EXECUTIVE SUMMARY

1.0 Titanium Dioxide is one of the top 20 inorganic chemicals of industrial importance. It is the most important pigment material used. Titanium Dioxide has the highest refractive index among the known materials and hence it imparts best pigment properties such as hiding power, opacity, etc. Titanium Dioxide is the whitest of the White Pigments. It is used extensively in paint, paper, plastic and other industries. High purity titanium dioxide is an important electronic material.

2.0 First successful attempt to produce relatively pure titanium dioxide from ilmenite ore was made by Rossi in USA in 1908. The first titanium pigment company which intially produced composite pigments commenced production at Niagara Falls in 1918. Since those days and even today USA has been in the vanguard of development of titanium dioxide industry. Another important landmark in the history of titanium dioxide was development of improved method of thermal hydrolysis by Blumenfeld in 1920 in France. The technology was licensed to a number of companies in Europe as well as in USA.

3.0 The event that revolutionized the titanium dioxide industry was the development of Chloride Technology by M/s. Du-Pont around 1959. The chloride technology took the US industry by storm and in a short span, most of the sulphate route plants were closed or replaced by chloride route plants.

4.0 In the 1960s and 1970s major investment was made in the titanium dioxide plants in Europe. M/s. Tioxide of UK, M/s. Kronos of Germany and M/s Thann and Mulhouse of France have emerged as the leading European companies in the field of titanium dioxide. The Japanese industry has picked up in recent years and the Japanese production has now reached a level of about 280,000 tonne, M/s. Ishihara are the leaders of the Japanese titanium dioxide industry.

5.0 In India the titanium dioxide industry arrived almost with the dawn of independence. First plant was set-up by the erstwhile State of Travancore in 1950. However, thereafter the growth of the Indian industry has been rather sluggish.

6.0 The per capita consumption of titanium dioxide in USA is about 3.4 Kg. The consumption in Asia-Pacific region is about 0.2 Kg. The Indian consumption, however, is extremely low at less than 0.05 Kg.

7.0 Titanium dioxide is produced and marketed in two grades. These are Rutile and Anatase. Rutile has close packed structure whereas Anatase has more open structure. Rutile has higher density, higher refractive index, better resistance to chalking and higher hardness.

8.0 Because of high refractive index, titanium dioxide pigments exhibit the highest hiding power. If the hiding power of Rutile is placed at 100, that of Anatase is 78. The hiding power of other common pigments such as zinc sulphate, lithophone, white lead etc. ranges between 39 to 10.

9.0 There are three main fields of applications of titanium dioxide. These are:

i) Coatings (paints)

ii) Paper

iii) Plastics

iv) Miscellaneous usages

The percentage of consumption in different sectors varies from country to country. In USA coatings account for 51%, paper 24%, plastics 14% and other usages 11%. In most countries, however, the share of usage in paper industry is lower at about 6-9%. The share of the plastic industry is growing in all the countries.

10.0 Use of Rutile grade is preferred for applications in paints, plastics, Ceramics, etc. Anatase grade imparts a bluish tinge and is preferred by the Paper Industry. Similarly, Anatase grade has less hardness and is thus less abrasive. Hence Anatase grade is invariably used for delustering of synthetic textile fibres.

11.0 The present (1991) requirement of titanium dioxide in the country is estimated at 47,480 tons. Out of this, about 31,530 tons (or 66.4%) is consumed by the Paint Industry. The Paper and Plastic industries requirements are about 3,000 and 5,000 tons respectively. The miscellaneous demand is about 8,000 tons. Out of the total requirements, about 65% is for Rutile grade and 35% for Anatase grade. It is anticipated that the requirement of Rutile grade will increase in the future at the expense of Anatase grade. The demand determinant sectors namely Paints, Paper and Plastics are expected to grow at the rate of 7%, 2.6% and 10% in the years upto 2000. The total demand of titanium dioxide is projected to increase to 61,620 tons by 1995 and 82,890 tons by the year 2000. This corresponds to growth rate of about 6.9% which seems very reasonable. If India could make even a small dent in the export market, the total annual requirement of titanium dioxide will cross 100,000 tons by the year 2000.

