

MATERIALS OF CONSTRUCTION FOR PETROCHEMICAL INDUSTRIES

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Presented at the Silver Jubilee Celebration, National Welding Meet, 1998 of the IIW, Mumbai Branch, on 21st February, 1998. Theme : "Welding in Petrochemical & Refinery Sectors"

INTRODUCTION

Petroleum is a heavy, liquid, flammable oil stored under the surface of the earth and originally formed as the by-product of the action of bacteria on marine plants and animals. It consists chiefly of carbon and hydrogen in the form of hydrocarbons, including most of the liquids of the paraffin series, together with some of the gases and most of the solids of the series from $C_{17}H_{36}$ to $C_{27}H_{56}$. While petroleum is used primarily for the production of fuels and lubricating oils, it is one of the most valuable raw materials for a wide range of chemicals. The name "petrochemicals" is used in a general sense to mean chemicals derived from petroleum, but it does not mean any particular class of chemicals (sulfur, helium by products). Petroleum from different localities differ in composition, but tests of oils from all parts of the world give the limits as 23 to 87% carbon, 11 to 14% hydrogen, [1] with sulfur, nitrogen and oxygen in amounts from traces to 3%. The crude oil is split by distillation into naphtha, gasoline, kerosene, lubricating oils, paraffin and asphalt. It may also be split by

cracking, that is by subjecting it to violent heating in the absence of air; this process yields a higher proportion of volatile products because of the breaking down of the more complex molecules by the high heat. Liquefied petroleum gases, including propane, butane, pentane, or mixtures, are marketed under pressure in steel cylinders as bottled gas. Liquid gas is also used for internal combustion engines, as a solvent and for making many chemicals. Certain highly refined oils used in medicines as laxatives and used in other specialized applications are referred to as mineral oils. About half the world production of crude oil is in the western hemisphere (first wells in the USA were opened in 1859), but the largest single field is in the Persian Gulf area.

The Indian Petrochemical industry has undergone a metamorphosis over the last few decades. The chemical industry was identified in earlier years with heavy chemicals comprising sulfuric acid, caustic soda, and soda ash on the one hand and pharmaceuticals on the other. Subsequently the petrochemical industry came on the scene and oc-

cupied the centre stage. The changed profile of the chemical industry has also led to greater divisions mainly due to the proliferation of intermediates, process chemicals, catalysts and the like, from the commodity chemicals like heavy chemicals and petrochemicals. These speciality chemicals received a boost in the nineties with the liberalization of economic policy. In the changed scenario, easier availability of technologies through joint ventures and larger markets due to globalisation have initiated an acceleration in this area. Besides, these chemicals involve high technology/chemistry and involve multi-step reaction/operations. Speciality chemicals can be classified technologically into four broad areas - inorganic base (includes water treatment, electroplating, photographic, fire retardants); organic base : which includes drug intermediates, textile auxiliaries, leather chemicals etc; petrochemical base, namely, rubber chemicals, plastic compounding chemicals, cosmetic intermediates, emulsifiers, fragrance additives, anti-oxidants; and finally agro-base extractions and derivatives like castor, jojoba, natural

colors, essential oil derivatives and the like. In India, the total capacity of petrochemicals is expected to increase to eight million tonnes by the turn of the century from the present 5.4 million tonnes.

Petrochemical industry has been delicensed except for the following 13 items, as these involve hazardous processes : ethylene, propylene, butadiene, benzene, toluene orthoxylene, monoxylene, paraxylene, mixed xylene isomers, monoethylene glycol, ethylene oxide, low density polyethylene (Sp. gravity <6.94), polycarbonates (phosgene based) and poly methyl methacrylates (hydrocyanic acid based). Expansion of the naphtha cracker will help step up production of propylene and ethylene.

SELECTION OF MATERIALS

Ever increasing temperatures, pressures, equipment sizes and throughputs in chemical, petroleum and petrochemical industries are stretching capabilities of available commercial materials to their limits. Unscheduled shutdowns of such large equipment from weldcracking or corrosion leaks are much more serious than they are with smaller equipment. The throughputs of other plant equipment connected to failed units have to be adjusted during shutdown and production losses increase.

