosity of test oil at 38 °C

L = viscosity of the standard oil at 38 °C having a VI of zero

H = viscosity of the standard oil at 38 °C having a VI of 100

Oils of gulf origin (containing napthalenes) are assigned an arbitrary VI of zero, while those of Pennsylvania (containing straight chain paraffins) are assigned as VI value of 100. Any test oil is compared at 38 °C with zero VI and 100 VI oils.

Therefore by and large light oils of low viscosity are used in plain bearings for high speed equipment such as turbines, spindles and centrifuges, whereas high viscosity oils are used with plain bearings of low speed equipment.

Measurement of viscosity

Viscosity measurements are based on time in seconds for a given quantity of an oil to pass through a standard orifice under a given set of conditions. There are many instruments for measuring viscosity and are known as viscometers. For example Redwood viscometers are commonly used in England and Kinematic and Saybolt universal viscometers are used in the United States.

The Redwood Viscometer:

These are of two types.

a) Redwood viscometer No. 1 (RW1) b) Redwood viscometer No.2 (RW2)

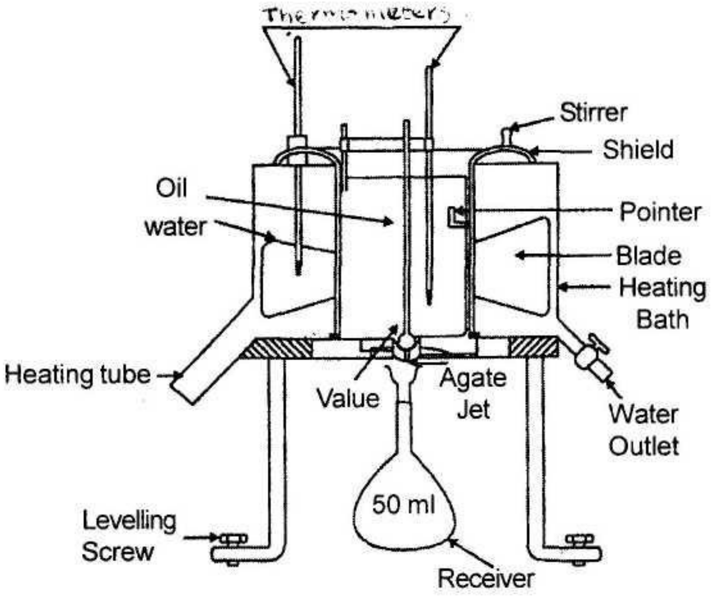
The basic differences between the two viscometers is outlined below :

Redwood Viscometer No. 1	Redwood Viscometer No. 2
1. This is used for determining viscosities of thin lubricating oils like kerosene, mustard oils etc.	1. This is used for determining viscosities of thick oils like fuel oil, mobile oil, glycerol etc.
2. Redwood viscometer No. 1 will correctly indicate viscosity for a liquid having flow time between 30 seconds to 2000 seconds.	2. Redwood viscometer No. 2 indicates viscosity of a liquid having a flow time more than 2000 seconds.
3. The dimensions of the orifice through which the oil flows is 1.62mm in diameter and 10 mm in length	3. The dimensions of the orifice through which the oil flows is 3.8 mm in diameter and 50 mm in length.

Inspite of the above differences, the two viscometers RW1 and RW2 are identical in principle, shape and mode of testing.

Description of viscometer

The viscometer consists of cylindrical brass oil cup (90 mm in height and 46.5 mm in diameter) which is open at the upper end and it holds the sample of the lubricating oil. This is cleaned with the help of a suitable solvent *eg:* CCl_4, ether, benzene or petroleum spirit and is properly dried to remove any traces of the solvent. The viscometer cup is fitted with an agate jet in the base, which can be kept closed or opened by a ball valve, so that the flow of the oil can be started or stopped. There is also an pointer fitted in the viscometer cup, which indicates the level upto which the oil should be filled (fig. 8.6). The lid of the cup IS provided with an arrangement to fix a thermometer to indicate the oil temperature.



Redwood Viscometer

Working of viscometer

1. Initially the brass ball is placed in position so as to seal the orifice.
2. The oil under test is poured carefully into the oil cup upto the pointer in the cup.
3. Place the 50 ml flask in position below the jet.
4. Keep stirring the water in the bath and the oil in the cup and adjust the bath temperature until the oil attains the desired constant temperature.
5. When the necessary temperature of the oil is attained, lift the ball valve and simultaneously start the stop watch and then note the time taken for 50 ml of oil to flow into the flask.
6. Replace the ball valve in position to seal the cup to prevent overflow of the oil. Repeat the experiment at five elevated temperatures say 45 °C, 55 °C, 65 °C etc., and note the respective time of efflux in seconds.