12.0 Presently titanium dioxide is being manufactured in India by three companies. These are M/s. Tavancore Titanium Products Limited, Trivandrum, M/s. Kerala Minerals and Metals Limited, Quilon and M/s. Kolmac Chemicals, Calcutta.

M/s. TTP are the oldest manufacturer of titanium dioxide in India. They use sulphate process and their plant has present installed capacity of 24,500 tonne. The present production level is about 10,000 tonne. The technology for the sulphate process was obtained from M/s. Tioxide of U.K. who are also the equity partners.

M/s. KMML have set-up a plant to manufacture titanium dioxide by chloride process. The plant has an installed capacity of 22,000 TPY but the production is only around 9,000 TPY. The technology was provided by M/s. KMCC of USA.

M/s. Kolmac have a small plant at Kalyani near Calcutta and they produce about 1,300 TPY of anatase grade pigment. The technology was developed indigenously. After several years, the operation of the plant seems to have stabilized now.

13.0 The present demand (1991) has been indicated as 47,480 tons whereas the present production is about 21,800 tons. A new project of 15,000 tons capacity is being pursued actively. It is anticipated that another project of 15,000 tons shall be set up before the end of the century. On these assumptions it is projected that the domestic production of titanium dioxide will increase to 33,800 tons by 1995 and 50,800 tons by the year 2000. Correspondingly, the demand shall increase to 61,620 tons and 82,890 tons. This would mean that the present demand supply gap of 25,680 tons will increase to 27,820 tons by 1995 and 32,180 tons by the year 2000. If a provision is made for exports then, the gap between demand and availability will exceed 40,000 tons.

14.0 There are two distinct technologies used for manufacture of titanium dioxide. These are Sulphate process and Chloride process. The sulphate process has been in existence for more than 70 years. The process involves the following steps:

i. Digestion of Ilmenite or Titania Slag in Sulphuric Acid

ii. Reduction and Crystallization

iii. Hydrolysis

iv. Calcination

v. Dry Milling

The product obtained by sulphate process is usually Anatase which can be further treated to obtain Rutile. The feed stocks used for sulphate process are mainly ilmenite or titania slag. The major disadvantages of the sulphate process is that large quantities of waste products, (about 10-12 tonnes per tonne of finished product) are generated in the form of spent acid and copperas. The problem of copperas can be reduced by using titania slag as the feed stock instead of ilmenite.

15.0 The chloride process was developed by Du-Pont around 1959. The main process steps are as follows:

i. Chlorination of Synthetic Rutile or other raw materials.

ii. Purification of titanium tetra chloride.

iii. Oxidation of pure titanium dioxide.

iv. Finishing of raw titanium dioxide.

The main advantages of the chloride process are as follows:

i. Product obtained is Rutile and is of a better quality.

ii. Process is continuous.

iii. The waste products generated are in small quantities.

16.0 A technical comparison of the Sulphate and Chloride processes indicates that the chloride process gives a product which is finer in particle size, is low in impurity contents and less waste products are generated. As a result more and more manufacturers are progressively shifting to the chloride process. Presently about 55% of the titanium dioxide is produced by sulphate process. It is anticipated that by 1995, this proportion will drop to 5% or even lower.

The elemental sulphur which is used for manufacture of sulphuric acid, required in the sulphate process has to be imported in India. The raw material assembly cost for the sulphate process under the Indian conditions is about 1.0% higher than for the chloride process.

17.0 So far four compaies have sourced technology from abroad. M/s TTP obtained sulphate technology from M/s. Tioxide of U.K. M/s. Tioxide also joined TTP as equity partner. M/s KMML obtained technology from KMCC of U.S.A. M/s. Kanoria Chemicals signed an agreement with M/s. KMCC for technology. However, the project was not implemented. M/s. Prodhvi Industry have an agreement with Czechoslavakia for provision of sulphate technology.

18.0 On the pollution aspects, the Indian industry leaves far to be desired. M/s TTP are presently discharging copperas and waste acid in the Arabian sea.