The basic consideration in selecting a construction material is economics (Fig.1). The ideal material would re-

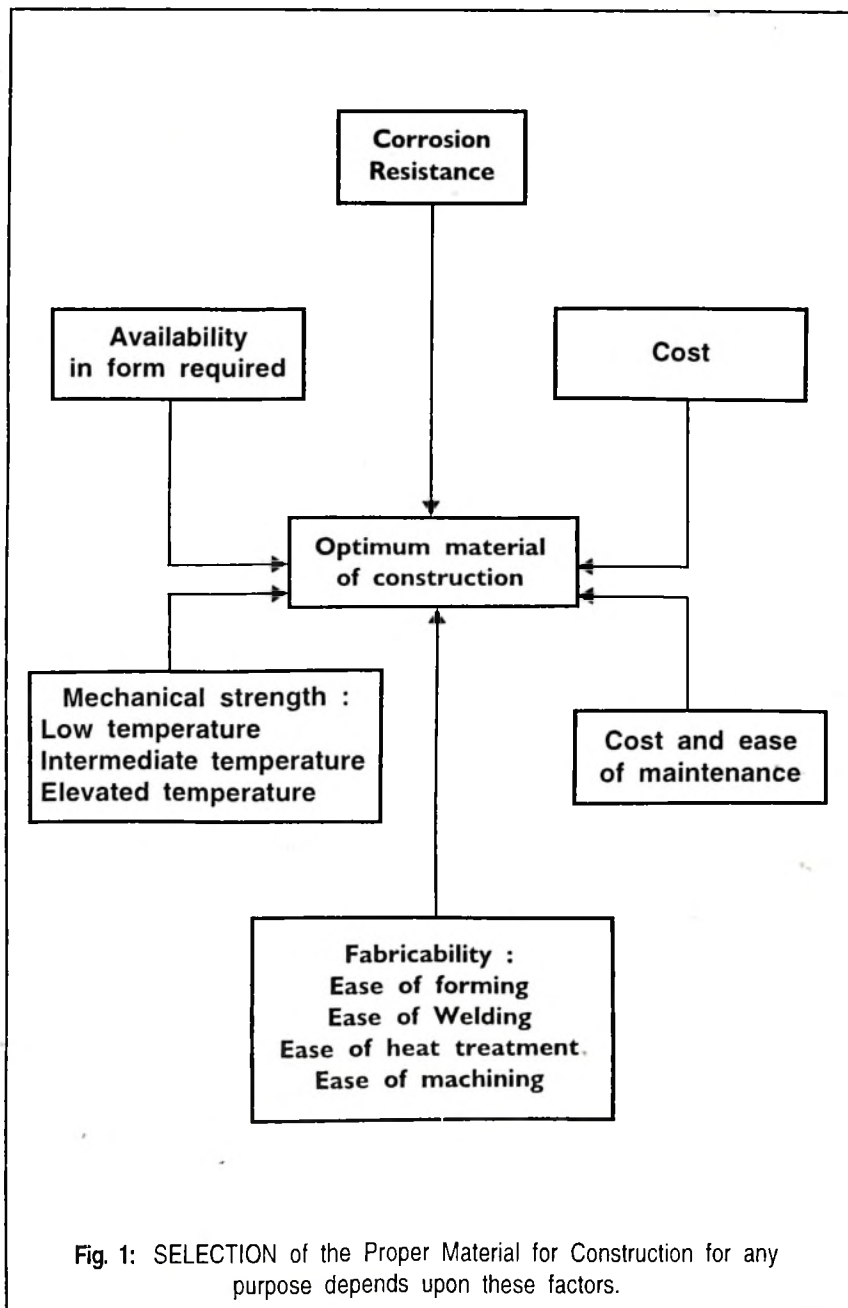


Fig. 1: SELECTION of the Proper Material for Construction for any purpose depends upon these factors.

