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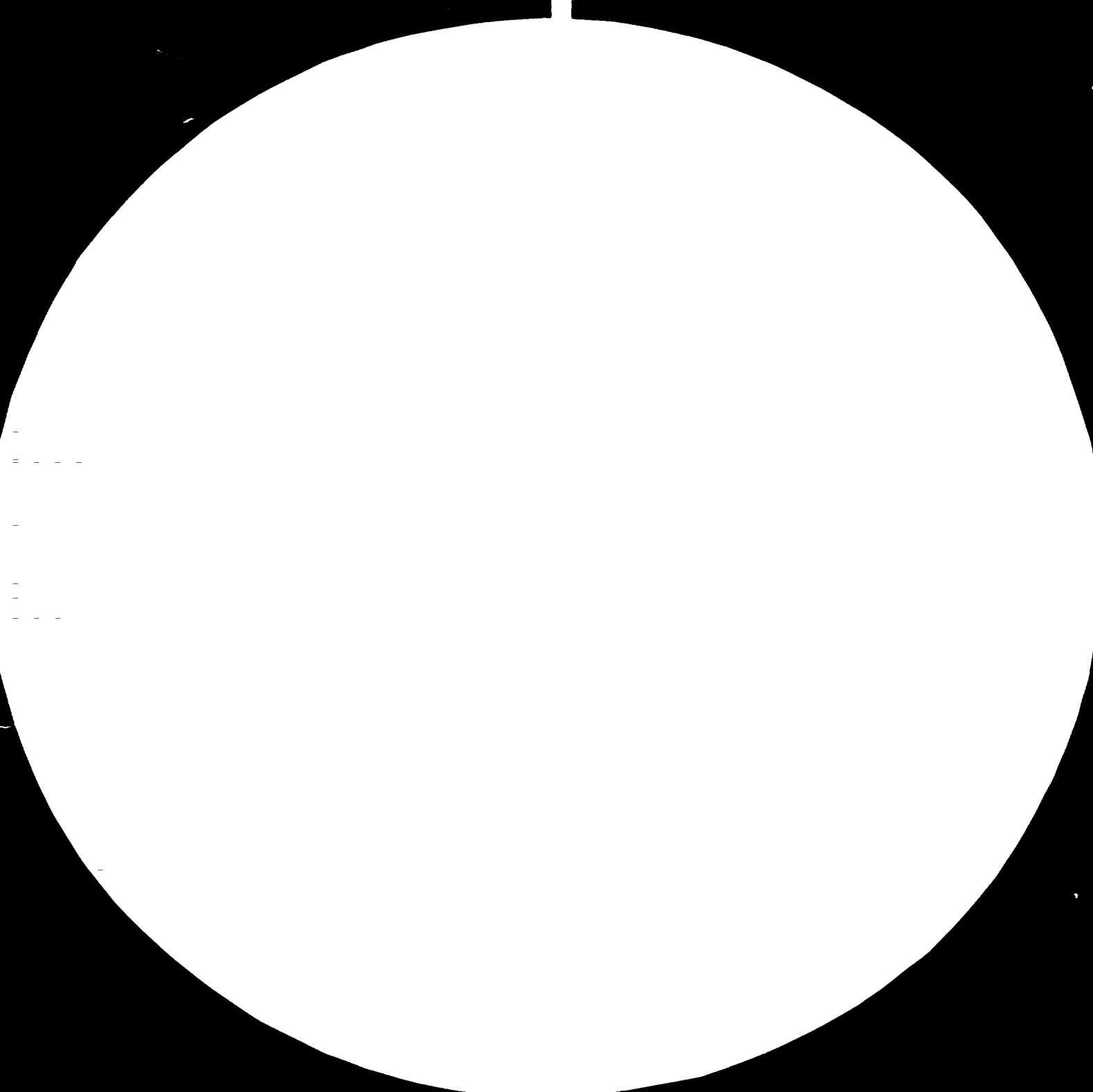
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ASSISTANCE  
TO  
CEYLON MINERAL SANDS CORPORATION:  
PROCESSING OF ILLITE SANDS  
SRL/78/031  
SRI LANKA

(R) Technical report:  
Titanium dioxide and synthetic rutile production

Prepared for the Government of Sri Lanka  
by the United Nations Industrial Development Organization,  
executing agency for the United Nations Development Programme

001..

Based on the work of Somo T. Wilka, consultant  
in titanium dioxide and synthetic rutile production

United Nations Industrial Development Organization  
Vienna

This report has not been cleared with the United Nations Industrial Development Organization which does not, therefore, necessarily share the views presented.

ABSTRACT

In the consultant's opinion, titanium dioxide pigments and/or synthetic rutile production from ilmenite sands should be established in Sri Lanka. Preference should be given to pigment manufacture provided that an interested and qualified foreign partner can be found to form a joint venture.

It is suggested that the sulphate process be used for pigment production. Since this involves a sulphuric acid plant being built, the process should be integrated with other heavy chemical process industries, to be developed within a common master plan. The most important of these will be fertilizer production.

Key words: 1) titanium dioxide pigment, 2) synthetic rutile, 3) upgraded ilmenite, 4) sulphuric acid, 5) phosphate fertilizers, 6) process integration

- 1) - пигмент, краситель, сыпучая краска (диоксид титана)
- 2) синтетический рutil (содержит ~~2%~~ окись титана)
- 3) upgraded илменит (титанистый железняк)
- 4) - серная кислота
- 5) производство удобрений.

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## INTRODUCTION

The present report covers the duties performed by the writer in the capacity of Consultant in Titanium Dioxide and Synthetic Rutile Production as a part of the Project DP/SRL/78/031, "Assistance to Ceylon Mineral Sands Corporation: Processing of Ilmenite Sands". The purpose of project is to improve and upgrade present mineral sands mining and beneficiation operations of Ceylon Mineral Sands Corporation (CMSC), and to evaluate the feasibility of introducing new processes for the conversion of ilmenite sands to more valuable intermediate products. Specifically, the expert was expected to carry out technical and economic studies to determine the feasibility of economically entering titanium dioxide and/or synthetic rutile production in the country, including definition of basic conditions, investment costs, market projections, etc., required in these studies.

It was soon found that the studies should be mainly concentrated on technical matters, because no reliable information has ever been given by the respective producers specifying investment or operational costs (in the fields of titanium dioxide pigments or synthetic rutile). Furthermore, especially in the pigments field, both investment and operational costs are largely dependent of the production program: which pigment grades are to be produced, and to what quality requirements (anatase vs. rutile type, base vs. treated pigments, standard vs. premium grades, etc.).

Therefore, this report deals rather extensively with different procedures for making the products, and the properties of pigment to be achieved. The purpose is to help the decision-makers by providing them with background information that in many cases is very hard to find from literary sources, or is not made public at all. However, economic facts have also been presented in the report whenever the writer considers them relevant and reliable.

The manufacture of titanium dioxide pigments is closely connected with environmental implications. Therefore, these have been considered very important. In many cases, especially during the last decade, environmental factors have been decisive in choosing both the manufacturing process and the location of the plant. The opinions presented in this report are based largely on the writer's own experience gained during his active work



in titanium dioxide pigments production.

The present writer soon realized that pigment production cannot be considered separately from the country's other heavy chemical process industry, especially if the sulphate route (for making titanium dioxide pigments) is to be selected. Therefore, with the approval of the Chairman & Managing Director of CMCC, he expanded the scope of his work to include a proposal for an integrated sulphuric acid, ammonia, and fertilizer industry. This led to a contact with a foreign company unique in covering all important heavy chemical process industries inclusive of titanium dioxide pigments production. Negotiations were held in Colombo and Pulmeddai (15.-21.11.80), during which the writer provided advice and assistance to the Government.

The present writer is not going to repeat the findings and facts concerning the infrastructure of the present ilmenite factory site, because they already appear in a previous Technical Report (Titanium slag production, by W. Harrach). Further, because slag production is not in his programme, he is not going to comment on the recommendations of Mr. Harrach, or the report except that he does not share the sentiments of expressions such as "handling dangerous chemical compounds" or "sophisticated chemical equipment" or agree that ordinary water treatment is a "sophisticated process".

As far as any recommendations for the sites of future industrial units, and transportation facilities are concerned, it has become apparent that the present writer's knowledge of local conditions and government politics is too limited for giving competent advice in this respect.

## I. RECOMMENDATIONS

1. It is recommended to establish a sulphate process titanium dioxide pigment plant in co-operation with a qualified foreign company, preferably on a joint venture basis. The recommended capacity, 67,000 tons/a corresponds to the planned capacity of the proposed wet magnetic separation plant, 150,000 tons/a. Local conditions provide an opportunity for free discharge of waste acid without detrimental environmental effects.
2. If the capacity presented above is considered too high at present from a marketing point of view, but feasible in the future, a staged development program should be worked out, and as much of the excess ilmenite exported in the meantime as is possible.
3. If a lower capacity is definitely decided on, for instance, 33,000 tons/a of pigment based on 75,000 tons/a of ilmenite, synthetic rutile should be manufactured from the remaining ore. This plant can be licensed, or built by buying know-how.
4. If no interested and qualified partner for the pigment production is available, the previous recommendation (3.) will apply for the whole amount of ilmenite produced. In this case, the Benilite company should be contacted at the first place because of its experience in the chemical upgrading field.
5. Provided that titanium dioxide pigment production is to start as recommended under (1.), (2.) or (3.), a sulphuric acid plant should be set up. It must be integrated with the pigment plant to make use of the excess energy produced by the acid plant.
6. Taking into account the country's need to establish heavy chemical process industries, the capacity of the sulphuric acid plant must be high enough to cover all demands that can be foreseen, especially those by the pigment and fertilizer industries, which should be integrated. This could provide an opportunity to use at least a part of the waste acid from the sulphate process in fertilizer production.

7. It is recommended that in the negotiations with prospective foreign partners their experience and competence in the widest possible field in integrated process industries should be decisive. In an ideal case, the successful company will be able to present sufficient references covering the whole area of the heavy chemical process industries, and will be ready to co-operate over the full range of the integrated industries.
8. It is recommended that a very thorough study be undertaken as to how to provide the process industries with a sufficient amount of water meeting the qualifications set for different units. The present water treatment plant that is actually a pumping station must be equipped with proper treatment facilities. Flocculation is required for pre-treatment, thereafter continuous clarifiers based on flotation and/or settling, and finally filtering by means of rapid sand filters. At least the household and drinking water must be properly chlorinated.
9. It is recommended that a possibility to set up an ammonia plant in the vicinity of the coming oil refinery at Trincomalee should be examined in co-operation with Rizaco International, and the joint venture partner for the pigment and fertilizer industries. At the same time, it should be made clear whether there are possibilities to get sulphur from this particular oil refinery as well as from the Ceylon Petroleum Corporation refinery at Sapugaskanda.
10. A careful examination is necessary concerning the location of the industrial units recommended above as well as existing and future transportation facilities.

## II. CONCLUSIONS

### A. Alternatives for future development

In the present writer's opinion, there are three alternatives for planning further processing of the ilmenite. It is assumed that the ilmenite output will be 150,000 tons/a having a mean content of 53 %  $TiO_2$ .

Alternative 1. Production of titanium dioxide pigments by the sulphate process, and using the whole amount of ilmenite for the purpose. Hence, the capacity of the pigment plant would be about 67,000 tons/a. The production could start at a lower capacity, excess ilmenite being exported.

Alternative 2. Production of titanium dioxide pigments as above but using only a part of the ilmenite, for instance, one-half, in which case the capacity of the plant would be about 33,000 tons/a. The rest would be upgraded to synthetic rutile by chemical means.

Alternative 3. Production of synthetic rutile only.

Alternatives for manufacturing the pigments by the chloride process, and upgraded ilmenite in the slag form are excluded. In the writer's opinion these processes do not fit into a master plan for the country's heavy chemical process industries where the production of sulphuric acid plays a predominant role.

In the writer's opinion, the Alternative 1. is recommended. Next comes the Alternative 2., but only if it is concluded that there does not exist and most probably will not exist sufficient demand for titanium dioxide pigments at a capacity level of 67,000 tons/a. In the following discussion, both alternatives will be kept in mind. The Alternative 3. is recommendable only if no foreign partner can be found for the pigment production.

