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The chlorine industry

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Abstract: Numerous products, such as polymers, chemicals or pharmaceuticals and ultra-pure metals, which often do not actually contain chlorine, are produced using either chlorine or its derivatives. They are essential in all industrial sectors and in our daily lives. New chlorine production units have adopted the membrane electrolytic process, but the century-old diaphragm and mercury processes retain their high-performance characteristics when appropriately modernised and improved

INTRODUCTION

Chlorine, an exceptional agent in synthesis, is essential to the chemical industry in the same way that salt, from which it is obtained, is essential to life. Among halogens, the most active class of chemical elements, chlorine is by far the most abundant in nature and is also the easiest to produce and to use.

This explains its predominant and irreplaceable role in the chemical industry, in all industrial sectors and in our day-to-day life :

- Forty million tonnes of chlorine were produced in the world in 1995.
- More than 85% of all pharmaceuticals and more than half the products marketed by the chemical industry are derivatives of chlorine chemistry. 1500 of these products have been listed: they are used in all industrial and economic sectors such as health, agro-food, building, textiles, transport, leisure activities, cosmetics, etc.,

As one of the most abundant and easy to collect and process raw materials on earth, sodium chloride is the trunk of an impressive tree of applications of the chlorine chemistry as shown in Fig. 1.

Some of the most technically and socio-economically important among these applications are reviewed in this paper.

CHLORINATED DERIVATIVES

PVC, polyvinyl chloride

With an annual global production of more than 20 million tonnes, PVC is the second-largest tonnage of all thermoplastics after polyethylene, and accounts for slightly more than 30% of the outlets for chlorine.

Produced industrially since the thirties, PVC has benefitted from considerable technological research. The presence of chlorine contribute to its specific properties:

- resistance to fire: PVC is classified as a 'difficultly flammable' material, just after concrete.
- impermeability towards gases and excellent resistance to bacteriological contamination.
- easy processing with an extensive variety of formulations due to compatibility with many products, additives or copolymers. This results in a vast range of PVC materials, transparent or opaque, flexible or rigid, with a long durability and properties which can vary to a great extent.

With chlorine coming from salt, PVC has the advantage to be independent, for more than half of its mass, from limited energetic resources.

The main applications of PVC are summarized hereunder

Building sector: 55% of all PVC is used in the building sector, including window profiles, roller shutters, water pipes, electrical insulation, floor coverings etc.

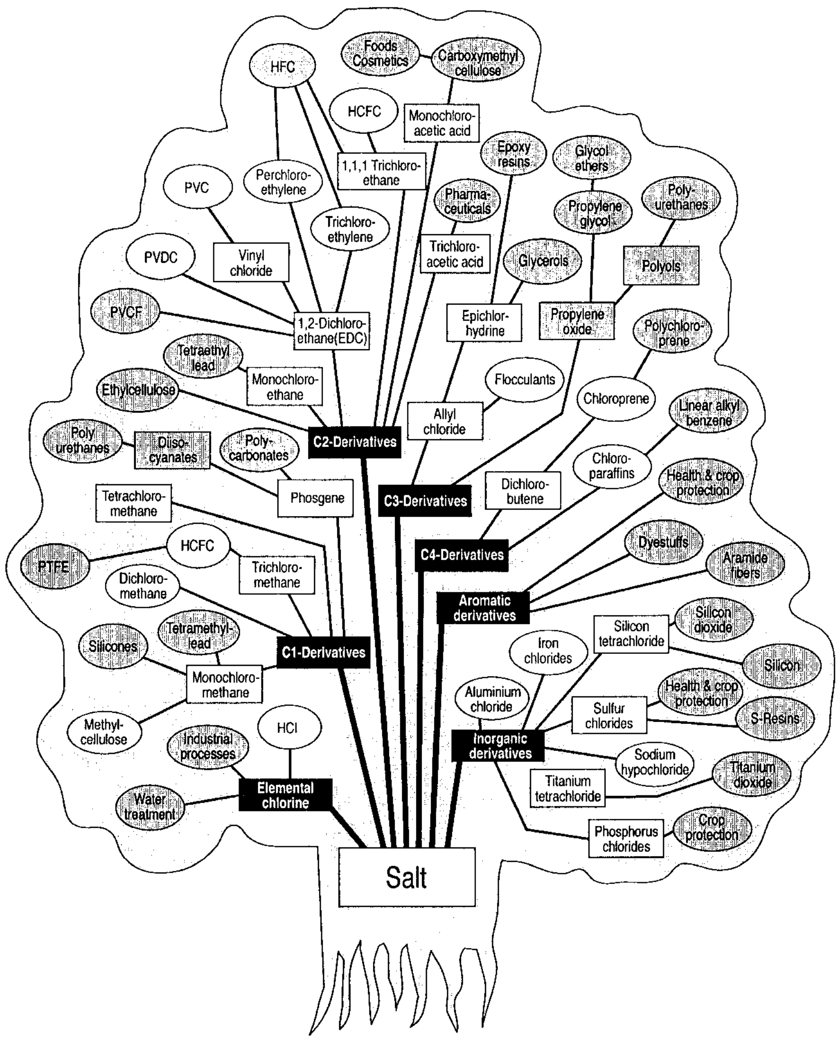

Fig. 1 The chlorine tree.