sist all corrodents, not deteriorate at high temperatures and pressures, be easy and inexpensive to fabricate and above all be cheap. **“The material that comes nearest to this specification is steel-in carbon, low-alloy, and stainless varieties - which is the major material used in petro-**

leum and chemical industries. The steels are supplemented by copper and nickel base alloys, titanium, plastics and refractories”. All of these materials have their shortcomings, which can be minimized or designed around in order to produce optimum cost equipment. When selecting the

construction material, the following questions must also be answered : Is the material selected available in the form required, e.g. plate, tubes, castings, forging? Is the material available as an "off-the-shelf" item (e.g. valves, rotating equipment are generally made of some standard materials, which would cost more money and time to obtain them in special materials).

Carbon steels predominate the materials field because of their low cost, versatile mechanical properties, availability in fabricated forms, and procurability as off-the-shelf equipment. The desired mechanical properties can often be obtained by changes in composition and heat treatment. Carbon steel is easy to fabricate and is less sensitive to the effects of fabrication than more highly alloyed materials. The material costs of carbon steels are about 1/6 to 1/10 the cost of stainless steels, 1/3 of lead and zinc, 1/6 of Aluminium, 1/6 to 1/5 of copper alloys and 1/20 of nickel base alloys and tin.

Carbon steels and low alloy steels with ferrite-pearlite or ferrite-bainite microstructures are used extensively at elevated temperatures in petroleum processing plants apart from some power plants. Carbon steels are often used upto about 370°C under continuous loading. They are predominantly used in pressure vessel fabrication because of their low cost, versatile mechanical properties

and the availability in fabricated forms. They are most common materials used in non-corrosive environments in the temperature range of -29 to 425°C in oil refineries and chemical plants. When the material is at or above 425°C for prolonged time the steel becomes weakened due to graphitization. Carbon steels are also affected by creep temperatures above 370°C.

Creep resistant low alloy steels usually contain 0.5 to 1.0% Mo for enhanced creep strength, along with chromium contents between 0.5 and 9% for improved corrosion resistance, rupture ductility, and resistance against graphitization. Small additions of carbide formers such as vanadium, niobium and titanium may also be added for precipitation strengthening and/or grain refinement. The effects of alloys elements of transformation hardening and weldability are additional factors.

Chromium-molybdenum steels are widely used in oil refineries, chemical industries and electrical power generating stations for piping, heat exchangers, superheater tubes and pressure vessels. The main advantage of these steels is the improved creep strength from molybdenum and chromium additions and the enhanced corrosion resistance from chromium. The creep strength of chromium-molybdenum steels is derived mainly from two sources : Solid solution strengthening of the matrix ferrite by carbon molybdenum

and chromium; and precipitation hardening by carbides. Chromium molybdenum steels are available in several product forms.

Modified chromium molybdenum steels : To achieve higher process efficiencies in chemical processing plants and 'Petrochemical' refining plants, several modified versions of chromium molybdenum pressure vessel steels have been investigated for operation at higher temperatures and pressures than those currently encountered. The higher temperatures affect the elevated temperature strength, the dimensional deformation and the metallurgical stability of an alloy, while the higher operating pressures require either higher strength alloys or thicker sections. Three categories of modified chromium molybdenum steels investigated for thick section applications in a hydrogen environment are 3Cr-1Mo modified with vanadium, titanium and boron. This steel is approved for service upto 445°C 9Cr-1Mo steel modified with vanadium and niobium strengths capable of meeting or exceeding the allowable stresses of stainless steel. Approved for use to more than 600°C, 2¼ Cr-1Mo steel modified with vanadium, titanium and boron is fully hardenable, resists hydrogen attack, exceeds the strength of normalized and tempered 2¼ Cr-1Mo steel.

Corrosion : Although the mechanical properties establish the allowable design-stress levels, corrosion ef-

fects at elevated temperatures often set the maximum allowable service temperature of an alloy. Three common forms of corrosion that occur at elevated temperature are oxidation, sulfidation and hydrogen attack.