Report the value as Redwood viscosity No. 1 at T°C = t seconds.

Further the Redwood viscosity obtained above for different temperatures can be converted into kinematic viscosity by using the formula given below:

$$V = At - \frac{B}{t}$$

where V = kinematic viscosity of the oil in centistokes

t = time of flow of oil in seconds.

A and B = the instrument constants

The value of A = 0.264 and B = 190, when t = 40 to 85 seconds. A =

0.247 and B = 65, when t = 85 to 2000 seconds.

Viscosity values are used in evaluating load carrying capacity, in denoting the effect of temperature changes, for determining the presence of contaminants in used oil during service. Absolute viscosity values are required for use in all bearing design calculations and other lubrication engineering technical design problems. Whereas kinematic values are applied in oil blending procedures.

In Saybolt viscometer the time required for 60 ml of oil to run through the orifice is measured and is reported as Saybolt universal seconds at that temperature. On the other hand in a kinematic viscometer for a fixed volume of sample, time is measured for the sample to flow through a calibrated capillary under a constant temperature. From the measured efflux time, the kinematic viscosity is calculated.

Kinematic viscosity in centistokes (cst) = C x t

where, C = viscometer constant and

t = observed flow time in seconds

Conversion Formulas Let time of

efflux = t seconds Saybolt: cst =

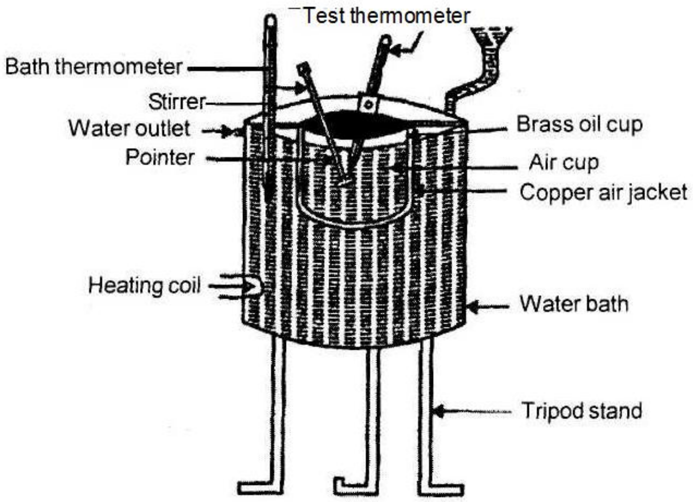
0.22t-180/t Redwood : cst =

0.26t -171 /1

Flash and fire point

A lubricating oil selected for a job should have a flash point which is reasonable above its working temperature. It also should not volatalise under the working temperatures. Even if some volatalisation takes place, the vapours formed should not form inflammable mixture with air under the conditions of lubrication. Therefore a knowledge of flash and fire points in lubricating oil aids in-precautionary measures against fire hazards.

" The flash point of an oil may be defined as the lowest temperature at which it gives off vapours, which will flash if brought into contact with a flame."



Abel's flash point apparatus

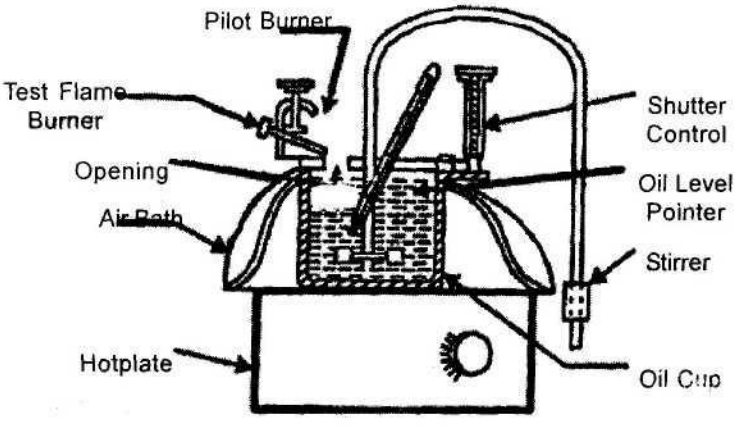
"The fire point of an oil is defined as the lowest temperature at which it will give enough vapours, which on rising will begin to produce a continuous flame above the oil for at least 5 seconds". In most of the cases, the fire point of an oil is about 5 to 40 °C higher than its flash point.