Consumer goods: articles for the house or office, credit cards, mineral water bottles, toys, footwear and other goods made from synthetic leather, raincoats, etc. One of the special uses of PVC is in the coating of fabrics (oil-cloth, covers for trucks) and for wall coverings.

Packaging: PVC, impermeable to oxygen, like other chlorinated polymers, is used in the packaging of agro-food products, cosmetics and pharmaceuticals.

Medical equipment: PVC, has received the agreement of the medical profession and is widely used for perfusion and transfusion pouches, probes and other medical and surgical products.

The global rate of growth of PVC will, according to experts, be in the range 4% to 5% a year from now until the end of the century. This figure will be 7–8% in Asia. Consumption should grow strongly with the economic development of many countries. In North America and Europe the annual per capita consumption is in the region of 14 kg, whereas on a global scale it is only from 3 kg to 4 kg.

Other chlorinated polymers

Smaller tonnages of various chlorinated polymers are used in specific applications where the properties conferred by chlorine are used to advantage.

Polyvinylidene chloride, PVDC, is used as a barrier material in multi layer films for food packaging. In copolymerisation the monomer adds to other monomers its own specific properties, such as providing flame resistance to acrylic fibres.

Polychloroprene is an elastomer valued for its high resistance to fire and oils and its excellent weathering characteristics. It is used in cable coverings and gaskets.

Organic syntheses and active pharmaceutical principles

Many chlorinated derivatives are essential agents in organic syntheses. For example the chloromethanes, allyl chloride, monochloracetic acid, epichlorhydrin, phosgene and other chlorinated derivatives are frequently used in various chemical reactions which give rise to a multitude of chemical products, whether or not they finally contain chlorine. These products are essential in all industrial sectors and in our daily lives. They enter in the composition of: food additives, cosmetics, detergents, photographic products, paints, adhesives, materials, etc.

The vast majority of active pharmaceutical principles is dependent on chlorine chemistry : many drugs often the most widely prescribed, are based on chlorine-containing compounds. More than 90% of all agrochemicals contain chlorine.

Chlorinated synthons are also valuable tools for research. A recent example is the synthesis of an organosilane obtained from trichlorosilane and allyl chloride which is used as the coupling agent for the silica used in the so-called 'green tyres'.

Chlorinated solvents

Chlorinated hydrocarbons possess properties which combination is unusual in organic solvents, such as high volatility—and consequently speed of drying—and non-flammability. Chlorinated solvents have the advantage, when compared with aqueous solutions, of concentrating dissolved products in a very small volume. They are easily recycled by distillation. However for ecological considerations their consumption has been strongly reduced and they represent now less than 4% of the total usage of chlorine.

Alternative solutions are available, but for certain applications chlorinated solvents remain essential, such as dry cleaning, special metal degreasing as in the electronic industry, extraction of natural products for the agro-food industry, cosmetics, pharmaceuticals, etc.

Inorganic chlorine-containing derivatives

Metal chlorides have many applications, including the use of aluminium and iron chlorides as important catalysts in synthesis and as flocculants in water treatment. Zinc chloride is used in galvanisation.

The phosphorus and sulphur chlorides are widely used as intermediates for agrochemicals such as pesticides and herbicides: they are also used in the production of plasticisers, stabilisers and colouring materials for plastics materials, etc.

The hypochlorites (bleaching solutions) are well known for their disinfecting and bleaching properties. Chlorine dioxide has replaced elemental chlorine in new processes for bleaching paper-making pulps.

Chlorates and perchlorates are used in the explosives industry and as rocket propellents, in fireworks and matches and also as herbicides.