Oxidation from steam or air is a serious problem that can occur at elevated temperatures. When metal is exposed to an oxidizing gas at elevated temperature, corrosion can occur by direct reaction with the gas. This type of corrosion is referred to as tarnishing, high temperature oxidation or scaling. The rate of attack increases substantially with temperature. The surface film typically thickens as a result of reaction at the scale/gas or metal/scale interface due to cation or anion transport through the scale which behaves as a solid electrolyte. Alloys intended for high temperature applications are designed to have the capability of forming protective oxide scales. Silicon and chromium provide oxidation resistance. If variables affecting oxidation are changed, such as gas composition, the heating method, temperature, pressure or velocity, different rates of scaling can be expected. Elements such as sulfur, vanadium and sodium can change the nature of metal oxidation, sometimes increasing it to a catastrophic level.

At elevated temperatures, steam decomposes at metal surfaces to hydrogen and oxygen and may cause steam oxidation of steel which is

more severe than air oxidation at the same temperature. Fluctuating steam temperatures tend to increase the rate of oxidation.

In a water environment, corrosion is significantly influenced by the concentrations of dissolved species, pH, temperatures, suspended particles, and bacteria.

Sulphidation : Corrosion by various sulfur compounds at temperatures between 260 and 540°C is a common problem in many petroleum refining processes and occasionally in petrochemical processes. When the sulfur activity (partial pressure and concentration) of the gaseous environment is sufficiently high, sulfide phases, instead of oxide phases can be formed. Sulfur once it enters the alloy, redistributes the protective scale forming elements near alloy surface interfering with the process of formation-reformation of the protective scale. Once sulfides have formed in the alloy, there is tendency for the sulfide phases to be preferentially oxidized by the reaction front and for the sulfur to be displaced inward forming new sulfides deeper in the alloy. In this way, finger-like protrusions of oxide/sulfide can be formed from the alloy surface inward, which may act to localize stress or otherwise reduce the load bearing section. The relative corrosivity of sulfur compounds generally increases with temperature. Depending on the process particulars, corrosion is in the form of

uniform thinning, localized attack, or erosion corrosion. Corrosion control depends almost entirely on the formation of protective metal sulfide scales that exhibits parabolic growth behaviour. **“In general nickel and nickel rich alloys are rapidly attacked by sulfur compounds at elevated temperatures, while chromium containing steels provide excellent corrosion resistance as does Aluminium. As a rule austenitic stainless steels are required for effective corrosion control”.**

When selecting steels for resistance to high-temperature sulfide corrosion in the presence of hydrogen, the possibility of high-temperature hydrogen attack should be considered. Conceivably this problem arises when carbon steel and low alloy steels containing less than 1% Cr are chosen for temperatures exceeding 26°C and hydrogen partial pressures above 700 kPa and when corrosion rates are expected to be relatively low.

Hydrogen damage : Hydrogen damage includes hydrogen embrittlement, hydrogen attack, and hydrogen blistering. In ferrous alloys, embrittlement by hydrogen is generally restricted to those alloys having a hardness of 22 HRC or greater. The other form of hydrogen damage, such as hydrogen attack or hydrogen blistering, are associated with low alloy or carbon steels. Hydrogen attack is a damage mechanism that is associated with carbon and low

alloy steels exposed to hydrogen-containing environments at temperatures above 220°C. With hydrogen at elevated temperatures and pressures there is increasing availability of atomic hydrogen that can easily penetrate metal structures and react internally with reducible species. Exposure to the environment is known to result in a direct chemical reaction with the carbon in the steel. The reaction occurs between absorbed hydrogen and the iron carbide phase, resulting in the formation of methane. Unlike nascent hydrogen, the resulting methane gas does not dissolve in the iron lattice. Internal gas pressures develop, leading to the formation of voids, blisters or cracks. The generated defects lower the strength and ductility of the steel. Hydrogen attacks occur in carbon steels and can lead to fissuring of the steel. Alloy steels with stable carbides (Cr,Mo) are less susceptible to this form of attack. "**Hydrogen attack does not occur in austenitic stainless steels**". Hydrogen blistering is a mechanism that involves the hydrogen damage of unhardened steel near ambient temperature. Entry of atomic hydrogen into steel can result in its collection, as the molecular species, at internal defects or interfaces. The resulting internal pressure will cause internal separation (fissuring or blistering) of the steel. Such damages typically occur at large, elongated inclusions and result in delaminations known as hydrogen blisters.