### B. Foreign co-operation

It is evident that in order to succeed in the titanium dioxide pigments production foreign expertise in some form is definitely needed. The production involves an immense amount of experience obtained by intensive research and development work, and, it must be admitted, by trial-and-error during the relatively short existence of the pigment industry. In general, the following alternatives exist:

Alternative 1. Purchasing the know-how at a lump sum, or having the process licensed. Performance guarantees usually exist but tend to be rather limited.

Alternative 2. Establishing the factory on a turn-key basis including performance guarantees. These are, however, limited to a certain period of time for instance one year. Guarantees do not, as a rule, take into account the need of continuous development of existing pigment grades, and of course not any new grades.

Alternative 3. Forming a joint venture with a reputable foreign company well established in the field.

Alternative 4. Basing the production totally on foreign investment.

Here, the Alternative 4. has been mentioned for the sake of completeness only, and will not be discussed further.

Of the remaining alternatives the present writer prefers the Alternative 3., a joint venture, provided that:

- a) The prospective foreign company is well known in the world market, and its products competitive regarding both quality and price, the former being more important of these two.
- b) The company is specialized in export trade, and possesses a global marketing system that covers practically all pigment importing countries.
- c) The company has created an efficient sales service system, and has established full confidence amongst international clients in this respect.
- d) The company is known to be research and development minded - actually a prerequisite for any success in the field - and it must have well-equipped laboratories for the purpose.
- e) The status of the company is financially sound, and it is able to meet the investment and other costs as agreed upon.

Of the provisions presented above, the a) is a basic one. At the present time, it is extremely difficult, if not impossible, for a new unknown producer to penetrate the international pigment market. Therefore, it is easy to understand that all recent titanium dioxide production units are connected with well-known parent or joint companies, and usually carry their trade mark on the products.

Further, creating an effective global marketing system is a very costly and time-consuming business. The same applies to sales service activities, a very important part of the sales promotion. And last but not least,

only extensive research and development work ensures success in creating new or improved pigment grades, as needed, in hard competition. This can be performed in modern and well-established research laboratories and pilot plant installations only by a highly competent staff. Within a joint venture, all R & D work can be carried out in the partner's central laboratory, and process control laboratories only are needed at the factory site.

C. Sulphate process pigment plant located at Pulmoddai

Raw materials

Raw materials for manufacturing the titanium dioxide pigments are sulphuric acid and ilmenite plus a number of additional chemicals. The writer suggests that sulphuric acid will be produced at an integrated plant. The matter will be discussed more detailed in section E. of the present chapter.

Process water

Both the quantity and the quality of the process water are critical. Main problem is to store enough water during the rainy monsoon period. At present, the process water used in the ilmenite factory is taken from the Yan Oya river that at the end of September this year appeared to be nearly dry. The flow of the river is regulated by several dams upcountry. In the writer's opinion the present conditions do not seem to be favourable for new installations to be established, because even the present ones have been suffering from the shortage of water. It is suggested that possibilities to build a dam at the mouth of the Eya Oya river should be examined so as to form a lake separated from the sea. The same procedure should be examined at the mouths of other rivers and lagoons located at the nearby area.

As far as the quality of water is concerned, daily analyses during the period of 14.10.-11.11.1980 have shown values for the chloride ion from a minimum of 291 mg/l to a maximum of 666 mg/l, the hardness being from 332 to 706 mg of  $\text{CaCO}_3$ /l, respectively. The rainfall, however, has been unusually low, and the effect of the monsoon period appears first on 18.11.1980: chloride 244 mg/l, and hardness 279 mg/l, on 26.11.1980, 163 and 254 mg/l, respectively.

## Effluents

Disposal of the waste acid and iron sulphate is the most critical environmental problem, as discussed in detail elsewhere in this report (p.37). In the U.S. it has been the main reason for the progress of the energy intensive and more costly chloride process.

It has been commonly accepted that a free discharge of the effluents, whenever feasible, is the most economic solution. As stated by the writer (p.38), under certain conditions this type of disposal is certainly possible, and in his opinion such conditions exist at Pulmoddai. The continental shelf there is comparatively narrow, at a certain point north of Arisimalai about 10 km only, after which the depth of the sea rapidly increases to 300 m. The writer is assured that if the effluents are disposed of, say, at a distance of 11 km from the coast at the place in question, no harm whatsoever will result. Another possibility could be its use, at least partially, in integrated fertilizer production. This matter is discussed in a separate chapter.

### D. The production of synthetic rutile

As stated under A. in this chapter, the writer does not favour the production of synthetic rutile, if the titanium dioxide pigments production can be realized. The market price of the product is not very attractive, and the competition heavy, especially after the establishment of the Richards Bay operations. On the other hand, the process itself is straightforward, and the need for continuous research and development less demanding.

The Benilite process enjoys the widest popularity for the time being. It can be easily integrated with sulphate process operations as shown in the Preliminary plan (p. 14). There is no doubt that this process can be brought into operation by purchasing the necessary know-how, or by licensing. Especially if there is an integrated sulphate process for pigment production carried out as a joint venture, the synthetic rutile process can be realized on know-how basis.

E. Pigment production and other chemical-process industries

In the present writer's opinion, the production of titanium dioxide pigments by the sulphate process is closely connected with the development of the country's other heavy chemical industry. As is well known, sulphuric acid plays a key role in many chemical processes, and the sulphate process for manufacturing the pigments needs a sulphuric acid plant.

On the other hand, there is a very valuable phosphate rock deposit in the country, at Eppawala, with a content of 33 to 36 %  $P_2O_5$ . This is comparable with the best phosphates on the international market. To obtain modern fertilizers from the apatite rock sulphuric acid is needed again.

Nowadays, phosphoric acid is produced first from the apatite by means of sulphuric acid, waste gypsum disposed of, and the acid used for making different fertilizers by adding other main or minor nutrients (nitrogen in the form of ammonia or nitrates, potassium chloride or sulphate, etc.).

Phosphoric acid may also react with the apatite producing a fertilizer very high in phosphorus. Normal superphosphate is made by using less sulphuric acid, and leaving the gypsum in the product.

The relative investment and production costs diminish with increasing capacity of the plant. According to information originating from the USSR, the following relationship exists:

| Capacity, thousand tons | Investment cost per ton (roubles) | Production cost per ton (roubles) |
|-------------------------|-----------------------------------|-----------------------------------|
| 180                     | 55.5                              | 27.4                              |
| 360                     | 47.2                              | 24.6                              |
| 2 x 360                 | 42                                | 22.45                             |

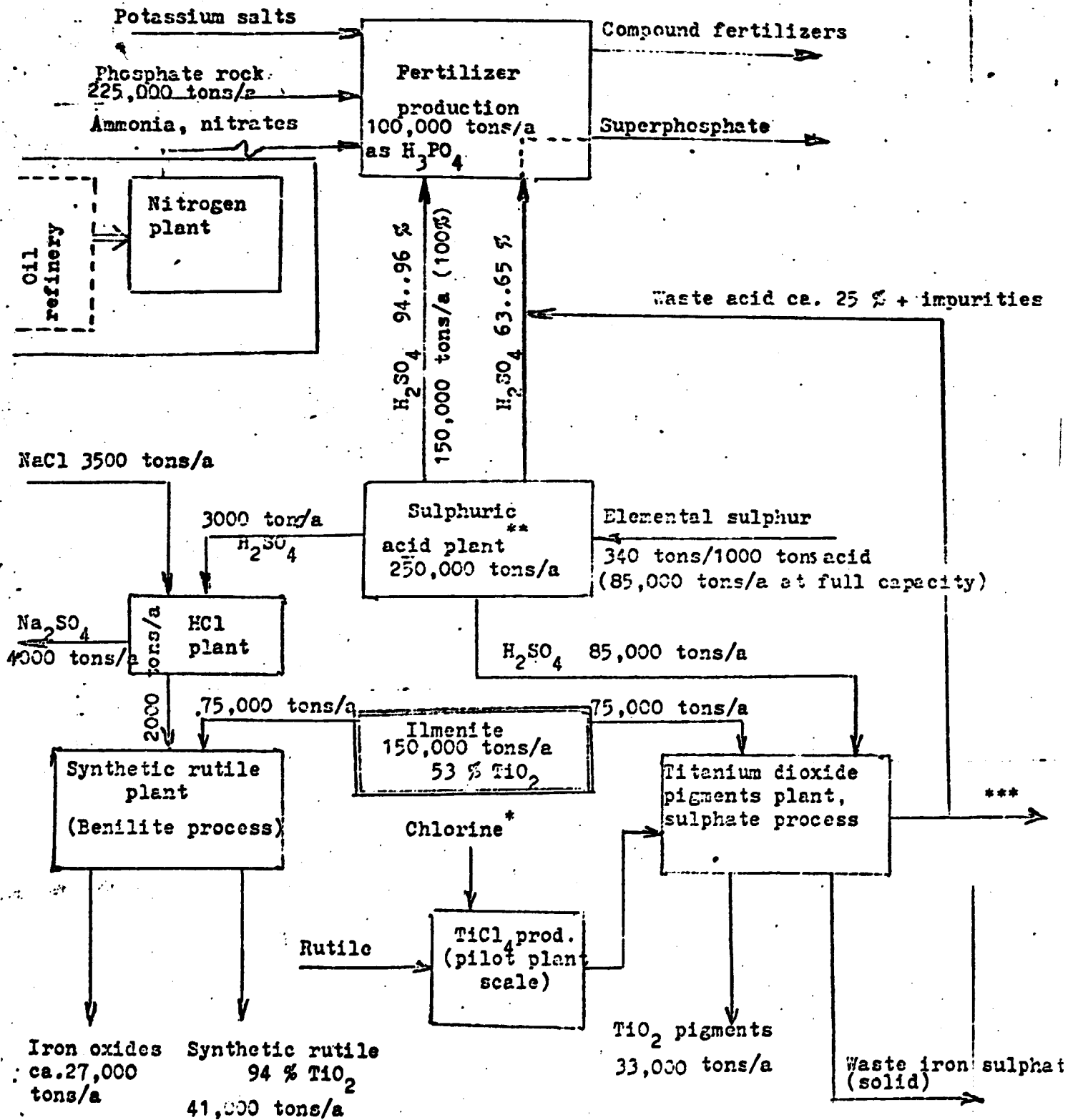
(Source: Malishkov P.S. Khim.promyslennost, 1971, No.9, 643-646)

Therefore, in the writer's opinion, the sulphuric acid plants needed for both pigment and fertilizer production should be combined, and integrated with the production of titanium dioxide pigments as shown in "Preliminary plan" on the next page. As suggested, it is possible, in principle, to use waste acid from the pigment production for the fertilizer process. However, because of impurities, mainly iron, present in the acid, its use is subject to further investigation, actually going on in the writer's research laboratory at the University of Technology, Lappeenranta, Finland. The most suitable product in this respect could very well be the ordinary superphosphate.



Figure 1. PRELIMINARY PLAN

for integrated production of titanium dioxide pigments, synthetic rutile, and fertilizers in Sri Lanka, with an approximate materials balance based on 150,000 tons/a of ilmenite, and 100,000 tons/a of  $H_3PO_4$  produced.



\* Chlorine from HCl or bought      \*\*\* Excess waste acid disposed of  
 \*\* Plant capacity depends on the fertilizer production

Seppo Wilska, UNIDO consultant, 24 October 1980  
 The plan is based on the Alternative 2. (page 9)  
 The Ishihara process (p. 43) is not excluded.

According to recent information published in local newspapers, a very large oil refinery will be set up at Trincomalee, about 60 km from Pulmoddai. As mentioned, ammonia and nitrates are needed in making compound (NPK) fertilizers. A natural location for an ammonia plant is in the vicinity of an oil refinery (or oil field, for that matter) so as to be able to make use of its gaseous effluents and other less valuable fractions as starting material. This possibility is also shown in the plan.

Although the whole production of the new U.S.-company owned refinery is intended for export only, negotiations should be carried out about using its heavy and light fuel oil in the pigment production because of the proximity of the installation.

Preferred raw material for making sulphuric acid is elemental sulphur. Depending of the quality of the crude, oil refineries produce variable amounts of sulphur as by-product. The writer suggests that this possible source of sulphur be examined from the existing national and from the coming refinery. If not sufficient or not available, the balance of sulphur can be imported from India. ?

### III. ECONOMIC ASPECTS IN UPGRADING THE ILMENITE

It is self-evident that further processing adds greatly to the value of mineral products. For example, the current market price per ton of ilmenite containing 53 % of  $TiO_2$  is about US\$ 18, i.e. US\$ 34 per ton of  $TiO_2$ . Titanium slag (Richards Bay) sells at about US\$ 159 per ton of  $TiO_2$ , and the international market price of standard grade titanium dioxide pigments varies between US\$ 1400 and 1700 per ton (all prices are given on FOB basis).