The flash point is determined either by the open-cup or closed cup apparatus. The open-cup apparatus commonly employed is Cleveland's apparatus in which the oil is heated with its upper surface exposed to the atmosphere. On the other hand the closed-cup apparatus in common use are Abel's apparatus and Pensky-Martens apparatus. The closed-cup apparatus gives more reproducible results and also the flash point obtained with an open-cup apparatus is generally about 10 to 30 °C higher than that obtained with closed-cup apparatus.

Cleveland's open-cup apparatus is generally used for determination of flash point of fuel oils and other oils having flash point below 175 °C. The Abel's closed cup apparatus is best used for oils having flash point below 120 °C, while the Pensky Marten's apparatus is used for oils with flash point above 120 °C.

Description and procedure of Pensky-Marten's apparatus

This is the most commonly used apparatus for the determination of the flash point of a lubricating oil. The essential features of the apparatus are shown in the figure.



Pensky - Marten's flash point apparatus

The apparatus consists of a brass cup which is 5 cm in diameter and 5.5 cm in depth. This cup should be dried and no moisture should be allowed to remain inside it. The level upto which oil is to be filled in the cup is marked at about 1 cm below the top of the cup. The lid of the cup is provided with four openings of standard sizes which are meant for a special type of stirrer, a standard thermometer, an inlet for air and the fourth for introducing a flame. At the top of the cup, a shutter is provided. By moving the shutter, openings for the test flame and air are opened and the flame exposure device dips into the opening over the surface of the oil. The whole assembly is kept on an electrical heater which can be heated in a controlled manner.

The oil sample under test is poured into the oil cup upto the mark. The cover incorporating the stirring device, the thermometer and the flame exposure device is fixed on the top. The apparatus is heated so that the oil temperature (as recorded by the thermometer dipped into the oil sample) increases by about 5 to 6 °C per minute, while the Stirrer is rotated at approximately 60 revolutions per minute. When the temperature rises to within upto 15 °C of the anticipated flash point the test flame is dipped into the oil vapour for about 2 seconds at every degree rise in temperature. The temperature (t, °C) is noted at the time, when the test flame applied causes a distinct flash in the interior of the cup. The oil sample is further heated at a rate of about 1 °C/min and application of the test flame is done after every 1 °C rise in temperature of the oil. The temperature (t_2°C) at which the vapours of the oil sample gives a clear and distinct blue flame, is recorded as the fire point of the given sample.

Precautions:

1. Stirring of the oil sample should be stopped at the time of application of test flame.
2. Oils containing minute quantities of volatile organic substances are liable to flash below (freaky flash) the flash-point of the oil. Although a small flash may be observed in such cases, it should not be confused with the true flash, since its intensity does not increase with increased temperature.
3. Presence of moisture in the lubricant may increase or decrease the flash point.

Cloud and pour point

In order to understand the suitability of lubricants in cold conditions, we make use of cloud point and pour points. Usually lubricating oils derived from petroleum contains dissolved paraffin wax and other asphaltic or resinous impurities. These impurities tend to separate out of the oil at lower temperatures. Further sodification of lubricant normally causes jamming of the machine.

The cloud-point is the temperature at which crystallization of solids in the form of a cloud or haze first becomes noticeable, when the oil is cooled in a standard apparatus at a standard rate. The pour point is the temperature at which the oil just ceases to flow when cooled at a standard rate in a standard apparatus.