CHLORINE FOR NON-CHLORINE-CONTAINING PRODUCTS

Chlorine and certain chlorinated derivatives are excellent synthesis intermediates because of the high reactivity of the carbon-chlorine bond which :

- allows the introduction in the molecule of such diversified groups as –OH, –SH, $-NO_2$, –F, –CN;
- give access to the organo-metallic chemistry and especially to Grignard reagents leading to acids and ketones.
- leads to alkylation and acylation of aromatic compounds through Friedel-Crafts reactions.
- is used in the manufacture of industrial isocyanates and (poly)carbonates by the phosgene route.
- allows the introduction of double bonds by elimination reactions (often of HCl) and thus the manufacture of unsaturated compounds used as monomers.

This makes it possible to synthesize many products which do not contain chlorine themselves in their molecule.

In order to avoid the use of chlorine various replacement processes have been studied, in particular for the isocyanates, silicones and polycarbonates, but these are more complex to use industrially, are less reliable and of lower performance than processes using chlorine. Such processes are well-known and have been constantly improved throughout many years, give excellent yields and consume very little energy.

When it plays a role as a chemical intermediate, chlorine can be eliminated at the end of the process as an inert inorganic chloride, but more frequently it is recycled. For example hydrogen chloride resulting from chlorination of organic products or from the incineration of chlorinated residues can be used in production of vinyl chloride monomer, VCM, by catalytic oxychlorination of ethylene to 1,2-dichloroethane (which is then thermally dehydrochlorinated to VCM.)

It can be evaluated that more than a third part of the total chlorine produced is recycled within the chemical industry.

As shown in Table 1 chlorine chemistry leads to the manufacture of various polymers, many of them being non chlorinated.

Polyurethanes

With a world annual tonnage of the order of 6 million tonnes polyurethanes absorb about 10% of the total chlorine production.

The two agents used in polyurethanes synthesis depend on the chemistry of chlorine. The chlorohydrin process still accounts for half the world production of propylene oxide, and isocyanates are obtained by reacting phosgene with amines.

Polyurethanes, mainly in the form of foams, have many different applications:

- flexible and semi-rigid foams in furniture, beds, the automobile industry, etc.
- rigid insulating foams in building and refrigeration;
- elastomers for footwear, floor coverings, sports goods and domestic electrical appliances.

Table 1 Chlorine in the manufacture of polymers

Polymer	Structural unit	Chlor. raw mat.	Applications
PVC	[$CHCl$–CH_2]	$CHCl$=CH_2	Various
PVDC	[CCl_2–CH_2]	CCl_2=CH_2	Barrier films
PVDF	[CF_2–CH_2]	CCl_3–CH_3	Anti-corrosion films, piezo- and pyroelectric polymers
PTFE	[CF_2–CF_2]	$CHCl_3$ → $CHClF_2$	Coatings, mechanical parts
PC	CH_3 O [O–φ–C–φ–O–C] CH_3	$COCl_2$	CD, appliance housings, protection helmets, cameras, electromechanical devices
PPS	[φ–S]	Cl–φ–Cl	HT electrical parts, under-the-bonnet automobile parts
Polyolefins	[CH_2–CH] R	Catalysts	Packaging, fuel tanks, household parts, toys, appliance, bumpers, business machines, fiber
PUR	[R–NH–CO–O–R′]	$COCl_2$ → TDI	Furniture and insulation foams, ski boots
Epoxy	CH_3 [O– CH_2– CH_2– CH_2–O–φ–C–φ–O] CH_3	CH_2Cl–CH–CH_2 O	Sport, aeronautics, tanks, moulds, adhesives

From G.J.Martens in *Chlorine and Life*, Ed. L.Puigjaner, UPC, Barcelona (1995), p.59.

Technical polymers

Technical polymers, derived from the chemistry of chlorine, suit a wide range of often very sophisticated uses:

Polycarbonates, produced from phosgene and bisphenol A, have very high resistance to impact and heat combined with excellent optical properties: they are used for synthetic lenses, protective shields, visors for cosmonauts, compact discs, medical equipment, prosthesis, etc.

Epoxy resins are produced from epichlorhydrin. They enter into the composition of anti-corrosion coatings, very powerful two-part adhesives used for example in aerospace composites, and in highly resistant paints and varnishes.

Silicones are synthesized from chloromethane and silicon to give chlorosilanes, subsequently hydrolysed and polycondensated in polysiloxanes better known as 'silicones'. Used in the form of fluids or technical components they have remarkable properties of lubrication, electrical insulation, chemical inertness and thermal stability. They find their outlets in all industrial sectors especially those demanding high-quality materials such as surgical goods: implants, catheters, drains etc.

'Special' polymers

Special high added value polymers are produced in small tonnages using chlorine chemistry:

Fluorinated polymers, are very resistant to heat, corrosion and chemical agents.They are used as gaskets or sheaths of pipelines or other equipment for example, in the chemical industry.