Although not comparable as such (the value of pig iron obtained from slag process has been omitted) the figures show that the country of origin certainly profits more from upgraded, and still more from final products. The great difference between the prices of intermediate vs. final products favours strongly the latter. Of course, as has been shown elsewhere in the present report, pigments production involves high investment cost, imported raw materials and energy plus higher operational costs. However, it is commonly known that this particular branch of the chemical industry is profitable provided that it is properly managed both technically and economically. Once a sufficient share of the world market has been obtained, the cash flow in foreign currency is throughout satisfactory, although foreign capital cost and imported raw materials inclusive of fuel take their share.

On the other hand, the future of upgraded ilmenites does not look very promising after the Richards Bay products entered the world market.

#### IV. ORE RESERVES AT PULMODDAI AREA AND ITS VICINITY

Regarding the ore reserves reference is made to two recent investigations. One of them is a "Report on the demarcation of the western boundary of heavy minerals at 5 % cut-off between Mullaivivu and Kuchchaveli - north-eastern coastal stretch of Sri Lanka", prepared by H.S. Ranasinghe and S. Babusukumar, Geological Survey Department, September 1979. The study covers the ilmenite resources on-shore, and although preliminary of its nature, gives a reliable estimate of the reserves in addition to those already established at the Pulmoddai area. The other, an off-shore study carried out by a foreign company using the so-called vibrocore technique added new knowledge of the location of the deposits. It did not, however, give promises for deposits deeper in the seabed. For details the reader is referred to two extensive reports prepared by the company, filed at the CMSC Office.

As a whole, it can be concluded that the mineral sands deposits within reasonable geographic limits from the present ilmenite factory site justify the expansion of the present capacity to at least 150,000 tons/a of ilmenite. Hence, decisions for upgrading the ilmenite based on this yearly output are sound, and the supply of the raw materials is guaranteed for a sufficient long period, according to Harrach (*loc.cit.*) for more than 50 years.

The Table on the next page has been taken from the Geological Survey Report mentioned above. It is self-explanatory and shows the situation according to the most recent study on-shore.

TABLE 1. Estimate of tonnages of heavy mineral sands (tentative)

| Location of Deposit   | No. of Holes | No. of Pits | Area of Deposit (in acres) | Average Heavy Mineral % | Average thickness (feet) | Tonnages (tentative) (in million tons) |
|---|--------------|-------------|----------------------------|-------------------------|--------------------------|--|
| (a) THEVIALLEU  | 33           | 07          | 650.0                      | 16.03                   | 7.21                     | 1.78                                   |
| (b) PUDAVAZADDU   | 30           | 02          | 1475.3                     | 17.69                   | 6.89                     | 4.51                                   |
| (c) NAYANU  | 15           | 03          | 316.4                      | 18.35                   | 7.75                     | 1.09                                   |
| (d)* The remaining stretch of coastline in the area investigated upto the 5% heavy mineral cut-off boundary | 56           | 05          | 3578.1                     | 10.30                   | 6.41                     | 5.74                                   |

\* This excludes deposits (a), (b) & (c) and the stretch between Arisimalai and Kokkilai.

Note - The average weight of a cubic foot of heavy minerals was taken as 125 lbs.

Source: Report on the demarcation of the western boundary of heavy minerals at 5 % cut-off between Mullaitivu and Kuchchaveli - north-eastern coastal stretch of Sri Lanka. N.S. Ranasinghe and S. Boousukumar, Geological Survey Department, Colombo, 1979.

\*\* Actual Pulmoddai deposit, estimated to be 4.5 m tons (1971)

## V. TITANIUM DIOXIDE PIGMENTS AND THEIR PRODUCTION

### A. Short introduction to pigment physics and chemistry

There is no clear and commonly accepted definition of a pigment, and sometimes one does not even differentiate between pigments and dyestuffs, the latter actually being organic compounds, as a rule soluble in the media to be coloured. Actually, the pigments form a rather inhomogeneous group of finely ground, usually inorganic solid particles having colouring and/or hiding properties when applied onto surfaces or as ingredients to different media. Here again, paint and paper manufacturers use different terms. In the paper industry, all solid materials used to increase the opacity of the paper are called pigments, while in the paint technology ingredients such as talc, clay, micronized limestone are merely extenders. To be called a pigment the material must either have a high refractive index or possess colouring properties. Typical paint extenders are colourless (white) very finely ground solids having a low refractive index.

The impression of colour depends on the spectrum of the incident light, and its behaviour on the surface illuminated. An absolutely white pigment does not absorb different wavelengths of the light selectively (in fact, no absorption should occur), the colours again are caused by a selective absorption of the spectrum. Hence, a white pigment appears white (colourless) at daylight, while at coloured light the surface reflects exactly the colour of the incident light.

The second important property is the hiding or covering power. A paint film of less than 0.1 mm thickness is able to completely hide a surface provided that the pigment used in the paint is effective enough. For economy reasons a part of the pigment(s) is usually replaced by suitable extenders. In the same way, a pigment or extender added to paper increases its opacity. Hiding power of a surface coating, in most cases paint, is caused almost exclusively by the pigments and extenders used as a part of the paint formula, coloured or white. Binders and organic dyestuffs do not produce hiding but are more or less transparent.

Hiding power of white pigments is based on an optical phenomenon called scattering. Scattering results from a very high number of subsequent reflectance and refraction steps of the incident light, caused by very small pigment particles. The refraction phenomenon is the decisive of these two, and therefore the higher the refractive index, the better the hiding power of the pigment or extender. As the refraction occurs at the pigment/binder

interface, the difference of the corresponding indices is actually determining.

The refractive indices of some interesting substances are shown in Table 2.

Table 2. Refractive Index Values

| Substance         | Refractive Index |
|-------------------|------------------|
| Air               | 1.00             |
| Water             | 1.33             |
| Linseed Oil       | 1.48             |
| Barium Sulphate   | 1.64 - 1.65      |
| Calcium Carbonate | 1.55 - 1.68      |
| Silica            | 1.54 - 1.56      |
| Zinc Oxide        | 2.0              |
| Zinc Sulphide     | 2.36 - 2.38      |
| Diamond           | 2.42             |
| Titanium Dioxide: |                  |
| Anatase           | 2.49 - 2.55      |
| Rutile            | 2.61 - 2.90      |

The Table is self-explanatory. Of all white pigments, titanium dioxide has by far the highest refractive index. The difference of the indices of typical extenders barium sulphate, calcium carbonate, and silica on one hand, and the classical binder linseed oil on the other hand is so small that no effective hiding can be expected. It is interesting to note further that even the lowest index value of the anatase type of titanium dioxide pigment is higher than that of diamond.

Particle size is another important factor that influences the hiding power. It has been shown theoretically, and also confirmed by practical experience that the optimum particle size for titanium dioxide pigment lies between 0.3 and 0.5  $\mu$ m. The size distribution is of great importance, it must be as narrow as possible, and oversize particles must be completely absent.

High refractive index and nearly complete whiteness are the basic properties of titanium dioxide particles. It is the task of the manufacturer to produce pigments that make maximum use of these properties given by the nature.

Unfortunately, nature has provided the titanium dioxide particle with an inconvenient property. It is an effective photocatalyst, able to promote

certain chemical reactions when under the influence of light especially at short wavelengths. Anatase is more effective in this respect, and the anatase type pigment cannot be used in outdoor paints because of rapid deterioration of the binder. Outdoor paint pigments are without exception those of the rutile type, and their photocatalytic tendency has been minimized by means of appropriate surface treatment.

The most important properties of the titanium dioxide pigment are brightness, whiteness, hiding power, weathering resistance, tone and undertone, dispersibility in different solvent or water based binders, and the gloss of resulting paint surfaces. However, all these properties cannot be obtained, improved, and upheld simultaneously in the production. Therefore different pigment grades must be produced for different applications, for instance, solvent based paints, emulsion paints, baking glossy enamels, plastics, paper coatings and laminates, etc. This results in a selection of normally up to twenty different pigment grades. Very active R & D work is needed to develop new grades, and to keep the quality of the products competitive in a rather tight world market.



B. The titanium dioxide pigment process

Base pigment production

The Chloride and Sulphate processes represent alternative means of extracting essentially pure titanium dioxide from the titanium bearing ores, slags or other beneficiates, and at the same time providing a base pigment within very narrow quality specifications. There are two main modifications of the base pigment representing two polymorphic forms of the titanium dioxide crystal, namely anatase and rutile. As a rule, the anatase type pigment, used mainly in the paper industry, does not require other improvement than dry milling, and in some cases air classification, whereas almost all rutile pigment grades undergo a series of different improvement operations frequently called coating or after-treatment of the pigment.

The sulphate process

In the sulphate process the starting material is ground ilmenite, ilmenite beneficiate, or slags that contain, in addition to their main components titanium and iron, many minor elements such as vanadium, chromium, phosphorus, manganese, aluminum, magnesium, etc. Of these, especially the elements that may affect the colour (tone) of the white titanium dioxide pigment are problematic, chromium and niobium being the most harmful. At the first step, finely ground mineral is digested with concentrated sulphuric acid in huge reactors. The reaction is initiated by adding a small amount of water or diluted acid. The liberated heat of dilution of the acid is able to start the strongly exothermic reaction that proceeds very rapidly, and generates large amount of steam in few minutes. Because of the violent reaction small droplets of acid are carried out with the steam. Hence, to protect the environment, efficient gas washers are installed to separate the acidic mist.

During the reaction the mineral components form corresponding sulphates: titanyl sulphate  $TiOSO_4$  and iron sulphates  $FeSO_4$  or  $Fe_2(SO_4)_3$ . Most minor components react with the acid as well. Finally a solid cake is formed. The cake is allowed to mature as to ensure a complete reaction, and thereafter the soluble salts are leached out by using cold water together with recycled acid from the process. Batchwise operation has been replaced by a continuous one

in some more recent installations.

Next, trivalent iron is reduced to the divalent form as to eliminate the strong adsorbing tendency of the ferric ion onto the surface of the titanium hydrolysate at a later stage of the process. The reduction is usually made by means of scrap iron. Recently an electrolytic reduction has been applied as well. The latter eliminates the risk of getting harmful impurities occasionally present in scrap iron (Cr, Mn, Ni) but tends to be more expensive. A small amount of  $Ti^{4+}$  is reduced to  $Ti^{3+}$  to ensure that all iron will remain in divalent form. For this reason the solution turns from black to blueish after the reduction.

A part of the ilmenite remains undissolved and is separated by settling and filtering. The addition of suitable flocculants causes an effective settling and the resulting sludge is pumped to a filtering and washing unit, usually a drum filter. Before dumping the sludge is neutralized by means of lime. The acidic filtrate is recycled.

The overflow from the clarification is cooled until a considerable amount of the dissolved iron crystallizes from the solution. The crystals are separated and washed by continuous centrifugation.  $FeSO_4 \cdot 7 H_2O$  (sometimes called "copperas") so formed is disposed of in solid form. A minor amount can usually be marketed mainly for waste water treatment purposes, but otherwise it is typical waste material. No economic solution for its use has been found so far, the only exception being the German Bayer Co. that produces different grades of iron oxide pigments using a technology of their own.

Before the next step, vacuum evaporation, the solution is filtered to remove all solid particles. Drum filters and suitable filter aid materials are commonly used for this purpose. The vacuum evaporation is effected by means of indirect steam. The concentration of the liquid is followed closely by density measurements, because the specification in this respect varies with the pigment grade to be produced.

Next step, hydrolysis, is very critical regarding the quality of pigment. After adding seed crystals or other nuclei the concentrated liquor is heated by indirect steam to effect the hydrolysis of the titanyl ion to corresponding hydrated titanium, the composition of which cannot be presented by an exact chemical formula. Several additions of water are made during the hydrolysis step in order to control it. The nuclei are usually prepared from aqueous  $TiCl_4$  solution by neutralizing it with sodium hydroxide solution. The procedure is again very delicate and specific for different pigment grades.

The precipitate from the hydrolysis is collected by filtration. Resulting waste acid that still contains considerable amount of iron can be partly recycled, but to avoid the accumulation of minor impurities most of it is discharged.