Hydrogen embrittlement : Unlike hydrogen attack (blistering) this can occur without immediate and resolvable damage within the metal structure. This is a reversible process. Susceptibility to hydrogen embrittlement is strongly influenced by the strength level of the metal or alloy. In steels, untempered martensite is the most susceptible phase.

Low Temperature Applications : Critical structural components must be fabricated from steels that exhibit adequate low temperature fracture toughness because of the serious consequences of failure due to brittle fracture. Fracture toughness requirements are specified by different design codes API, BSI, ASTM.

Three major factors contribute to service failure of steel structures : Brittle failure due to the presence of fabrication defect; fatigue crack developments; crack development as a result of accidental damage. It is not practical or economical to fabricate defect free structures. Use of appropriate inspection and quality control procedures can limit size of defects. Proper fatigue design practices and in-service inspection can control the growth of fatigue cracks : Currently, all design guidelines, codes or standards for critical applications emphasize fracture control procedures that provide for the evaluation of properties such as fracture toughness, weldability and strength.

Many significant advances in steel making processes have been made

by steel companies to meet the demand for high quality lower cost structural steels with higher strength, improved weldability and increased fracture toughness. Advances in the steel making process have resulted in major improvements in structural steels, including significant control of alloying elements (C, Mn, Nb, V and Aluminium), major reductions in impurities (S,P,N) and improved uniformity of composition and properties. Recent advances in computer control and rolling capacity have allowed the development of a new class of high strength low alloy steels viz. TMCP steels.

Nickel and nickel alloys : These are used for a wide variety of applications, the majority of which involve corrosion resistance and/or heat resistance.

Iron-Nickel-Chromium Alloys : The development of this series of alloys took place in the early 1950s. Incoloy Alloy 800 was designed as a leaner nickel version of the nickel-chrome series of materials. It offered good oxidation resistance. This series of alloys has also found extensive use in the high temperature petrochemical environments, where sulfur containing feed stocks (naphtha) and heavy oils, are "cracked" into component distillate parts. Not only were they resistant to chloride-ion stress corrosion cracking, but they also offered resistance to polythionic acid cracking. Some alloys of commercial im-

portance include : **Alloy 800** (Fe-32 Ni-21 Cr), the basic alloy in the Fe-Ni-Cr system; resistant to oxidation and carburization at elevated temperatures.

Alloy 800H. Modification with controlled carbon (0.05 to 0.10%) and grain size (>ASTM5) to optimize stress rupture properties. Alloy 800HT similar to 800H with further modification combined titanium and Aluminium levels (0.85 to 1.2%) to ensure optimum high temperature properties.

Alloy 801. Increased titanium content (0.75 to 1.5%), exceptional resistance to polythionic acid cracking.

Alloy 802. High carbon version (0.2 to 0.5%) for improved strength at high temperatures.

Alloy 825. (Fe-42 Ni-21.5 Cr-2 Cu), stabilized with titanium addition (0.6 to 1.2%), also contains molybdenum (3%) for pitting resistance in aqueous corrosion applications. Copper content bestows resistance to sulfuric acid.

Alloy 925. Addition of titanium and Aluminium to 825 composition for strengthening through age hardening.

The 800 alloy series offers excellent strength at elevated temperature (creep and stress rupture). These alloys are consequently useful for catalytic cracking tubes, pigtailed and reformer tubes, for optimum

performance in the new millisecond design of crackers. Alloy 800HT internally finned tubing is being used. This offers greater heat exchanger wall area. For environments where polythionic acid can form during down time periods, Alloy 801 offers optimum resistance. Alloy 802 offers competitive high temperature strength capabilities because of its high carbon level and has been used extensively in sinter deck plate applications for handling abrasive, high temperature environments.