Synthesis of fluorinated monomers always involve chlorinated molecules (C1 and C2 hydrocarbons). Chlorine atoms can be replaced by fluorine atom using hydrogen fluoride.

Polytetrafluoroethylene is obtained by fluorination of trichloromethane wish give chlorodifluoromethane subsequently cracked in PTFE with elimination of hydrogen chloride. This product is well-known as non-sticking coatings used for cooking equipment.

Phenylenesulphide, result from condensation between dichlorobenzene and sodium sulphide. PPS has a very high resistance to heat, and is used for automobiles injectors and in the manufacture of components in the aeronautical industry

Polyaramides are used, in the manufacture of fire-resistant fibres for protective fabrics, tyre carcasses and to replace asbestos in brakes. To obtain these aromatic polyamides fibres, such as Kevlarâ, paraphenylene diamine is reacted with terephtalyl chloride.

CFC substitutes

Hydrofluoroalkanes have recently been developed as substitutes for chlorofluorocarbons in order to help protecting the ozone layer. They show excellent toxicologic and flammability resistance properties while being excellent refrigeration fluids. They provide the best overall energy balance of all refrigeration systems and help in that way to limit the greenhouse effect. As for the large majority of fluorinated compounds, they are produced by halogen exchange between a chlorinated hydrocarbon and hydrogen fluoride.

Metallurgy, ultra-pure metals

Certain metals are obtained from their chlorides; these can be either natural or be obtained by reaction with hydrogen chloride or by carbochlorination of the ore. The metal chlorides are often sufficiently volatile to be easily purified by distillation . The metal is extracted from the purified chloride either by electrolysis of the molten salt, as in the case of magnesium, sodium or lithium, or by reduction as in the case of titanium or zirconium, etc.

Silicon, high purity (>99.99%) used in the manufacture of microelectronic components or in solar panels, is obtained by distillation of trichlorosilane followed by reduction to the metal and crystallisation by the Czochralski process. Produced hydrogen chloride is recycled to the chlorination of metallurgic grade silicon (about 97%) to its trichloride.

Zirconium is used in the manufacture of the rods containing pellets of nuclear fuel: it must not contain any hafnium since this element absorbs neutrons. Zirconium is therefore purified by very careful distillation of its chloride and then obtained by reduction.

Inorganic products

Various non-chlorine containing inorganic products need chlorine to be produced, these include:

Titanium dioxide, universally used white pigment, is manufactured using the titanium tetrachloride process. This is now the generally used process in new plants because of its kinder environmental impact than the older sulphate process.

Bromine is obtained from bromides, present at trace levels in sea water, by oxidation using chlorine. It is used in the synthesis of pharmaceutical and agrochemicals specialities, in fire-proofing agents and in anti-knock additives.

THE THREE ELECTROLYSIS PROCESSES

Chlorine and its co-product caustic soda have been obtained industrially for a century by electrolysis of brine, a saturated solution of sodium chloride. The two older processes, the mercury process which was predominant in Europe, and the diaphragm process, predominant in America, are constantly being improved and coexist with the recent membrane process. Installed in Japan on a massive scale about ten years ago the membrane process is now used in new units.

In all processes chlorine is produced at the anode. Initially made from graphite the anodes are now made from titanium with special coatings (dimensionally stable anodes DSA). Their shape, often complex, has been the subject of many studies aimed at improving the gas release and minimising inter-electrode spacing in order to improve energy efficiency. Catalytic coatings also contribute towards lowering the voltage.

Mercury cathode process

Sodium forms an amalgam with mercury which flows into a decomposing vessel where the addition of water results in the release of hydrogen and the formation of a pure soda solution at the commercial concentration of 50% wt. The mercury is recycled to the electrolysis cell.

Mercury losses in this process have been considerably reduced over the years. They have fallen by more than 90% over the last twenty years: for the European industry, according to Euro Chlor, losses of mercury in liquid effluents are less than 2.5 g of mercury per tonne of chloride and discharges to the atmosphere are already conform to the standards fixed, by the Commission de Paris for the end of 1996, at 0.2 g of mercury per tonne of chlorine produced. Taken overall the losses of mercury arising from the production of chlorine account for less than 0.1% of all industrial rejects of mercury. These losses can be even further reduced by the modernisation of the units in Eastern Europe.

Diaphragm and membrane processes

The separator, whether a diaphragm or a membrane, forms the boundary of the anode compartment which is supplied with a saturated aqueous solution of sodium chloride, and of the cathode compartment where the soda solution is produced. Chlorine and hydrogen are produced at the anode and cathode respectively.