After the first filtration step the cake is slurried in water, the resulting slurry is filtered, slurried again and washed until the purity of the filtrate meets very strict specifications. The  $Ti^{3+}$  ion originating from the reduction step has by now disappeared and a new reduction step is necessary to guard the hydrolysate against the  $Fe^{3+}$  ion. There are two different methods: the use of zinc powder, or an electrolytic reduction. In both cases an addition of pure sulphuric acid is made for an effective desorption of unwanted ions.

Before the next, calcination step the hydrolysate is pretreated by adding certain chemicals. The purpose is to aid and control the pigment particle formation that occurs in the rotary kiln used for calcination. Different pigment grades again require different pretreatment. Typical rotary kilns used have a capacity of 100 tons/d or more, the temperature at the outlet being near  $1,000^{\circ}C$ . The feed loses first its moisture, thereafter sulphuric acid still adsorbed in the cake, and finally different sulphates present decompose and exit gaseous  $SO_3$  and  $SO_2$ . The kiln is heated directly by light fuel oil (diesel oil grade) or gas. Heavy fuel oil and solid fuels cannot be used because of impurities in the ash.

The calcination process is controlled by X-ray diffraction analysis, especially the anatase content in the rutile type of pigment must be minimized. Samples for this purpose are taken usually every hour. The most important variables of this unit process are the calcination temperature and the rotation speed that controls the residence time.

During calcination the primary crystals, either rutile or anatase, grow until they reach the specified mean particle size. The particles tend to sinter as to form aggregates that must be broken by dry grinding after the calcination. The sizes and shapes of the particles, as they appear in electron photomicrographs are characteristic of the main grades of titanium dioxide base pigments. These micrographs are used for the determination of particle size distribution, an important pigment property.

A flow diagram for the sulphate process to base pigment is shown in Figure 2., and a block diagram indicating, a.o., the significant energy inputs in Figure 3.

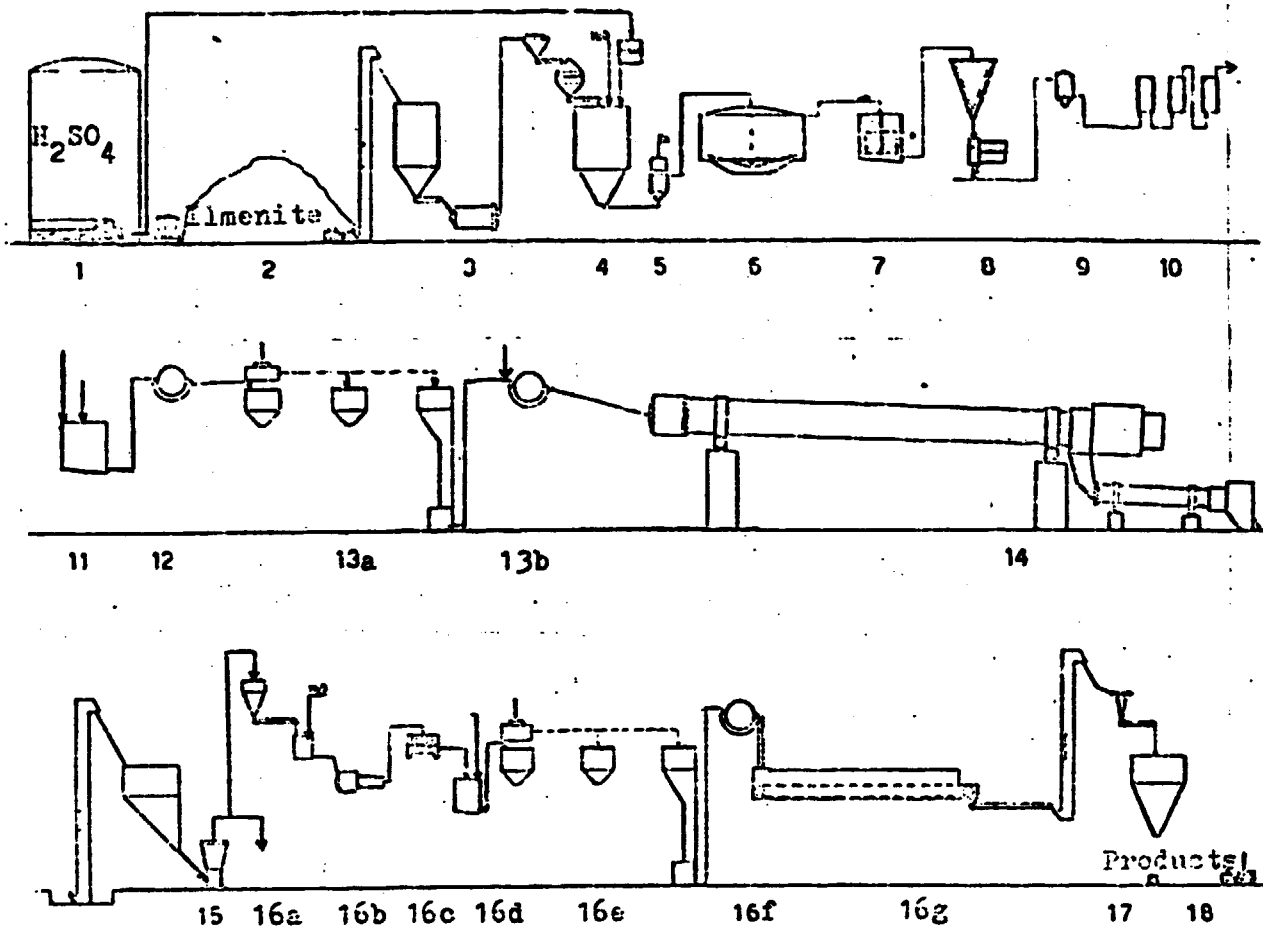


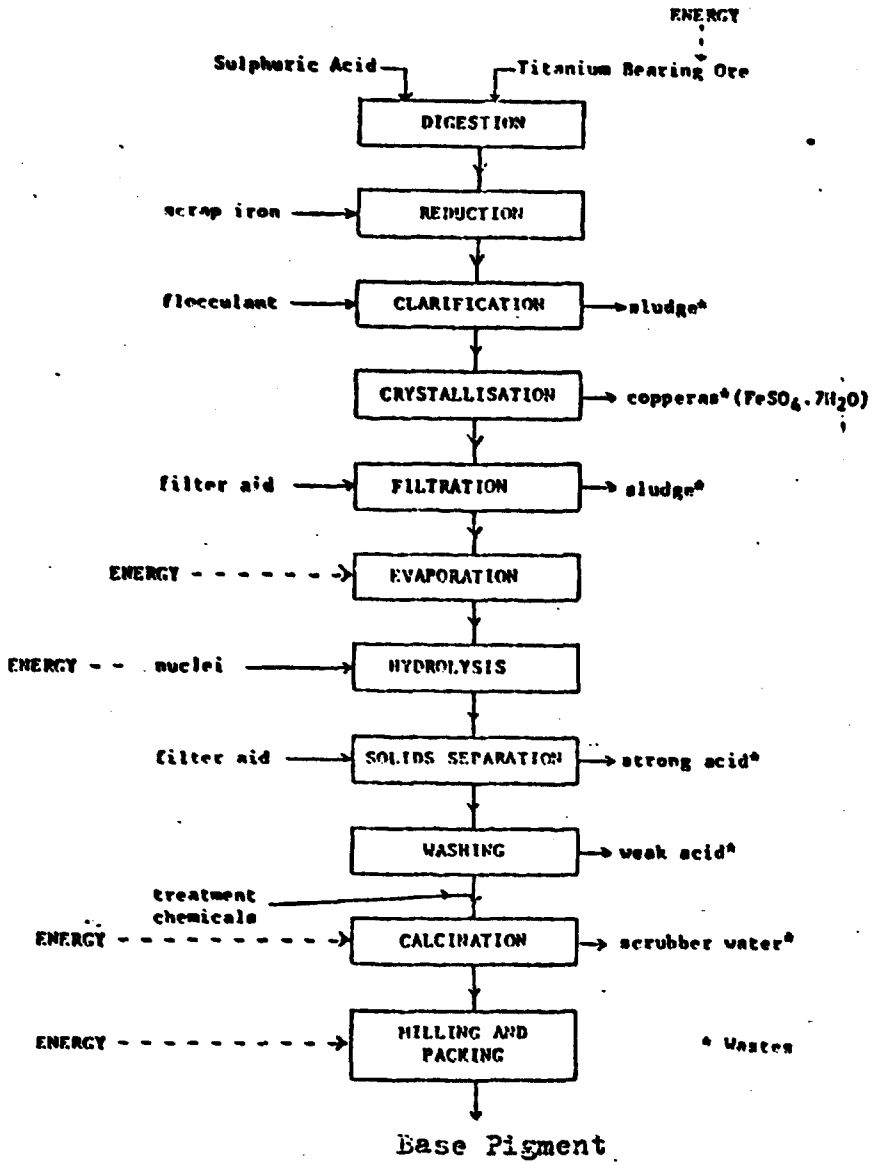
Figure 2.

FLWSHEET OF THE SULPHATE PROCESS

LEGEND:

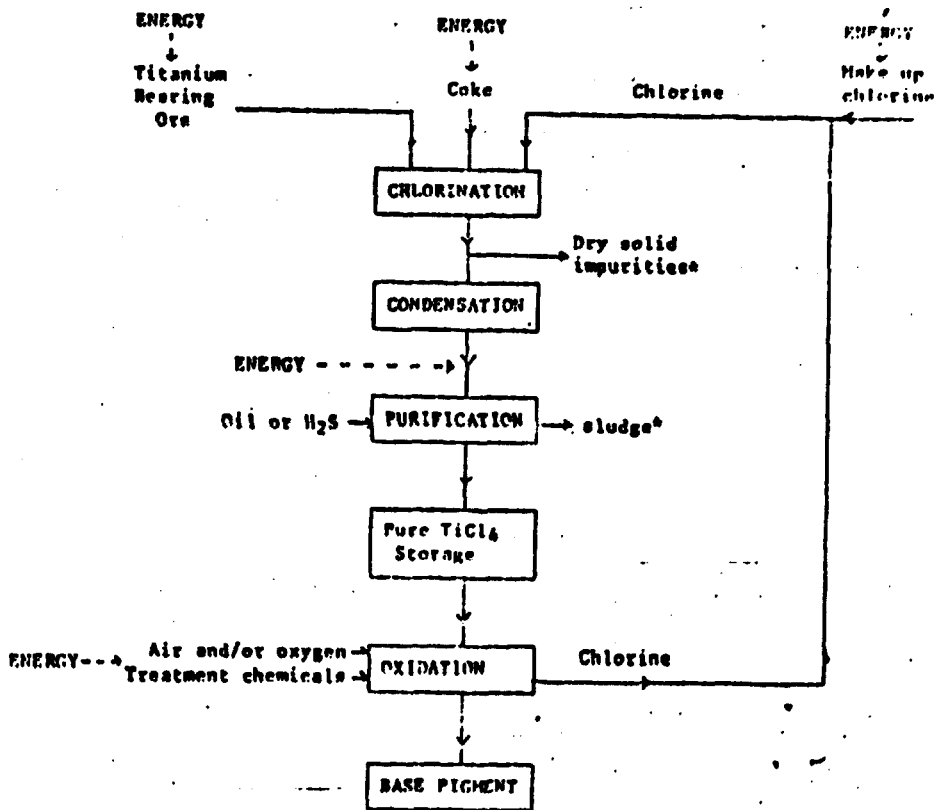
- |     |                           |     |   |
|-----|---------------------------|-----|---|
| 1,2 | Raw materials             | 14  | Calcination   |
| 3   | Grinding                  | 15  | Dry grinding (base pigment, anatase, untreated rutile grades) |
| 4   | Reactor                   | 16a | Slurrying (base pigment, above)                               |
| 5   | Reduction                 | 16b | Wet grinding  |
| 6   | Clarifier                 | 16c | Classification  |
| 7   | Crystallization           | 16d | Coating process   |
| 8   | Centrifugation            | 16e | Washing   |
| 9   | Filtration                | 16f | Filtration  |
| 10  | Vacuum evaporation        | 16g | Drying  |
| 11  | Hydrolysis, seeding       | 17  | Micronizing   |
| 12  | Filtration                | 18  | Packing and transportation                                    |
| 13a | Washing, acidic reduction |     |   |
| 13b | Filtration, modifying     |     |   |