19.0 On the international scene, the titanium dioxide industry is going strong and despite occasional recession in the market, the industry continues to grow at an average rate of about 2.5%. The industry is dominated by U.S.A., U.K., Germany, France and Japan. About half a dozen multi-national companies account for more than 60% of the world capacity. A number of new projects are in pipe line which include Du-Pont ventures in Taiwan, Korea and Brazil, Kronos project in USA, Tioxide projects in Canada and Australia, Projects in Saudi Arabia and Malaysia, etc. It is anticipated that by the year 1995 the installed capacity will cross 4.0 Million tonne.

20.0 Comparison of 1990 installed capacity and demand for the year 2000 indicates that there would be a short fall of about 625,000 tonne. Thus additional capacity will have to be created before the end of the century. This would mean scope for setting up of atleast 10 new projects of about 60,000 TPY capacity.

21.0 Despite the plentiful resources of titanium minerals in the country, the growth of the titanium dioxide industry in India has been constrained mainly because of the following factors:

i) Non-availability of technology.

ii) Capital intensive nature of the projects.

iii) Complex technology necessitating long gestation periods.

iv) Pollution problems.

22.0 The major technology gaps identified are as follows:

i) The Sulphate Technology available in the country is relatively old. Important developments have taken place in the sulphate technology in 1970s after emergence of the Chloride Technology as a competitor. These developments are not available indigenously.

ii) Pollution problems in sulphate technology are alleviated by manufacture of a number of by-products. The by-product technology is well developed in Japan. This is not available in India.

iii) A number of developments have taken place to overcome the pollution problems. These developments are also not available in India.

iv) There have been some lacunae in technology transfer while setting up of the Chloride-route plant in the country. As a result the technology has not been effectively transferred. As of today, the plant is manufacturing a single purpose grade of titanium dioxide. The quality of this product, according to users, has been deteriorating year by year. Thus the chloride technology as practised in the country needs to be updated and expanded.

v) Critical equipment such as Vapour Phase Oxidiser Assembly used in the chloride process is not available indigenously. This being specialised equipment is not readily available even from abroad. Hence indigenous development work is essential to develop capability in the manufacture of this equipment. This will call for a very sound knowledge of chloride technology itself.

23.0 CONCLUSIONS

23.1 India has a wealth of titanium minerals with very low ratio of resource-to-utilisation. A sound titanium dioxide industry is essential to ensure optimum utilisation of these resources as well as to develop a vibrant industry in the field of this strategic mineral.

23.2 Although some technology base is available in the country for both sulphate and chloride processes of titanium dioxide pigment manufacture, additional imports of know-how and technology are considered essential to update the existing sulphate and chloride technologies in the country.

23.3 The Indian raw materials may be upgraded to synthetic rutile or titania slag before being exported to fetch better returns. Presently synthetic rutile is being manufactured in the country by IRE, KMML and three other private companies. Another major project is likely to be set up for manufacture of synthetic rutile. However there is no project to manufacture titanium slag which can be used for sulphate process, chloride process and also for manufacture of titanium sponge. This gap needs to be bridged at the earliest.

Similarly research and development in the field of environment friendly process for upgrading ilmenite (viz., Becher Process) needs to be given priority. The process will find ready acceptance to replace Benelite-Woodall process being used for manufacture of synthetic rutile since the latter is very energy intensive.

23.4 The titanium dioxide industry is growing world wide. A number of new projects are on the ground. There is scope for another 10 major projects worldwide before the end of this century. Considering the wealth of mineral and technology resources we have, we must ensure a due share of this global expansion of titanium dioxide capacity for India.

23.5 As mentioned in the Report, there is scope for setting up of a new chloride route project of about 60,000 TPY capacity on the basis of indigenous demand-supply gap alone. This is on the assumption that atleast two sulphate route projects of 15,000 TPY capacity shall be set up before the end of the decade. It has to be reckoned that titanium dioxide is a product which has to be sold basically in the international market in competition with multi-nationals. Thus only a well planned technologically and financially sound project will succeed. The advantages under the Indian environment are ready availability of good quality feedstock, low labour cost and less stringent pollution laws.

The disadvantages are lack of technology, high power cost and uncertain power availability.

23.6 Sound base is available in the country for manufacture of equipment required in the sulphate or chloride processes. This base should be further strengthened by developing data and theoretical conceptual models for critical operations such as vapour phase oxidation, plasma oxidation, surface chemistry of titanium dioxide particles etc.