The corrosion resistant series of alloys (825, 925, 20 cb3) all contain molybdenum for enhanced corrosion resistance. This series of alloys has excellent resistance to sulfuric acid. The alloys have found extensive use as tubing and plate for production of fertilizer and associated products.

Alloy 925 has found use for downhole components in sour gas wells. Alloy 825 is used for downhole tubular components where hydrogen sulfide, carbon dioxide and sodium chloride are at elevated temperatures. For every aggressive corrosion sour gas environment, the nickel chromium-iron-molybdenum series of alloys has to be considered.

CONCLUSION

It is obviously necessary to have comprehensive information on all the chemicals in the process : raw materials, intermediates and final products. It is important to know whether

a chemical can be safely handled both in process and in storage and transport. The problem has two main aspects. One is the hazard of instability of a single component such as a reactant, intermediate or product, when undergoing physical processing in the plant and when stored and transported. The other aspect is the hazard of instability of the reaction mass in a chemical reactor. Unit processes (w.r.t the chemicals and petrochemical industries) are described as alkylation, condensation, cracking, hydrogenation, polymerization, sulphonation etc. (about 30); a particular unit process tends to have certain characteristic features which include "materials of construction". Similarly there are a number of unit operations like mixing, dispersion, precipitation, granulation etc. A no. of equipment are associated with these unit operations. Operation at extremes of pressure and temperature has its own characteristic problems and hazards. Extreme conditions may occur at (1) high pressure, (2) low pressure, (3) high temperature and (4) low temperature. Some general characteristics of these operating conditions are described in literature (among others ASME, appendix 28, materials, pressure vessels and piping).

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APPENDIX

BUTADIENE : Butadiene is a basic raw material, used in the manufacture of synthetic rubbers and an intermediate for the production of styrene copolymers (process steam cracking-naphtha, gas oil, butanes, propane, dehydrogenation). Non-corrosive, colourless flammable gas with mild aromatic odour. Insoluble in water; soluble in ethyl alcohol. M.P. 109.9°C steel or Aluminium closed containers are employed; copper and its alloys act as oxidizing agents, must not be used. Highly inflammable and forms explosive mixtures with air over a wide concentration.

BENZENE : (Process from petroleum by catalytic reforming from Toluene by

hydrodealkylation, from coal, petroleum gas); colourless, refractive liquid with a characteristic odour. In cold weather, benzene solidifies to a white crystalline mass. Highly inflammable, burning with a sooty flame. The vapour forms explosive mixtures with air over a wide range. Soluble in ethyl alcohol but only slightly soluble in water. Half of world production is alkylated to ethyl benzene which is the prime feedstock for producing styrene. Second most important outlet for benzene is cumene, the starting material for the manufacture of phenol and acetone. Having practically no corrosive effects of metals, iron and steel containers are usually employed for storage. Any sulphur compounds present as impurities may affect copper and Aluminium which precludes their use.

ETHYLENE : Ethylene is the largest volume hydrocarbon used in petrochemical industry. Employed exclusively as a chemical intermediate, its impressive growth since world war II has been due to its ready availability at competitive prices from an abundance of economically priced feedstocks.

Ethylene is produced by steam cracking from a wide range of hydrocarbons including ethane, propane, butane, naphtha, Liquid petroleum gas (LPG) and gas oils. Refinery off-gases and light hydrocarbons recovered from natural gas are sources of ethane, propane and butane. Feedstock patterns vary in different countries. Colourless gas with faintly pleasant odour. Highly inflammable, forming explosive mixtures with air. Slightly soluble in water. Soluble in liquid hydrocarbons. MP-169.2°C.

The most important outlet is polyethylene which consumes 55% of total ethylene demand. Polyethylene can be broken down to LDPE and HDPE which account for 35% and 20% respectively of ethylene consumption. Ethylene derivatives are also used in the preparation of two other high-volume polymers via their intermediates, vinyl chloride and

ethyl benzene. Most ethylene consumption is either captive or consumed locally. In order to provide continuity of supply, major pipelines have been constructed. Ethylene presents a dangerous fire and explosion hazard. Ethylene is normally stored as a liquid in refrigerated tanks at a pressure upto 7 bar or at room temperature at a pressure of 56-100 bar in underground cavities. Stable in closed containers at a room temperature, ethylene should be stored in a well ventilated area to ensure dispersal of any gas leakage. All sources of ignition must be avoided and electrical equipment earthed to prevent static build up; ethylene spontaneously explosive with chlorine in the presence of sunlight.