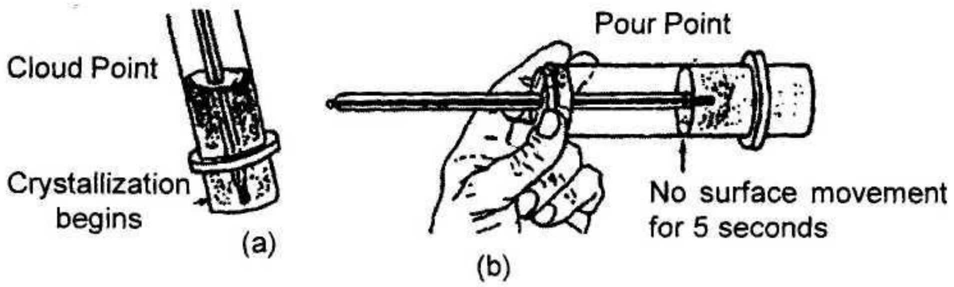
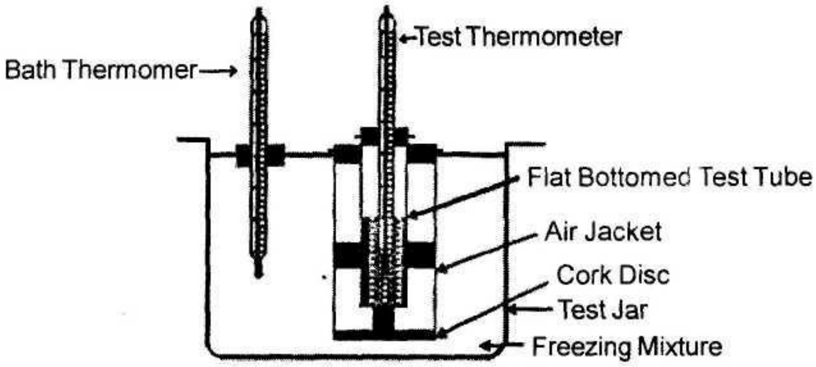


Fig. 8.9 : Cloud and pour points

The pour-point has a greater significance for lubricating oils. It determines the suitability of a lubricant or a hydraulic oil for low temperature installations. Important examples are refrigerator plants and air-craft engines, which may be required to start and operate at sub-zero temperatures.

Description and procedure of cloud point and pour point apparatus

The apparatus used for conducting both these tests are shown below. The apparatus consists of a flat bottomed tube about 3 cm in diameter and 12 cm in height enclosed in an air jacket. (Note : the flat bottomed tube should not be kept directly in the freezing mixture). This tube is placed in a glass jar having suitable freezing mixture and a thermometer. Different freezing mixtures are tried depending on the type of lubricating oil. Mixture of ice and salt, ice and water, ice and $CaCl_2$, solid CO_2 and acetone are commonly used.



Cloud and pour point apparatus

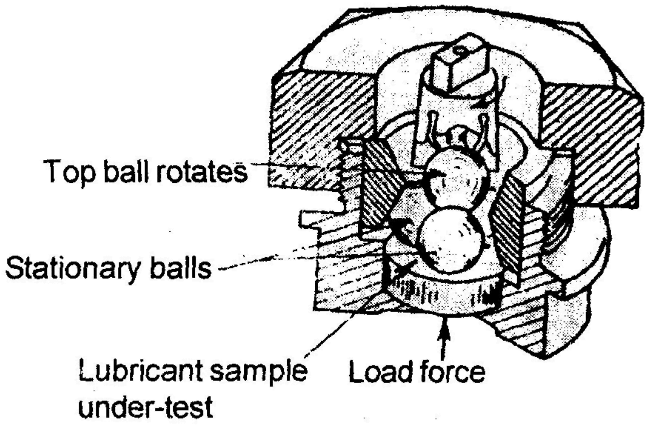
The oil is first dried by shaking it with small amount of anhydrous sodium sulphate and it is filtered through lintless filter papers. The oil is filled upto the mark inside the flat bottomed glass tube and the cork is fitted with a thermometer dipping inside the oil. The tube is then kept in the freezing mixture. The temperature of the oil falls on cooling. The tube is taken out of the freezing mixture, for every degree fall of temperature of the oil and then inspected for a moment. The temperature at which cloudiness or haziness is first noticed represents the cloud-point. As the cooling is further continued, at a particular temperature, the oil just ceases to flow or pour as observed from tilting the test jar. This particular temperature at which the oil does not flow in the test jar for 5 seconds on tilting it to horizontal position is reported as the pour point

Significance of cloud and pour point

Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become clogged because of seperation of wax. Pour point values of petroleum and non-petroleum lubricants are necessary when functioning under sub-freezing conditions.

Mechanical stability

Mechanical stability determination is useful for judging the lubricant under conditions of high pressure. This is determined by the four balls extreme pressure lubricant test.



Four-balls extreme-pressure lubricant tester

In the equipment the three lower balls remain stationary while the fourth upper ball rotates in the presence of the lubricant under test. If the lubricant is satisfactory under the given load, the ball bearings after the test comes out clean. However, when the load is progressively increased, and if liberated heat welds the balls, then the lubricant is said to have failed completely. Therefore this test enables one to determine the maximum load that can be carried out safely by a lubricant.