23.7 The existing titanium dioxide plant in the country do not seem to be paying adequate attention to pollution aspects. Necessary awareness in this regard has to be created. The current practice of dumping waste acid and other products into the sea may be stopped.

23.8 Similarly, the existing units, probably because they are in sellers' market, have not paid due attention to R&D to improve process and to development of new grades required by user industries. The user industry is not fully satisfied with indigenous product quality. Immediate action on the part of the domestic titanium dioxide manufacturers is essential to improve upon, this situation.

23.9 A Research and Engineering Team (RET) be constituted to consolidate the existing indigenous expertise available, to set up a pilot cum semi-commercial plant and to enable better assimilation of imported technology so that perpetual dependence on imported technology is avoided.

The RET could co-ordinate various Research & Development Projects to be farmed out to various investigating agencies in the country.

24. RECOMMENDATIONS

After reviewing the status of titanium dioxide technology and production in the country, availability of indigenous raw materials, demand-supply situation, scope for setting up of new projects and the corresponding international scenario etc. the following recommendations are being offered with a view to develop titanium dioxide and in turn Titanium Industry in India. Since a wealth of natural resources is available in the country, it is imperative that the industry is developed to fetch better value for natural resources as well as to make a mark in the field of sophisticated, hightech and strategic Titanium Products.

24.1 Upgradation of Indigenous Technology

India has been manufacturing titanium dioxide pigment for the last 40 years. A small titanium dioxide plant has also been setup with indigenous technology though the product is not equivalent to international specifications. The chloride route plant (KMML) has been in operation for the last 7 years. Thus some base for both sulphate and chloride technologies is available. Additional inputs are needed to fulfill the following gaps:

A) **Production of Rutile:** Presently the TTP does not manufacture rutile grade although world over sulphate route plants manufacture rutile grades. The rutile grades can fetch much higher returns. A number of Indian Paint manufacturers are forced to use Anatase Grade because of non-availability of the rutile grade. Thus immediate action may be taken to develop rutile grade from indigenous anatase. The implementing agency for this development work may be TTP. It may be possible for them to get some inputs from their foreign collaborator namely M/s. Tioxide of U.K. In addition RRL, Trivandrum could also provide conceptual and laboratory experimentation support.

B) **Development of Specialised Grades:** Presently KMML manufactures only one grade of rutile. Different applications call for different grades with specific combination of properties. KMML may undertake development of different grades required by Paint Industry, Plastic Industry, etc. It is understood that know-how for the same is already available with KMML.

C) **Pollution Control:** The waste acid and other waste products generated at TTP & DCW are presently being let off into the sea.

Such a practice is unhealthy. Hence steps should be taken to tackle the pollution problem. For this purpose a suitable committee with representatives of TTP, DCW, State Pollution Control Board and other Experts in the country may be constituted to prepare a time-bound action plan to prevent further pollution and environmental damage.

D) **Development of Ultra Fine Rutile:** Ultra Fine Rutile grades are used in the manufacture of plastics to impart resistance to UVde gradation. The laboratory work on development of these grades may be taken up now since the production of plastics is growing rapidly in the country and in the coming years the plastic manufacturers will demand these grades. The laboratory work on development of these grades could be taken up by R&D section of KMML as well as by CSIR laboratories such as NCL Pune, RRL Trivandrum etc.

E) **Development of High Purity Grades:** High purity titanium dioxide has a number of important uses which have been mentioned in the Report. The laboratory work on development of high purity grades could be undertaken by organisations such as NFDC, Hyderabad, NCL, Pune, etc.

24.2 IMPORT OF TECHNOLOGY

It has been brought out in the Report that there is a clear scope for setting up of new projects for manufacture of titanium dioxide both from view point of indigenous demand supply gap as well as from view point of growth of the international market. India, as one of the major suppliers of the raw materials, cannot afford to miss this opportunity. Development of indigenous technology will take long time. Hence efforts may be made to obtain latest technology both for sulphate and chloride routes from abroad.

24.3 STRATEGIC PARTNERSHIP

An interesting alternative for indigenous development of chloride technology is, particulary because the foreign manufacturers are invariably unwilling to share their technology, to enter into partnership with some of the companies who have earlier developed this technology but abandoned their plans to implement the technology mid-way for their own reasons. Such companies include Thann & mulhouse, France, Bayers Germany, Stauffer and Cabot Corpn. USA etc. With such partners, two way collaborative R & D effort may be feasible. In this way, commercial Chloride Technology could be developed indigenously at a substantially lower cost.