The diaphragm allows the brine to percolate. The produced solution of caustic soda contains an important amount of sodium chloride. Concentration of the solution to this commercial concentration causes the salt to crystallise out. The residual level of salt is 1% which makes this grade of caustic soda unsuitable for some uses, such as artificial textiles and some organic syntheses, without additional purification.

The diaphragms generally consist of asbestos, reinforced with fibres of fluorinated polymers. When immersed the asbestos does not present any health hazards, but nevertheless stringent precautions must be taken when handling it. The increasing severity of the regulations controlling the level of fibres present in the air of workshops could accelerate the installation of new diaphragms without asbestos.

These newly developed diaphragms are based on polytetrafluoroethylene (PTFE) with inorganic fillers which role is to make these composite materials hydrophilic. They are currently undergoing tests at the major chlorine producers with some success, but for the time being their price seems prohibitive to the producers.

The diaphragm process is therefore likely to continue being used in the older units since it can undergo new improvements, both in regard to environmental concerns and also reduced energy requirements with the introduction of cathodic activations based on nickel alloys.

Ion exchange membranes produced from perfluorinated polymers have been developped by the Americans since the beginning of the seventies by grafting sulphonic groups on the main polymeric chain, and subsequently by the Japanese with carboxylic groups. Present membranes actually form double layers which combine the advantages of these two types of anion. They prevent the chlorine ions from entering the cathode compartment, so that the caustic soda is pure and free from salt. The caustic soda, at a concentration of 30%, requires only limited evaporation to reach the commercial concentration of 50% wt.

Total energy consumption of the membrane process is less than 3000 kWh per tonne of chlorine, so the energy balance sheet of this process is the best of the three processes, not only because of the reduced cost of evaporation as compared with the diaphragm process but also because of the reduction of the voltage loss in the separator which is less than 50 mV for a newly installed membrane, as compared with 500 mV for a reinforced asbestos diaphragm (the theoretical voltage being 2.15 V).

The membrane process thus combines the advantages of a lower energy consumption, a very high quality caustic soda and the best behaviour in respect of the environment so it has been adopted in all new units. However the investment corresponding to a new unit is very high, and it is probable that the three processes will coexist throughout the world for some time to come.

Electricity, the raw material

The two raw materials used in the production of chlorine and its co-product, caustic soda, are salt (either from the sea or from mines) which is available in practically inexhaustible amounts even if they are unequally distributed, and electricity which has the advantage that it can come from a variety of sources such as coal or oil or from nuclear or hydraulic generation. The consumption of electricity by chlorine producers is very high, in excess of 3000 kWh per tonne of chlorine. However the consumption for electrolysis is constantly adjustable and hence plays a regulating role in the distribution of electricity; since electricity cannot be stored and this fact is appreciated by the distributors of electricity. In Western Europe electricity costs account for nearly half the cost price of chlorine.

The electrolysis processes have been the subject of constant research, to the benefit of the whole electrochemistry sector. Research is continuing on the development of air cathodes (employed in fuel cells) which use would result in a substantial gain in the thermodynamic voltage of the cell and hence on electricity costs.

Caustic soda, the co-product

Production of one tonne of chlorine is accompanied by the production of 1.1 tonnes of caustic soda: which is an important product, with a very wide range of applications. More than half of caustic soda tonnage is used in the chemical industry and the other part goes in the production of consumer goods such as paper, soap and textiles, and in water treatment, aluminium production and oil refining.

Caustic soda can be easily transported throughout the world and is easy to store. For certain applications it can be replaced by soda ash. Its market is much more easily regulated than that of chlorine which, being dangerous to transport, is mostly used at its production sites in a variety of downstream units, in particular those for VCM/PVC. The operating levels of electrolysis plants are thus controlled by the demand for chlorine.

Forecasts

Chlorine, and its co-product caustic soda, are two intermediates which play an important role in the chemical industry. The markets for chlorine and its derivatives have arrived at maturity in Europe and it is therefore only in countries with high economic growth that an increase in the demand is expected. This is mainly due to PVC, which is increasing at 7% to 10% annual rate in the Asiatic countries. Units are projected in Asia, but investment costs, the limited availability of electricity and often of hydrocarbons and salt, lead to the assumption that Asia will continue for many years to rely on imports of dichloroethane, the precursor of VCM and PVC.

The world capacity for chlorine was 44 million tonnes in 1995. The major future production units will be built in regions having cheap electricity, salt and ethylene such, as Saudi Arabia which is currently considerably increasing its chlorine capacity, converting chlorine into dichloroethane, VCM precursor, for export.

According to specialists chlorine production will increase at a global rate slightly above 1% per annum.

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