Figure 3. Sulphate Process Block Diagram



\* Wastes

Figure 4. Chloride Process Block Diagram



\* Wastes

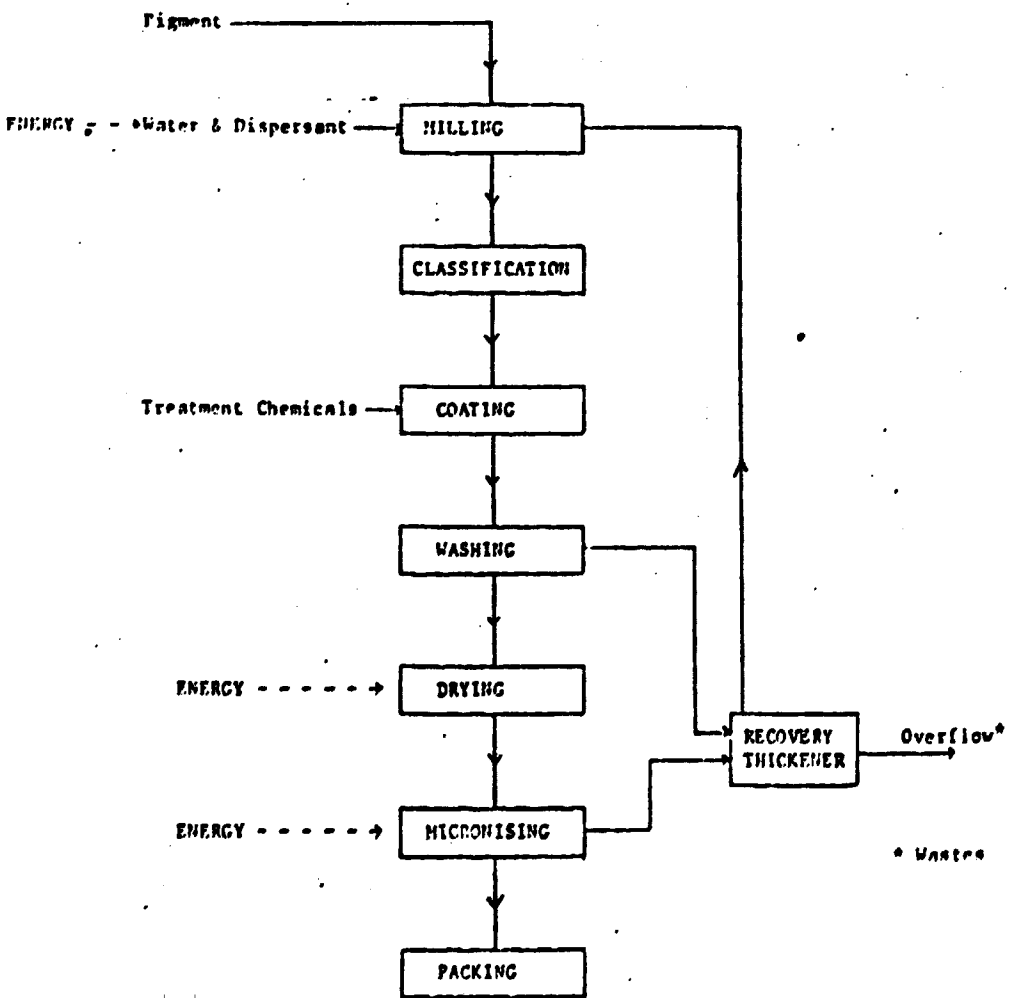
The chloride process

The chloride process for the manufacture of titanium dioxide consists of producing titanium tetrachloride by mixing the raw material with coke and reacting with chlorine gas at around 950°C. Purification of the crude titanium tetrachloride is effected by distillation and chemical treatment. The pure tetrachloride is burned with oxygen or oxygen enriched air to give chlorine, which is recovered and recycled to chlorination, and titanium dioxide. The reacting gases have to be preheated to approximately 1,000°C to ensure a satisfactory level of efficiency. The degassed titanium dioxide is then passed forward for further treatment.

There are potentially three naturally occurring raw materials suitable for the chloride process - mineral rutile, leucxene, and ilmenite, which is known to be used by one producer. Mineral rutile contains 94.96 % of TiO<sub>2</sub>. Ilmenite contains 45.60% titanium dioxide, while leucxene, which is naturally weathered ilmenite contains 65.30% titanium dioxide. A more detailed discussion of different raw materials appears elsewhere in this report.

A block diagram for the chloride process to base pigment is shown in Figure 4. indicating the significant energy inputs.

Figure 5. Surface Treatment Process Block Diagram



### Base pigment improvement

The titanium dioxide process used to end with the production of base pigment. Over the last twenty-five years, further processes have been developed to enhance the properties of the base pigment by further treatment. These are commonly known as surface treatment or coating processes.

The complexity of these processes may be judged by the fact that approximately one third of the total capital cost of a manufacturing plant for titanium dioxide pigments is required for the surface treatment equipment.

A number of important properties are given to the pigment by this additional processing, e.g. the dispersion of the pigment into polymers is vastly improved thereby saving the customer time and equipment. The opacity or hiding power is improved. The photocatalytic activity of the pigment is reduced and hence the durability of the system (mainly paint) is improved. The actual process can be tailored according to the users' application, but broadly follows similar principles.

The base pigment, from either the chloride or sulphate process, is slurred in water, dispersed and intensively ground. The product is classified and the oversize recycled. The product should conform to a particle size distribution, which provides optimum optical properties, with a complete absence of oversize material.

The individual particles are then coated by selective precipitation of small quantities of colourless, inert components, usually hydroxides or hydrated oxides of silicon, aluminium and titanium. The quantities and mode of precipitation are varied according to the final properties required.

The resultant slurry is washed over vacuum filters, to remove the soluble salts produced during the coating procedure. The soluble salt content is critical in some pigment applications, hence for top quality pigments de-ionized water (equal to distilled water) is used for the final washing.

The pulp is dewatered and dried through a tunnel or spray drier.

The dried product is fed to fluid energy mills, which generally use medium pressure overheated steam. The intensity of milling is varied according to the properties required.

A flow diagram for the surface treatment process is shown in Figure 2, and a block diagram showing main energy inputs in Figure 5.



Development trends of titanium dioxide pigment industry

The growth rate of the pigment industry in the decade 1960-1970 was 6.7 per cent per year. Since then the growth rate of titanium dioxide production has declined and in some countries even stagnated.

The ratio of production distribution between sulphate and chloride methods in 1973 was 3.9 : 1 and in 1974 3.4 : 1. Although more recent statistics are lacking, it is evident that this ratio has continued to change in favour of the chloride process because the technology is now established, and importantly for environmental reasons. The chloride process is favoured mostly in North America, particularly in the U.S. where it accounts for more than 50 per cent of total production. For instance, Du Pont, the world's biggest titanium dioxide producer, is putting a new 150,000 tons/a chloride process pigment plant onstream during the year 1980. The \$ 150-million plant gives Du Pont more than 50% of U.S.  $TiO_2$  capacity, which has previously been 885,000 tons/a.

In Europe the sulphate process is still predominant.

Raw materials estimate and energy consumption

Basis: Production of 40,000 tons/a titanium dioxide pigments,  
no. of effective days of operation 330 d/a, i.e. 121 tons/d.

Sulphuric acid needed: 100,000 tons ( $H_2SO_4$  100%)

For this amount: elemental sulphur 34,000 tons  
or pyrites 75,000 tons

Ilmenite, 53% of  $TiO_2$ , supposing a total yield of 85%:  
90,000 tons

Titanium tetrachloride, estimated 400 tons

Plus 30-40 different chemicals, the largest items being soda ash  
and caustic soda, alumina, sodium silicates, zinc and zinc oxide,  
magnesium oxide etc.

Scrap iron (theoretical) 7,500 tons

Energy consumption

Basis: as above, for an integrated plant  $H_2SO_4$  -  $TiO_2$  pigments

Total energy consumption /ton of product:

|                 |           |
|-----------------|-----------|
| Base pigment    | 30 GJ     |
| After-treatment | <u>20</u> |
|                 | 50 GJ     |

Less excess energy from  $H_2SO_4$

|                   |              |
|-------------------|--------------|
| plant (see p. 33) | <u>12 GJ</u> |
|                   | 38 GJ        |

Oil equivalent for 38 GJ: 0.9 ton

For 40,000 tons/a: oil 36,000 tons/a

Approximate breakdown: heavy fuel oil 85%  
light fuel oil 10%  
kerosene 5%

Heavy fuel oil can be replaced by any other fuel if considered  
more economical, light oil and kerosene by natural gas only because  
of the impurities resulting from solid fuels or heavy fuel oil.  
Kerosene is needed in the spray drying units only; if conventional  
drying by steam is applied, the portion of kerosene is to be added  
to that of heavy fuel oil.

Electric energy consumption (sulphate process)

Because of a high consumption of low-pressure steam it is possible to use back pressure turbines for the generation of electric energy. Hence, the plant may generate at least one-half of the electric energy needed in the production, the balance must be taken from the national grid. In the present estimate, the electric energy is included in the total energy consumption figures as presented above.

Water

Process water: Sulphuric acid plant: 80,000 m<sup>3</sup>/a  
approximately 250 m<sup>3</sup>/d

Titanium dioxide pigment plant:

Water demand is highly dependent of the effectiveness of returning the condensates, of the recycling ratio of the process water, of the quality (salt content) of fresh water, and of many other factors. Therefore, the figures presented below are approximate.

Waste acid contains about 4 m<sup>3</sup> of water/ton product,  
i.e. 500 m<sup>3</sup>/d

A careful estimate for different slurring and washing operations of the pigment gives 40 m<sup>3</sup>/ton product.

Assuming a recycling ratio of 0.25, net demand will be 30 m<sup>3</sup>/ton, i.e. 3.600 m<sup>3</sup>/d

Losses of steam (condensate), by evaporation,  
and blowdowns = boiler makeup water 100 m<sup>3</sup>/d

Cooling water: it is supposed that sea water can be used for cooling purposes.

Miscellaneous requirements: Those occurring in the plant (potable and sanitary water) present a small item and need not be considered at the present degree of accuracy. However, it must be remembered that total personnel of the new plants may amount to about 1,200, and the water needed in the industrial village must be treated preferably at the same water treatment plant. If it is assumed that the number of inhabitants will be 3,000, and their water consumption 0.2 m<sup>3</sup>/d per person, an additional need of 600 m<sup>3</sup>/d must be met.

Hence, the water treatment plant capacity will be:

Process water

- sulphuric acid plant 250 m<sup>3</sup>/d

- pigment plant 4,200

Household water 600

---

5,050 m<sup>3</sup>/d

210 m<sup>3</sup>/h

3.5 m<sup>3</sup>/min

(Basis: cf. page 30)

As far as process water is concerned, the above figures represent an optimum that can be achieved by a very careful planning and effective recycling only. The latter, for example, can be easily affected by a high salt content in the water. If sea water is not used for cooling purposes, an additional makeup for losses occurring in the cooling towers must be taken into consideration.

Total energy requirements (process vs. raw material)

It is possible to compare the energy requirements for manufacturing titanium dioxide base pigments, by making certain simple assumptions.

They are:

- a) The same ilmenite is used as the starting point for each route; and therefore the effect of the ilmenite itself can be ignored.
- b) Each of the energy inputs can be converted into primary fuels where appropriate. This, for example, implies that electrical power is not obtainable from hydro-electric or nuclear sources.
- c) The energy for extraction of the primary fuel is ignored.
- d) Apart from the direct energy requirements, only the energy associated with sulphur, carbon or coke, oxygen and chlorine are considered for the various process routes.

The following process routes have been selected for examination:

- A) Sulphate process using ilmenite, with free discharge of wastes.
- B) Sulphate process using slag with free discharge of wastes.
- C) Chloride process, using beneficiated ilmenite.
- D) Chloride process, using high grade slag.

The energy requirements for the four routes are shown in the following Table.

|                     | <u>Process Routes.</u> <u>Energy: GJ per ton product.</u> |           |           |            |
|---------------------|---|-----------|-----------|------------|
|                     | A   | B         | C         | D          |
| Preparation of Feed | -   | 45        | 40        | 50         |
| Base Process        | 30  | 25        | 45        | 50         |
| Credits             | -12   | - 8       | -         | -          |
| <b>TOTAL</b>        | <b>18</b>   | <b>62</b> | <b>85</b> | <b>100</b> |

It is to be noted that the above table has been compiled solely from the energy conservation point of view, and cannot be used for cost comparison between different processes. Therefore, credits are given for the energy generated by the sulphuric acid process, but not for the byproduct obtained in connection with slag production.