Saponification number

This test help us to identify whether the oil under reference is animal and vegetable or mineral or a compounded oil containing mineral and vegetable oils. It is defined as the number of milligrams of KOH required to saponify 1g of oil. Normally mineral oils do not saponify, while vegetable and animal oils saponify readily.

Neutralization number

This is a measure of acidic or basic impurities present in tbe lubricating oil. Determination of acidic impurities is most common and is expressed as acid value or number. Acid value is defined as the number of milligrams of KOH required to neutralize the acidic constinuents in 1 gm of the oil. Acidity in lubricating oil may be due to oxidation products of oil, additives used to improve processing of the lubricating oil. Generally lubricating oils have acid values of less than 0.1. Values greater than 0.1 indicates oxidation of oil leading to gum formation and corrosion of the equipment. Therefore determination of the acid value is useful for determining whether the lubricating oil has to be replaced.

Aniline point

The tendency of a lubricant to mix with aniline is expressed in terms of aniline point. This point gives an indication of the possible deterioration of oil in contact with rubber sealings, packings etc. to prevent leakage since aromatic hydrocarbons have a tendency to dissolve natural rubber and certain synthetic rubbers. Aniline point of a lubricant is a measure of its aromatic content. A lubricant with a low aniline point has high aromatic content and consequently low aromatic content in the lubricants is desirable.

Aniline point is determined by mixing equal volumes of the oil sample and aniline in a test tube. The mixture is heated till a homogeneous solution is obtained. The test tube is then allowed to cool under controlled conditions. The temperature at which the two phases (oil and aniline) seperate out as indicated by the sudden appearance of cloudiness throughout the medium, is recorded as the aniline point of the sample.

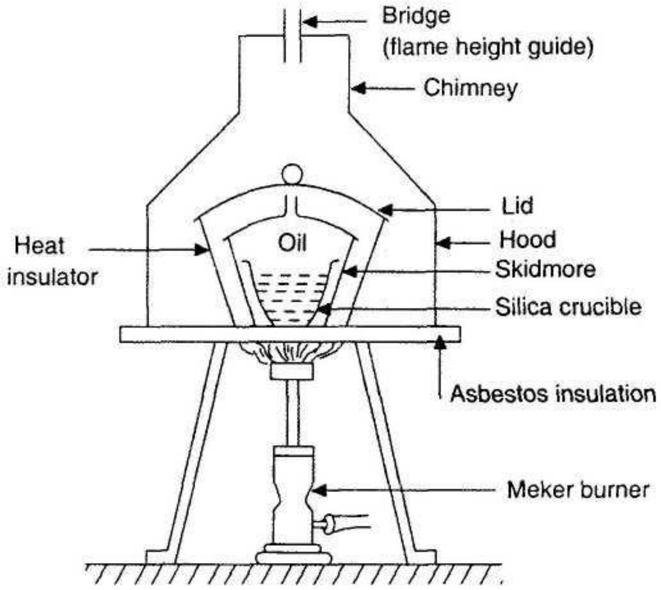
Oiliness

It is the property of the lubricant to stick on to the surface under the conditions of high speed and heavy load. It is an important property in selecting a lubricant for a particular application. Generally under the conditions of high speed and heavy load, the oil may be squeezed out from the sliding surfaces and the oil film may be reduced in thickness, with the result, the lubricating action will stop and direct metal to metal contact will take place. A lurbicant which does not squeeze out from the sliding surface under the conditions mentioned above and maintains a continuous film is known as oil having high degree of oiliness. Normally fatty oils have high degree of oiliness than those of lubricating oils obtained from petroleum. Further the degree of oiliness of lubricating oils obtained from petroleum can be improved by adding little quantity of oleic acid, stearic acid etc.

Carbon residue

A good lubricant should deposit least amount of the carbon. Lubricating oils contain high percentage of carbon in combined form. On heating they decompose, depositing a certain amount of carbon which is intorlerable particularly in internal combustion engines and air compressors.

The estimation of carbon residue is carried out by *Conradson method.* A weighed quantity of lubricant is taken in a silica crucible which is placed in a wrought iron crucible having a cover with a small opening for the escape of volatile matter.



Conradson's apparatus for carbon residue estimation

These are then placed in a third iron crucible covered with a chimney shaped iron hood and heated slowly for 10 minutes till flame appears. Finally strong heating is done for about 15 minutes till the substance burns completely. The crucible is then cooled and residue left out is weighed.

$$Carbon\,\mathrm{Re}\,sediu = \frac{Weight\ of\ Carbon\,left\ out}{Weight\ of\ Oil\,taken} \times 100$$