PROPYLENE : Propylene has become increasingly important as a chemical intermediate in the petrochemical industry. Produced from hydrocarbons by steam cracking. Its major chemical outlet is for the manufacture of polypropylene which accounts for 44% of total production. Copolymerization with ethylene with or without diene modifiers results in ethylene-propylene rubbers.

Propylene gas (MP-185°C) normally is stored as a liquid under a pressure of 20 bar in welded containers. It is non-corrosive and can be stored at atmospheric pressure. It must be kept away from strong oxidizing agents, because of flammability, the area must be well ventilated, sources of ignition avoided and electrical apparatus earthed to prevent static builds.

POLYPROPYLENE (PP) : Polypropylene was first produced commercially in the 1950s. With advancements in stabilization technology, PP has emerged as one of the most versatile thermoplastic raw materials with a wide range of uses. The global consumption is estimated at 20 million tonnes, slowly approaching the consumption level of PVC. The range of products made from PP is extremely wide. PP is the lightest among all commodity plastics with a unique

combination of properties, high tensile strength and dimensional stability, high heat resistance and excellent chemical resistance. PP is used in the automotive industry, household appliance components, textile industry, medical sector packaging. Fibre and filaments are growing areas of PP applications. Globally PP fibre is emerging as the second largest synthetic fibre material, approaching the consumption level of nylon after overtaking acrylic. PP is processed from propylene by gas-based polymerization (70-90°C, 25-35 bar) or by slurry polymerization (65-70°C, 5-30 bar) in the bulk process; liquid polypropylene is polymerized in a tubular reactor. Colourless; very good resistance to acids, alkalis, and inorganic chemicals. The one disadvantage is its brittleness below 0°C.

HDPE : The discovery of catalysts capable of polymerizing ethylene at lower pressures and temperatures than those used previously, revolutionized the production of polyolefins. The polymer formed by this new process had a more crystalline structure and higher density due to its linearity with only a few short chain branches in order to differentiate it from low density polyethylene; it was called high-density polyethylene. The addition of alpha olefins polymerization of ethylene results in a polymer which has a density similar to that of LDPE, but with the linearity of HDPE. This polymer is called linear, low density polyethylene. Suspension solution and gas phase polymerization from ethylene can be used for the production of HDPE. LLDPE is made the same way as HDPE except for the choice of comonomer and catalyst. Major outlet for HDPE is in blow moulding (40%) film and sheet (14%) extruded pipe wire cooling cable insula-

tion (14%). Largest outlet for LLDPE is in film applications (66-70%) where it is replacing LDPE. HDPE should not be exposed to flames as it gives off dense smoke on burning.

LDPE : Low density polyethylene was first produced in the laboratories of ICI; due to its versatility it is now the largest tonnage polymer in the world. Large scale production began in 1950. Large amount of heat is created by the reaction. Recent emphasis has been on raw materials and energy saving processes leading to the move from high pressure LDPE to low pressure linear low density polyethylene (LLDPE). LLDPE offers a cost performance over LDPE which it is replacing in many of its traditional outlets. Processed from ethylene by polymerisation in a tubular reactor or stirred autoclave. Film is the largest application for LDPE (60-70%) extrusion (14%) injection moulding.

Welding Instructor required for a Welding Training & Testing Unit at Bombay near International Airport

Should be a graduate Welding Engineer. Overseas experience is a must. Complete knowledge in accordance with ASME IX & AWS 01.1Exp. and conversant with SMAW, GTAW, SAW & TIG processes. Able to read & fully understand Welding Procedures. Candidates must have a minimum of 10/15 years experience in a Supervisory post with an ability to develop business. A matured personality with good leadership qualities will be preferred.

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