Of course, a relatively higher energy demand makes the process more vulnerable in case of rising energy cost.

The above data applies only to base pigment. The additional processes which are now installed to treat the base pigment to meet specific customer requirements can add up to a further 20 GJ per ton of product.

The recovery and re-use of the waste acid would require a further 25..30 GJ per ton of product. Therefore, titanium dioxide pigment production is associated with an expenditure of energy equivalent to between 38 and 120 GJ per ton, dependent on the feedstock, the process route, environmental standards and the nature of the pigment required.

It is of interest to note that, in comparison, one ton of crude steel requires only 25 GJ per ton.

C. The role of research and development in titanium dioxide pigment production, sales service

Manufacture of titanium dioxide pigments is of necessity highly research intensive. There are two main tasks in the R & D involved: product quality control, and developing of new and improving of existing grades. International competition is very fierce, but typically quality counts more than price. This is especially true if the manufacturer must rely mainly on the export market

Maintaining stable quality level is considered as important as the quality itself. Customers, mainly paint manufacturers, are usually conservative, so, reluctant to change their proven paint formulas once developed on the basis of a certain pigment grade with constant properties. If some of these, for example, dispersibility or hiding power, are different in different lots purchased independent of whether the new lot is better or worse in this respect, trouble in the production will occur.

Therefore, much skill, manpower, and cost is involved in the two main branches of control: process control and product quality control. Typically, the head of the process control unit reports to the production manager, while product quality control is independent of the production and reports directly to the plant manager. As an example of the thoroughness of quality control it may be mentioned that a representative sample is taken from every pigment lot produced, so every ton sold can be identified and in case of complaint, the sample can be re-examined. Small fluctuations in the pigment quality cannot be completely avoided, but computerized storage bookkeeping ensures that each customer always gets a new lot as similar as possible to the one delivered earlier.

**Sales service**

Sales service forms an important part of the sales promotion of titanium dioxide pigments. As a rule, sales service engineers contact the customers around the world, inform them about latest developments in the field, act as troubleshooters in the manufacturing process especially from the pigments point of view, and, what probably is most important, maintain fair and confidential relations between the producer and the customers. Ideally, sales service should be separated from selling, but it is not always feasible because of the cost involved.

Normally there is a sales service laboratory in the pigment plant where problems brought up by sales service engineers or customers can be studied and solved.

#### D. Economic considerations

Taking into account the expenses connected with research and development work, the cost of sales promotion, and maintaining a net of offices/agents worldwide, it is evident that a new producer may easily run into difficulties in competing with existing and established companies. These may maintain one central laboratory devoted entirely to research equipped with top quality staff and instruments. This is able to serve several production units in different parts of the world. Likewise, one and the same marketing and sales service organization is used worldwide. Therefore, the overall trend has been towards big concerns. Three companies through their international subsidiaries and affiliates account for more than 50 % of world titanium dioxide pigment manufacturing capacity. These are Du Pont (USA and Canada), NL Industries (USA, Canada, West Germany, Belgium, and Norway), and Tioxide (UK, France, Spain, Australia, Canada, and South Africa). Other major Western World producers are American Cyanamid (USA, and the Netherlands), Bayer (West Germany, Belgium, and Brazil), Laporte (UK and Australia), Kemira (Finland), Glidden Pigments (USA), Thann et Mulhouse (France), and Ishihara Sangyo (Japan).

Exact capacity figures do not appear in the literature, and it is still more difficult to make reliable estimates of the actual production and therefore of the degree of utilization. The latter figures are never published by the producers. In the writer's opinion, the following capacity figures are realistic:

| <u>Year:</u> | <u>World capacity million tons/a</u> | <u>Source of information</u> |
|--------------|--------------------------------------|------------------------------|
| 1925         | 0.005                                | Laporte                      |
| 1937         | 0.1                                  | "                            |
| 1976         | 1.8 - 1.9                            | Chemical Week Dec.12, 1979   |
| 1980         | 2.1                                  | Writer's estimate            |

U.S. titanium dioxide capacity was 985,000 tons/a prior the Du Pont startup of its 150,000 tons/a plant that makes the total to 1,035,000 tons/a in 1980 (Stanford Research Institute, Menlo Park, Calif.).



### E. Environmental implications

The environmental implications resulting from the manufacture of titanium dioxide pigments are related to the disposal of the byproducts and waste material inevitably generated. The implications for the upgrading of the deposits to obtain the feedstock for the pigment manufacturer will be treated elsewhere in this report. Quite clearly though, the concentration of the titanium dioxide in the feedstock defines the quantities of byproducts and wastes generated in the upgrading stage compared with that in the pigment process itself.

The two pigment processes - chloride and sulphate - depend upon attacking the raw material with either chlorine or sulphuric acid. The resulting titanium salts are subsequently decomposed to titanium dioxide, with the release of either chlorine or sulphuric acid. The remainder of the raw material is converted mainly into the relevant metallic chlorides or sulphates - essentially iron salts - together with some inert residues. With the chloride process, the chlorine set free can be completely recycled. This applies, however, to the titanium tetrachloride only, iron and other chlorides must be dumped. With the sulphate process, only a very limited quantity of the sulphuric acid released can be recycled in the pigment producing process (cf. p. 24 ). On the other hand, its reuse is possible in certain other applications. It must be taken into account that concentration of the waste acid by means of evaporation is uneconomical. The problem of the waste acid will be treated elsewhere in the present report.

As the sulphate process normally employs a weaker feedstock than the chloride process, it is self-evident that it will generate a much greater quantity of waste. If the ilmenite used as the raw material contains 44% of  $TiO_2$  (Norwegian), 55% (Australian); or slag of 71%  $TiO_2$  content, tons of sulphate waste per ton of product will be 6.5, 5.0, and 3.1, respectively. In comparison, the chloride process generates less than one ton of waste per ton of product, for those feedstocks employed in Europe (mostly rutile).

Most sulphate pigment companies have sited their plants so that they can discharge their waste products by pipe-line to east-flowing water, into the sea at considerable depth, or barge the wastes out to sea for disposal. Monitoring of these areas, over many years, has shown little impact on the ecology, providing that the disposal site has been selected wisely. In one particular case, the plant has been operated for nearly 20 years, and the effluents have been discharged into brackish sea water at 15 meters depth, 4.5 km from the shore. The ecological and chemical impact has been followed

systematically by taking water samples both from the discharging area and surrounding sea at different depths, further by studying samples of plankton and other organisms from the seabed and from the water. The monitoring has been followed closely by the Government Water Protection Agency. In short, it has been found that low pH values can be detected only at less than one km radius around the effluent outlet. It is evident that the effluent will be neutralized very rapidly by sea water in which there is an equilibrium between calcium carbonate and carbon dioxide, and it therefore contains bicarbonate ions, which react with the acid. A detrimental effect on sea organisms can be detected only in an area of about one square kilometre. Hence, it is evident that the waste sulphuric acid does not present any problem in the sea.

More troublesome is the oxidation of ferrous ion and subsequent precipitation as ferric hydroxide. While not poisonous, this substance is clearly visible and may cause sludge formation on the shores and on fishermen's nets under unfavourable conditions (during storms). In the present writer's opinion, if the outlet lies at a sufficient depth and distance from the shore, practically no ecological changes will result. On the other hand, careful hydrologic (oceanographic) studies are needed on sea currents prevailing at the area of the effluent outlet, if the sulphate pigment plant is to be integrated with the mineral water operation. Iron hydroxide precipitate should not be allowed to contaminate the heavy mineral deposits, which are constantly being added by wave action. This will not happen, if the water layers at the sea bed are moving outwards, and the outlet pipe is at sufficient depth so as to be beyond the wave action even during the most intense storms.

P. Elimination of the wastes

The pigment industry has been singled out for special attention by Environmental Agencies in many countries over recent years to find means of reducing these wastes.

As mentioned before, the wastes from the sulphate process consist essentially of solid ferrous sulphate heptahydrate or coppras, and aqueous solutions of waste sulphuric acid containing ferrous sulphate and other metallic sulphates.

Theoretically, it is possible to recover the sulphur values from coppras or the waste acid or alternatively convert them into saleable products. Unfortunately, these processes, at least those suggested so far, are not economic.

The degree of difficulty and the cost involved in recovering sulphur values is due to the following:

- a) The so-called "strong" waste acid from the process is between 10..20% strength. For re-use as a commercial acid it must be concentrated to 94..96% strength. Since vast quantities of water have to be evaporated, much energy is required.
- b) During the evaporation step, some metallic salts precipitate in a semi-colloidal form, difficult to separate from the liquid. Certain other salt remain in solution even at high acid strength. Recycling of these leads to deterioration of colour of the pigment.
- c) High temperature roasting of ferrous sulphate is energy intensive, and both this process and the acid evaporation evolve large quantities of water vapour containing a residual amount of sulphur dioxide.
- d) Process economics have been plagued with significant variations in fresh sulphur prices. Since 1973 the energy costs have soared. The relative price of energy to sulphur has dictated the manufacture of new acid rather than regenerating, even more so recently. This is despite the waste acid disposal difficulty. Further, in the production of sulphuric acid from sulphur, a very significant quantity of energy is released which can be easily utilized in the associated titanium dioxide plant. In fact, the value of the steam produced by the released heat energy is sufficient to cover the operation cost of the sulphuric plant.

## VI. MINERALS FOR TITANIUM DIOXIDE PIGMENTS PRODUCTION

### A. The Sulphate Process

There are two types of raw materials in use in the sulphate process: natural ilmenite and upgraded ilmenites. The need for the intermediates has increased because of environmental pressure. As these materials contain less iron and more titanium minerals, the amount of ferrous sulphate to be disposed of is smaller. The main process requirement for the intermediates is the acid solubility. Also, certain impurity element contents must be within limits.

A more detailed discussion of these materials appears in connection with the sulphate pigment process description.

### B. The Chloride Process

Traditional raw material for the chloride process is natural rutile (or related minerals). Rutile, however, has severely limited reserves and this is already posing raw material problems. The preferred solution lies in the manufacture of an artificial or synthetic rutile by the chemical or metallurgical beneficiation of the abundantly available ilmenite. The upgrading may well be performed at the mining site where the iron or iron oxide byproducts from this process can be disposed of more acceptably and energy and transport costs can be minimized.

The production of synthetic rutile from ilmenite is capital and energy intensive, considerably more so than mining. In optimum circumstances the latter could undercut the former. However, optimum circumstances are the exception and it is doubtful if any undiscovered mineral sand deposits exist that should supply the steadily increasing world demand for natural rutile, so the growth of chloride process titanium pigment production is likely to be based on upgraded ilmenite.

C. Statistics

World production figures.

The following information has been compiled from different sources, and at least to the year 1976 (inclusive) does not cover the whole world due to lack of information.

| <u>Year</u>     | <u>Production tons</u>                    |                  |         |
|-----------------|---|------------------|---------|
|                 | Ilmenite                                  | Rutile (natural) | Slag    |
| 1962            | 2 340 000                                 | 126 000          |         |
| 1963            | 2 440 000                                 | 201 000          |         |
| 1964            | 3 150 000                                 | 195 000          |         |
| 1965            | 3 300 000                                 | 224 000          |         |
| 1966            | 3 250 000                                 | 254 000          |         |
| 1967            | 3 600 000                                 | 299 000          |         |
| 1968            | 3 700 000                                 | 310 000          |         |
| 1969            | 4 000 000                                 | 390 000          | 635 000 |
| 1970            | 2 921 000                                 | 417 000          | 774 000 |
| 1971            | 2 582 000                                 | 390 000          | 779 000 |
| 1972            | 2 420 000                                 | 320 000          | 840 000 |
| 1973            | 2 700 000                                 | 340 000          | 860 000 |
| 1974            | 3 000 000                                 | 330 000          | 850 000 |
| 1975            | 2 600 000                                 | 360 000          | 750 000 |
| 1976            | 3 186 000                                 | 427 000          | 826 000 |
|                 | Tons of TiO <sub>2</sub> in ilmenite+slag | Do. in rutile    |         |
| 1977            | 2 103 000                                 | 315 000          |         |
| 1982 (estimate) | 2 392 000                                 | 442 000          |         |

Source for 1977 and 1982: SME-AIME Fall Meeting 1978: a special report. (Industrial Minerals 1978, 133:45,51)

## VII. UPGRADED ILMENITES

Commercialized processes only will be treated in the following text. This limitation reflects the present writer's opinion that the development of a process from bench scale through pilot plant operations to commercial production must have been carried out by the prospective tenderer, and satisfactory references must be available if and when considered. There are two exceptions in this respect in the processes included below. These have passed the pilot plant stage successfully but apparently not yet commercialized. These are the Summit process, ingenious and elegant, and the Kurso process that has gained much publicity through effective advertising

### A. The Group of synthetic rutiles

#### Benilite process.

Benilite Corporation of America has developed a synthetic rutile process called "ECA Cyclic Process" that has been accepted by several enterprises, in fact, by the majority of existing synthetic rutile producers. The process is based on leaching reduced ilmenite by hydrochloric acid, and the ferrous chloride formed is decomposed by the Woodall-Duckham process so as to regenerate the hydrochloric acid and to give iron oxide as by-product. The losses of HCl are about 5 %. Synthetic rutile produced contains 92.96 % of  $TiO_2$ , and is suitable to be used in the chloride process for making titanium dioxide pigments. Benilite has also developed a product containing 90 % of  $TiO_2$ , suitable for the sulphate process. It only requires a lower drying temperature (450°C) so that its solubility in sulphuric acid is not affected.

