0. EXECUTIVE SUMMARY

0.1 INTRODUCTION :

0.1.1. Hydrogen peroxide is an inorganic, weak acid. It is a powerful oxidizing agent. It is also a good reducing agent against more powerful oxidizing agents. On reaction, it releases oxygen and water. Thus, it is non polluting in nature, unlike many other oxidizing agents.

Its most prominent use is for bleaching of cotton textiles. It gives better whiteness than other agents. It is also used for bleaching pulp by the paper industry. It is used to manufacture many other peroxy compounds. It is a disinfectant and thus used in pharmaceuticals and for aseptic packaging. Because of its oxidizing property, it has many other uses, like, waste water treatment, in hydrometallurgy, refining of sugar and as an etchant in electronics. Hydrogen peroxide is also used as a propellant for rockets.

Hydrogen peroxide is normally prepared in 65-70% w/w strength. It is normally available in 50% w/w strength. However, it is also available at different strengths, mainly 3%, 6%, 35%, 70% and 90%. Most users require dilution at user's site. It is available in various grades. Technical grade product is most commonly used. It is a grade which is not ultrapure, contains stabilizers, has concentration of less than 50% w/w and is for general purpose use. For electronics, ultrapure grade is available. For food and pharmaceuticals, a separate grade product is available. In India, quality specifications are laid down in IS : 2080 for general use and in Indian Pharmacopoeia (1985) for pharmaceuticals use.

0.2 HISTORICAL DEVELOPMENT

0.2.1. Hydrogen peroxide was first discovered in 1818 in France. Initially a small quantity was used for bleaching purposes. However, it was only in 1870s that the first commercial process was developed.

0.2.2. Initially hydrogen peroxide was produced from barium peroxide, which was easily available. Many small units were established in Europe and North America as hydrogen peroxide was found to be a very useful

chemical. However, its large scale development took place only when its excellent properties could be profitably used in the textile industry. Around that time, new electrolytic processes were developed and the first large scale industrial production by electrolytic process started in 1909.

0.2.3. In 1930s laboratory scale production of hydrogen peroxide by autoxidation process was established. The first plant was set up in 1941-42 in Germany. With industrial development and with discovery of new uses, demand for hydrogen peroxide grew considerably. Large scale production was required to be established and it was found that autoxidation process was more economical for large scale production, compared to electrolytic process. Soon autoxidation process became the preferred route. Presently, almost the entire world capacity is based on autoxidation process.

However, process does vary from plant to plant. Variations occur in type of catalyst, in types of working materials, in types of working solutions and solvents. Modifications have been made to make the process more efficient but the basic process remains unchanged.

0.2.4. Recently, new processes have been reportedly developed at pilot plant scale.

0.3 PROCESS OF MANUFACTURE

0.3.1. Hydrogen peroxide can be manufactured by a variety of processes. Major processes have been :

a. Barium Peroxide Process

b. Electrolytic Process

c. Isopropyl alcohol oxidation process

d. Anthraquinone Autoxidation Process

However, at present, autoxidation process using 2-ethyl anthraquinone is the process of choice. Other processes have become economically unviable. Barium peroxide process stopped being used when electrolytic process was developed. Electrolytic process was used till recently, on lower scale of operation. However, rising cost of energy has made that process obsolete.

0.3.2. Autoxidation process essentially involves hydrogenation of 2-ethyl-anthraquinone to from 2-ethyl-anthrahydroquinone. This is subsequently oxidized to from hydrogen peroxide and 2-ethyl-anthraquinone. Thus, essentially, hydrogen and oxygen are used as raw materials.

2-Ethyl anthraquinone is dissolved in suitable solvents to form a working solution. A catalyst, normally palladium on inert support, is used for hydrogenation reaction. Hydrogen of very high purity is required. Air or oxygen is used for non-catalytic oxidation. Hydrogen peroxide is extracted with water and other solvents. Then it is concentrated and stabilized. Normally hydrogen peroxide of 65-70% w/w strength is produced. Working solution from which hydrogen peroxide has been stripped, is regenerated and recycled after adding make up requirements. Normal plant size is 20-30,000 tpa of 100% w/w hydrogen peroxide for economic operation. However, in India, 5000 tpa, is the maximum capacity that the market can sustain, though it does result in higher production costs.