24.4 NEW PRODUCTION CAPACITY

It has been shown in the Report that even after assuming that two new sulphate route projects of 15000 TPY capacity shall be set up before the end of this decade, there is scope to set up atleast one 60,000 TPY Chloride route facility to meet indigenous demand. As mentioned earlier world-wide there is scope for setting up of 10 new chloride route projects of about 60,000-80,000 tons capacity. Considering the ready availability of raw materials in India, setting up of two chloride route projects could even be considerd so that there is substantial capacity to launch in the export market. It will not be possible to enter the export market unless there is surplus production of atleast about 50-100,000 tons. It is recommended that the Govt. may encourage private entrepreneurs who already have part of the infrastructure such as Chlor-Alkali units (who have chlorine gas as by-product) to set up Chloride Route Projects based on proven imported technology.

24.5 UPGRADATION OF RAW MATERIALS

Beach sands are presently being exclusively mined by IRE. Mineral separation is also being done by them. The ilmenite obtained is being upgraded to synthetic rutile by KMML, IRE as well as by few other private companies. However at present there is no company in India which is manufacturing Titania Slags. Use of Titania Slag will reduce the quantity of waste products by 300-400%. World over titania slag is being manufactured by 4 companies. Out of these M/s. RTZ Corpn. through corporate financial participation controls the major world production. Hence users of titania slag are looking for alternate source of supply. There is clear scope for setting up atleast one titania slag project in India. The manufacture of slag indigenously will help the present and future sulphate route plants to combat pollution and will also help in earning better foreign exchange from upgraded rawmaterials. IRE as a sole mining agency for the beach sands, could take lead in setting up of such a project preferably in joint sector.

24.6 RESEARCH AND ENGINEERING TEAM

To achieve objectives mentioned above it is desirable that a Research and Engineering Team consisting of Scientists and Engineers who have already been exposed to this field be constituted by way of nucleus group. Such a team could be constituted by deriving experts from organisations such as KMML, TTP, MECON, SIMCON, NCL, RRL (Trivandrum) etc. At the apex level, the activities of the team could be organised and monitored by DSIR.

24.7 R & D PROJECTS

There are a number of topics on which R&D projects could be undertaken with a view to provide inputs to the existing and new industries likely to be located in the field of titanium dioxide. Some of these projects have been identified as follows :

A) Problems related to vapour phase oxidation

Vapour phase oxidation of titanium tetra chloride is a crucial step in the Chloride Route. The various problems encountered can be reduced by lowering the vapour phase oxidation temperature by selection of suitable materials and by study of alternate processes. These problems could be studied by RET with KMML as the lead institution since presently vapour phase oxidation technology is being followed at their works.

B) Direct chlorination of Ilmenite Stocks :

Technology for direct chlorination of ilmenite stock if developed will help in reducing the cost of the input stock. Presently only M/s. Du-Pont use this technology. The work on development of this technology could be undertaken jointly by KMML, IRE and RRL Trivandrum under overall responsibility of RET.

C) Use of Titania Slag as Feed Stock

If titania slags are manufactured in the country, some changes in the existing flow sheet of titanium dioxide manufacture would be necessary. Similarly pilot plant facilities will have to be developed to evaluate digestion characteristics of the slag by sulphuric acid. Such a project could be undertaken by TTP under the overall responsibility of RET since TTP already has substantial know-how in the field of slag digestion. Since some Titania Slag units are likely to be set up in the near future, priority should be accorded in farming out such a project. Similarly, in view of imminent indigenous manufacture of slag, studies to develop chlorination technology of slag could be undertaken.

D) Product Development

As mentioned in the Report there are a number of gaps in the titanium dioxide products available in the country. These include specialised grades of rutile for Paint, Plastic and other Industries, Microfine Rutile grades for Plastic Industry, Conversion of Anatase to Rutile in Sulphate process, etc. Projects for undertaking this product development could be undertaken by R&D Divisions of KMML and TTP in consultation with RRL (Trivandrum).