For the upgrading process, ilmenite is reduced before leaching so as to contain 80 to 85 % of total iron in ferrous state. The reduction is normally carried out in a rotating kiln at 900°C, with fuel oil or coke as the reductant. After the reduction step the ilmenite is cooled down rapidly to 250°C to prevent a re-oxidation. This can be done with water sprayed on hot ilmenite. Reduced ilmenite is leached with 18.20 % hydrochloric acid in a slowly rotating reactor at 143°C and 0.25 MPa pressure. This step takes about 4 h. Usually the leaching consists of two steps, one-half of the acid used at the second step is recycled to the first. Leaching acid is used about 20 % in excess. The reaction between hydrochloric acid and ilmenite is not sufficiently exothermic to maintain optimum leaching

temperature, so energy for this purpose must be provided by evaporating and heating a part of the leaching acid. Direct steam cannot be used for the purpose because of its diluting effect. After leaching, the solids are calcined at 270°C. The overall yield is about 95.96 %, and 90 to 95 % of the iron present is removed.

The following companies are using the Benilite process according to the information obtained in 1977:

| Company                         | Location                         | Capacity t/a             | Started/Will start |
|---------------------------------|----------------------------------|--------------------------|--------------------|
| Taiwan Alkali Co.               | Kaohsiung, Taiwan                | 30,000                   | I 1975 II 1976     |
| Malaysian Titanium Corporation  | Lahat, Ipoh, Malaysia            | 65,000<br>(full 100,000) | 1976<br>1978 1.)   |
| Kerr-McGee Chemical Corporation | Mobile, Alabama<br>USA           | 100,000                  | 1976 2.)           |
| Sakai Chemical Industry Co.     | Japan                            | 30,000                   | 1979 1.)           |
| Kerala Minerals & Metals, Ltd   | Chavara, Quilon<br>India         | 30,000                   | 1978 1.)           |
| Indian Rare Earths Ltd          | Chatrapur, Orissa<br>India       | 100,000                  | 1981 1.)           |
|                                 |                                  | Total                    | 355,000            |
|                                 | Further options for three plants | 150,000                  |                    |

Remarks:

- 1.) Not verified at the time of writing.
- 2.) Operations at Kerr-McGee's synthetic rutile plant in Mobile were suspended in early 1978, because of, as reported, technical difficulties and high production cost. According to recent information the company is expected to recommence at the end of 1980 to supply the company's Hamilton, Mississippi, titanium dioxide facility, thus replacing the need to buy natural rutile from external sources (Industrial Minerals June 1980).

Operating needs of a typical Benilite plant

Basis: 100,000 tons/a synthetic rutile of 94 %  $TiO_2$  production, along with 60,000 to 70,000 tons/a by-product iron oxide, using an ilmenite feedstock of 54 %  $TiO_2$ .

| <u>Item per ton of product</u>                            | <u>Consumption</u> |
|---|--------------------|
| Raw materials and utilities                               |                    |
| Ilmenite tons   | 1.83               |
| Makeup hydrochloric acid (31.5 %) tons                    | 0.15               |
| Heavy fuel oil tons (total heat energy req.)              | 0.54               |
| Steam (7 bar, sat.) tons                                  | 1.25               |
| Electricity kWh   | 300                |
| Cooling water $m^3$                                       | 11                 |
| Direct labour, men/shift                                  | 12.15              |
| Maintenance labour, total men                             | 12                 |
| Maintenance materials, % of capital investment, per annum | 3                  |

For a production based on 150,000 tons of ilmenite (82,000 tons of synthetic rutile):

|                     | <u>per annum</u> | <u>per day (330 d effective)</u> |
|---------------------|------------------|----------------------------------|
| Ilmenite tons       | 150,000          | 455                              |
| Makeup HCl tons     | 12,300           | 38                               |
| Heavy fuel oil tons | 44,300           | 134                              |
| Steam tons          | 100,000          | 303                              |
| Electricity kWh     | 24,000           | 73                               |
| Cooling water $m^3$ | 830,000          | 265                              |

The amount of steam is not sufficient to allow in-plant generation of electricity by means of back-pressure turbines (about 90 tons/h suggested as a minimum, in the present case 13 tons/h, being far too low). Hence, the electric power needed in the process (about 3 MW) must be generated or purchased separately.



Hydrochloric acid plant for the Benilite process

Assumed capacity 12,400 tons of hydrochloric acid (31.5 %), corresponding 3,900 tons of 100 % acid.

Raw materials

|                 |      |      |       |             |
|-----------------|------|------|-------|-------------|
| Sulphuric acid  | 94 % | tons | 5,000 | (15 tons/d) |
| Sodium chloride |      | tons | 6,000 |             |

Products

|                   |        |      |        |
|-------------------|--------|------|--------|
| Hydrochloric acid | 31.5 % | tons | 12,400 |
| Sodium sulphate   |        | tons | 7,600  |

Sodium sulphate is a valuable chemical used in the cellulose industry.

Flow sheet of the Benilite process appears in Figure 6.

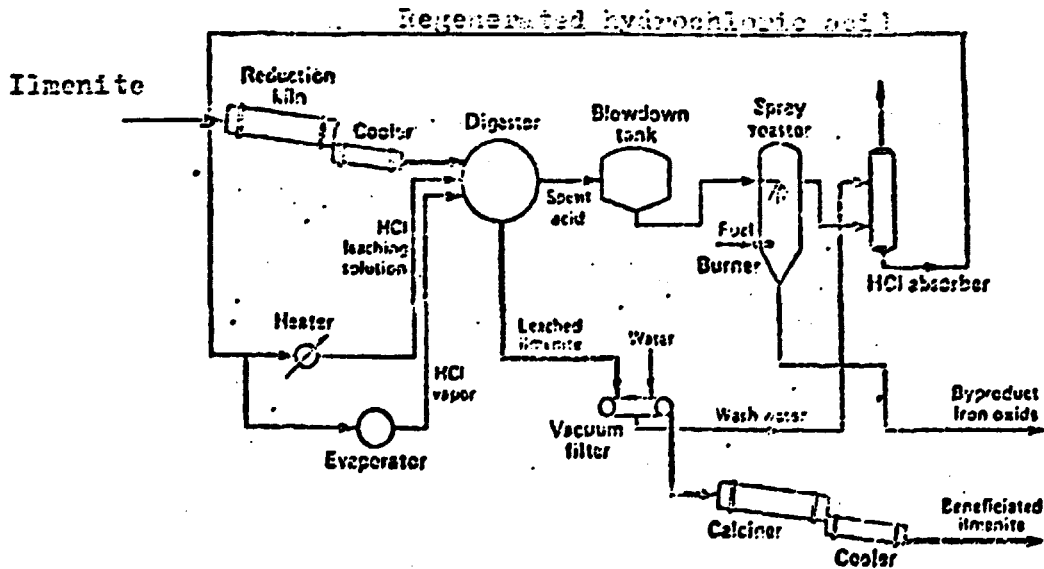


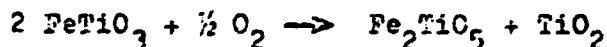
Figure 6. Flowsheet of the Benilite process

Western Titanium (A M A) Process

Western Titanium N.L., now Associated Minerals Consolidated Ltd (A M A), Australia, has produced synthetic rutile since 1968 according to a procedure developed by Western Australian Government Chemical Laboratories, and later Western Titanium together with CSIRO and Lurgi. The capacity in 1974 was 30,000 tons/a. A M A's announcement (half yearly results until 31 Dec. 1979) confirmed that the original ilmenite beneficiation plant at Capel has been refitted and brought back into action during January 1980 to bring total synthetic rutile capacity near to the 60,000 tons/a level. Plans to build another large scale unit (of around 60,000 tons/a) are understood to be proceeding. The production of synthetic rutile during 26 weeks to 26.12.79 was 21,507 tons (Industrial Minerals March 1980 p.9)

In the process, initially oxidized ilmenite is reduced until all iron is in metal form. Slurried in acidic water, the ilmenite is oxidized by air as to convert the metallic iron to its oxides, mainly  $Fe_3O_4$ . These can be separated mechanically. The product contains 91 .. 93 % titanium dioxide, and is suitable for the chloride process of titanium dioxide pigments. After certain process modifications the product is claimed to be suitable also for the sulphate process.

Going into detail, the ilmenite is oxidized before the reduction step to avoid sintering during reduction. Ilmenite is oxidized in a rotary kiln at 1000°C to pseudobrookite and rutile:



The content of ferrous iron is now 2.5 %. The reduction is also carried out in a rotary kiln at 1150°C. After a series of complicated reactions the bulk of the iron is reduced to metal. However, it is easily reoxidized so special precautions are taken in the process. The reduction is effected by coal mixed with the ilmenite in the feed, and the reduced ilmenite is cooled rapidly to 20..30°C.

After reduction, non-magnetic minerals are separated out and the material is slurried in water to form a suspension of 37 % solids. Air is blown through the slurry to oxidize the metallic iron to  $Fe_3O_4$  which precipitates on the mineral particles. After 13..14 h about 99 % of the iron has been oxidized. Because of exothermic reaction the temperature rises to a steady 80°C. The pH value is kept on the acidic side (0.02 %  $H_2SO_4$ ).  $NH_4Cl$  is

added to promote the oxidation. Iron oxide is separated by means of hydrocyclones. The material is drained and passed through the product drier and the final synthetic rutile product contains 91.93 %  $TiO_2$  and about 3.6 % Fe. In addition, it contains practically all other impurities present in the ilmenite concentrate. This fact will be discussed in more detail in connection with the Summit process (p. 51).

Main features of the Western Titanium process and a materials balance are presented in Figure 7.