0.4 STATE-OF-THE ART TECHNOLOGY AND CURRENT RESEARCH AREAS

0.4.1. Process for the manufacture of hydrogen peroxide is well standardized. Technology emanates from six or seven giant companies and they control most of the world production. Their processes are similar and hence operating parameters are more or less similar at all the plants. However, raw materials may differ.

0.4.2. Catalyst for the process is normally palladium. Nickel is also used. Efforts are made to improve catalyst activity, selectivity and life.

Working solution may contain different solvents. These are not standardized.

0.4.3. Oxidation may be based on use of air or oxygen. Very few plants are based on use of oxygen and that denotes inferior technology. Use of oxygen requires air separation units to get pure oxyen. Also, it implies a plant design which cannot take any impurity unlike the plants using air. Catalysts are normally not used. But attempts have been made to develop catalysts to make operation more efficient.

0.4.4. Regeneration of working solution is essential. Working solution is essentially used as a carrier of all reacting materials. Both, raw materials and

finished products, dissolve in working solution. However, it does not itself take part in reaction. Hence, it must be recovered, after stripping it of hydrogen peroxide, by removing by-products present, for recycling. Normally catalytic regeneration is practiced. Caustic soda based process is also used for regeneration.

0.4.5. Research efforts are directed at improving operational efficiency. These include better catalyst, lowering of working solution requirement per unit production, better regeneration techniques, new stabilizers etc.

0.4.6. Research is also directed at development of new processes.

Recently a new electrolytic process based on membrane technology has been developed. This process yields a dilute solution of caustic and hydrogen peroxide.

Also, a new process of direct catalytic oxidation of hydrogen has been reportedly developed.

These process have been developed at pilot plant level. They are not yet commercialized. However, both these processes are reportedly ready for commerical exploitation.

These two processes thus seem to be most likely new commercial processes in near future.

0.4.7. Hydrogen peroxide can be used in a variety of applications. New applications are being found which not only help the user but also the society at large due to non-polluting nature of hydrogen peroxide.

0.5. STRUCTURE OF THE INDIAN INDUSTRY

0.5.1. Indian chemical industry is well developed and has taken a lot of strides to achieve self sufficiency in many a field. However, when it comes to speciality chemicals, efforts have not been to the extent desired.

0.5.2. Hydrogen peroxide market in India is small, constrained by both, market size and monopolistic nature of industry. One large manufacturer has been producing for more than thirty years. Only one small scale manufacturer ventured for a while in this field. However, technological obsolescence has forced this small unit to close down. Thus, at present, there is only one manufacturer viz. National Peroxide Limited with 4200

tpa capacity situated near Bombay. One more 100% EOU unit is reportedly being set up with 5000 tpa capacity. This unit is in Andhra Pradesh. One more unit is expected to be set up in Madhya Pradesh with 6000 tpa capacity.

0.5.3. National Peroxide Limited has its own captive hydrogen production. Earlier, it relied on by-product hydrogen from a nearby chlor-alkali unit, supply from whom was erratic. Asian Peroxides Limited, the new unit in Andhra Pradesh will also have captive hydrogen production facility.

0.5.4. Production of hydrogen peroxide has been erratic, albeit growing. Production during 1986-87 was 2862 tons. Imports have also fluctuated reaching a high of 4076 tons in 1984-85. Imports in 1986-87 were 850 tons. A small quantity of hydrogen peroxide is also exported, largely to meet stipulated export obligation. Demand has been steadily growing and is expected to grow at more than 10% per annum. It is estimated that the domestic demand may reach 8630 tpa by 1994-95 and 16,500 tpa by the year 2000. Export demand could be 3500 tpa by 1994-95.

0.5.5. Presently, textile industry is the prominent consumer of hydrogen peroxide in India. Demand by paper and pulp industry is growing at good rates. Other use areas are also being developed. In the advanced countries uses in the manufacture of chemicals and for environmental protection are substantial.

0.6 TECHNOLOGICAL STATUS OF INDIAN INDUSTRY

0.6.1. The first plant, National Peroxide Limited, was established in 1956, using electrolytic process. Arat Electrochemicals, the second plant was also based on the electrolytic process. With the passage of time, electrolytic process became obsolete. NPL, having equity participation from its collaborator, Laporte, could get the new anthraquinone autoxidation technology and switched over to the same in 1972. later, while doubling its capacity, a new reversion process was introduced. Thus, one might say that the existing technology is probably very good and compares well with the best in other countries. Asian Peroxides Limited is importing a second hand plant, though it is also anthraquinone based technology and is comparable to the technology being used at present.

0.6.2. Indian technology is based on foreign know-how. India has adopted this technology to the extent that a similar plant can be set up indigenously. However, legal constraints may not permit such transfer of technology. Hence, it would be necessary to rely on foreign know-how for new plants.

0.6.3. Also, a lot of research abroad is directed at developing new processes. Indian research effort in this direction is nil.

0.6.4. Indian research institutions have also not paid any great attention to the technology of hydrogen peroxide. In fact, no major research centre has reported any work in this field. However, some universities are engaged in research on use of hydrogen peroxide. One area of research is use of hydrogen peroxide for removal of aphlatoxin from edible oils.

0.6.5. Hydrogen peroxide is available in many different grades. These include technical grade, pharmaceutical grade, electronic grade, propellant grade etc. Demand for most of these grades is small. Thus, it may not be economical to produce all grades. No new grades have been developed, apart from those for which technology has been imported.

NPL has claimed that it can produce various grades if sufficient demand exists.

However, it is also a fact that the Indian ability to produce a variety of grades is limited.

Higher strength grades require specialized knowledge. In high purity grades even stabilizers are not allowed as impurity.

0.6.6 Major raw materials are hydrogen and oxygen. Design and know-how for the manufacture of hydrogen from fossil fuel is now available in India, from major enginering consultants (with overseas principals). Also, by-product hydrogen of other industries can be used. Catalysts and some chemicals have to be imported.

0.6.7. On applications side, a lot of research is being directed to develop new use areas. NPL has developed some hitherto unexplored uses. For example, a cold bleaching process for cotton textiles has been developed. This is a useful application since many processors in India are not in position to use hot bleaching process. Also, processes have been just commercialized for use of hydrogen peroxide for bleaching of sugar. Commercial process is fully established for bleahcing of coir. Process know-how is ready for bleaching of high yield pulp, chemical pulp and metal polishing.

0.7 CONCLUSIONS AND RECOMMENDATIONS

0.7.1. Conclusions :

a) Hydrogen peroxide is being indigenously manufactured for more than 30 years. Production was 2862 tons in 1986-87. Growth rate is expected to be more than ten per cent per annum for the next few years.

b) Hydrogen peroxide manufacture is open to all sectors. It is a delicensed item since 1986. Quite a few letters of intent and registration are reported. However, at present, there is only one plant in operation, with one more being set up. A third plant is under active stage of planning and is likely to be set up.

c) NPL having been set up with foreign equity, has continuously upgraded its technology with the help of its collaborator. Technology and product are internationally comparable. The necessary capability and manufacturing technology to set up similar plants, is claimed. However, such indigenous know-how may not be available as NPL has to obtain its colloborators' approval before horizontally transferring the technology. New processes and technology have been reportedly developed abroad. These are claimed to be substantially cheaper than the existing technology. However, so far, only pilot scale development has taken place. They are yet to be commercialized.

d) Know-how has been closely guarded by a handful of companies in the world. For a relatively low scale of operation and limited market size, good technology has not been forthcoming so far. But this may change in future. FMC corporation and Du Pont are reported to be interested in setting up plants in India.

e) A large number of limited applications have been developed in India. Still, there is good scope for expanding applications.

0.7.2 Recommendations :

(i) NPL claim of capability to supply technology for hydrozen peroxide should be investigated. If found correct, NPL should be motivated to supply technology to other indigenous parties.

(ii) Technology import for hydrogen peroxide may be necessary if the requisite know-how is not available in India from NPL. However, new technologies are being developed and promising results have been reported. It would be worthwhile to follow the developments and weigh the options carefully.

(iii) Technology is closely guarded. Hence, to create competitive environment, it is necessary to get technology from available sources. Till, now, good technology was not easily available. But recent indications are that big foreign companies may be interested in supplying technology.

(iv) It is necessary that new applications are developed. Hence, any new technology should preferably be accompanied by the latest feasible application package, i.e. complete formulation of and technique of usage for different applications.

Development of new applications involves development of stabilizers etc., which are application specific.; Any new manufacturer of hydrogen peroxide will have to spend considerable time and effort to develop such stabilizers. Hence, it would help if such application package is also brought alongwith manufacturing know-how.

(v) Hydrogen peroxide usage in many areas have social benefits. Thus, its use needs encouragement. Fiscal benefits, coupled with development of competitive environment may be followed as an appropriate strategy. Also, one of the advantages of stricter compliance with pollution control laws could be to help increase consumption of hydrogen peroxide.