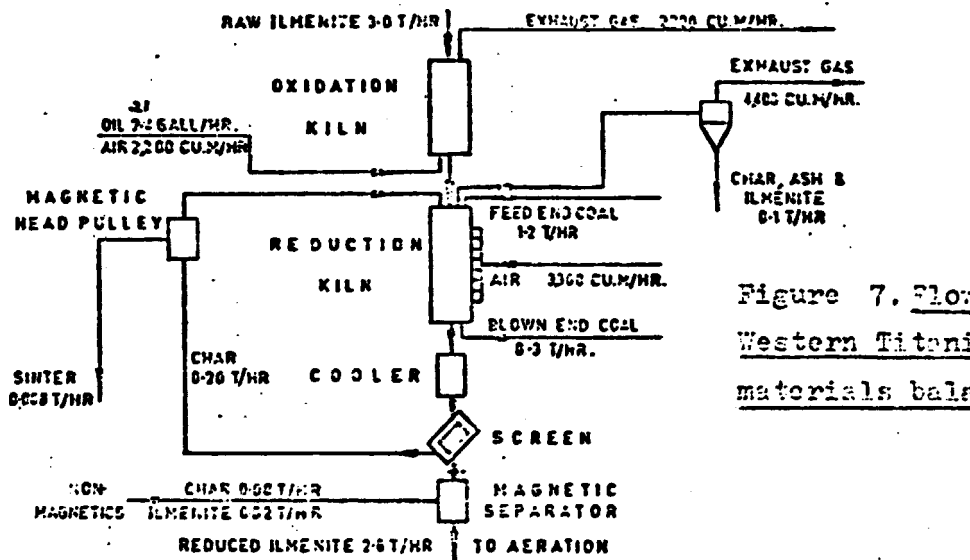
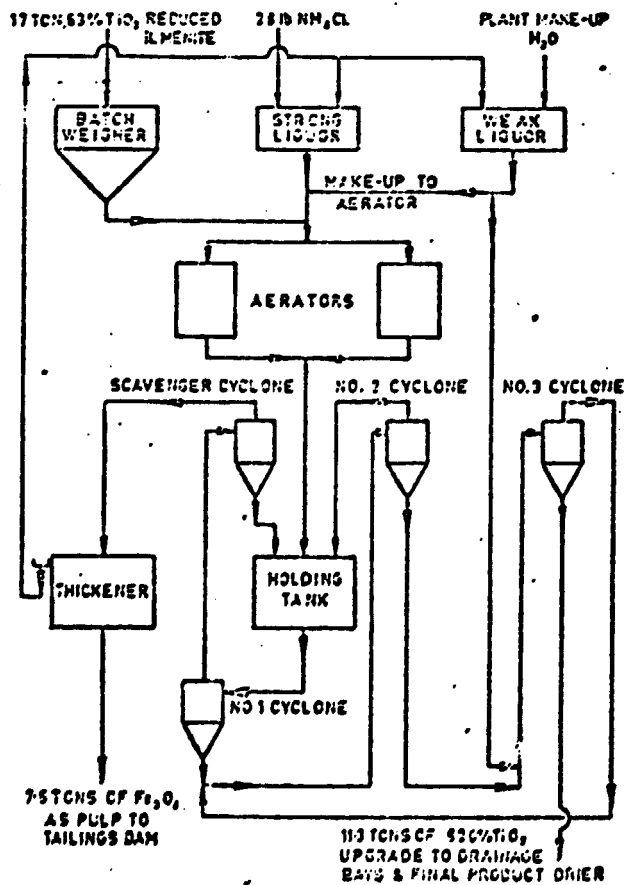


Figure 7. Flowsheet of the Western Titanium Process and materials balance



### Dragandra Chemical Works (Wah Chang) Process

Dragandra Chemical Works produces at Sahuruparam, Tirunelveli, Tamil Nadu, India, synthetic rutile since 1970 by means of the know-how from Wah Chang Corp., U.S.A. The capacity is 25,000 tons/a of synthetic rutile, representing little more than pilot plant scale. The Wah Chang procedure uses hydrochloric acid for leaching the ilmenite. The plant was originally founded to balance the demands of sodium hydroxide and chlorine from an electrolytic process, the demand of the former being much higher. Therefore, excess chlorine was converted to hydrochloric acid and used in the leaching process. Hence, it is clear that there is no need to recover the acid that is disposed of. It is not considered necessary to present further details of the process in this connection.

### Ishihara Process

Ishihara Sangyo Kaisha, Ltd, at Yokkaichi, has manufactured synthetic rutile since 1971 by using a process of their own. The initial capacity was 27,000 tons/a, and amounts to 48,000 tons/a according to recent information. The method is based on leaching the ilmenite by waste acid from the sulphate process, and is, therefore, designed to be integrated with  $TiO_2$  pigment production. However, this process does not eliminate waste problems, as it produces ferrous sulphate in the ratio 3 tons/ton product and waste acid, the whole amount of which cannot be used.

The present writer has been provided with a document prepared by Ishihara Sangyo Kaisha, Ltd, entitled "Preliminary Feasibility Study on Manufacturing Synthetic Rutile from Sri Lanka Ilmenite, December 1979". The study consists of laboratory experiments at "beaker scale" using sulphuric acid, stronger than usual waste acid from the sulphate process and not containing iron sulphate. Therefore, the results are of no practical value; besides, the properties of Pulmoddai ilmenite must be known to Ishihara without these trivial experiments.

Further, the report includes a flowsheet where the waste iron sulphate does not even appear. The neutralization of waste acid with ammonia, as suggested, is not realistic, at least not at the current price trend of ammonia. Ammonium sulphate is not an easily marketable fertilizer.

The report contains also a cost estimate for a synthetic rutile plant. It apparently implies the idea that Ishihara is willing to make a tender

to CMSC for a synthetic rutile plant to be established in Japan in order to help Ishihara to handle their waste acid problem. The present writer does not believe this to be in the best interest of CMSC or has ever been its intention. If selected for synthetic rutile production by CMSC, the Ishihara process would be feasible only in connection with CMSC's plant production in Sri Lanka.

As far as the report itself is concerned, it can by no means called a feasibility report, not even a preliminary one.

The flowsheet of the Ishihara process appears in Figure 8. Operational needs as given by Ishihara are shown on page 50. The amount of process water is tremendous; for a production of 40,000 tons/a of synthetic rutile the consumption of water is about 16,000 m<sup>3</sup>/a. Possibly this is an error.

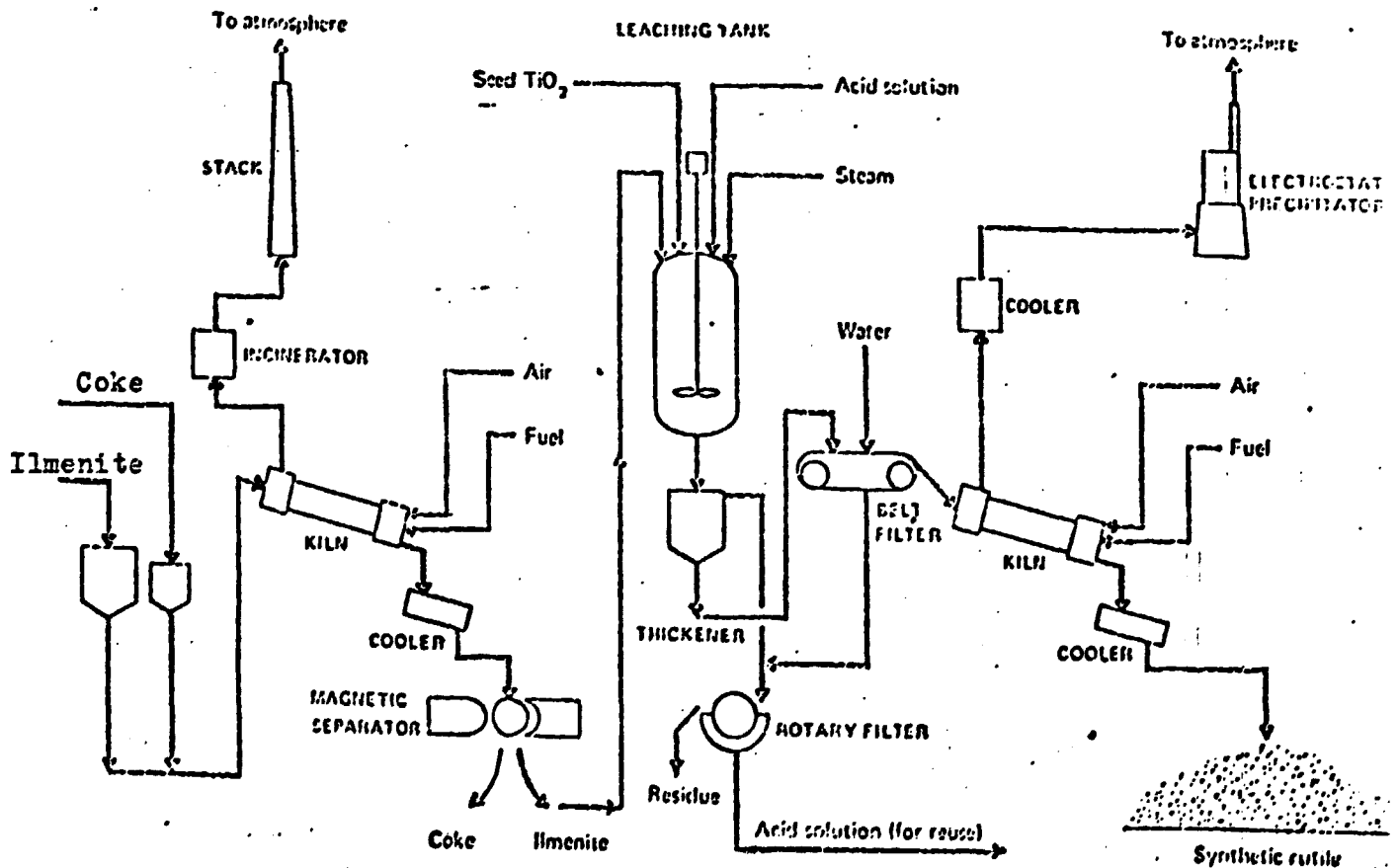


Figure 8. Flowsheet of the Ishihara process.

Operational needs per ton of synthetic rutile product in the Ishihara process are as follows: (Source: Ishihara Report December 1979)

1) Raw materials.

|   |            |
|---|------------|
| Ilmenite  | 2.13 ton   |
| Coal  | 0.21 ton   |
| Sulfuric acid( as 100% H <sub>2</sub> SO <sub>4</sub> ) | 1.51 ton   |
| Ammonium ( as 100% )                                    | 0.0075 ton |
| Scrap   | 0.04 ton   |
| Agent of aggregation                                    | 0.2 kg     |

2) Fuels

|                                 |       |
|---------------------------------|-------|
| Heavy oil for pre-Oxidation     | 70 l  |
| Heavy oil for partial reduction | 150 l |
| Heavy oil for calcination       | 70 l  |
| Kerosene for drying             | 25 l  |
| Kerosene for calcination        | 6 l   |

3) Utilities.

|               |          |
|---------------|----------|
| Electricity   | 220 kwh  |
| Steam         | 0.84 ton |
| Process water | 6.6 ton  |
| Sea water     | 60 ton   |

4) Additional utilities for vacuum crystalizer.

|               |         |
|---------------|---------|
| Electricity   | 46 kwh  |
| Steam         | 0.7 ton |
| Process water | 125 ton |

5) By-products.

|   |          |
|---|----------|
| Iron sulfate (FeSO <sub>4</sub> .7H <sub>2</sub> O) | 3.08 ton |
| Fine powdered synthetic rutile                      | 0.19 ton |

6) Personnel.

|                   |            |                  |
|-------------------|------------|------------------|
| Operators         | SR process | 10 persons/shift |
|                   | VC process | 2 persons/shift  |
| Officer           |            | 1                |
| Assistant officer |            | 1                |
| Engineer          |            | 1                |
| Foreman           |            | 1                |
| Supervisor        |            | 1                |

Processes at Pilot Plant stage

MURSO process

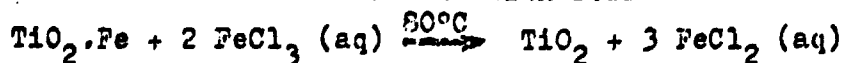
The MURSO process is probably the best known and most effectively advertized pilot plant process. It has been developed by the CSIRO (Commonwealth Scientific and Industrial Research Organization) and Murphys Pty Ltd, Australia, in co-operation with Mitsubishi Chemical Industries, Kurozaki, Japan, where the pilot plant tests have been performed. The process is based on leaching the ilmenite with hydrochloric acid and it is very similar to the Benilite process. It was first made public in 1969, and Murphys began technical and economic studies with the aim of bringing the process into commercial operation in 1971. A semicommercial plant of 10,000 tons/a capacity has been installed to prove the process. As announced, if the tests are successful, a 50,000 tons/a upgraded ilmenite plant will be built at Gladstone (Qld) with provisions of doubling capacity. As far as the present writer is aware, such a plant is not in operation.

Summit process

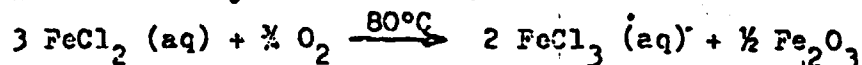
Of all processes in this category, this one appears the most attractive. The principle is amazingly simple and elegant, and eliminates problems frequently connected with the use of acids, especially hydrochloric acid, as well as those resulting from waste materials.

The process has been developed by Oceanic Process Corp., and another company, Tiron Chemical Corp. in Canada is planning pilot plant tests at a scale of 20,000 tons/a. The Summit process is based on leaching pre-oxidized and then reduced ilmenite by means of ferric chloride solution. The minimum  $TiO_2$  content of the product is reported to be 85 %, and the product is suitable for both chloride and sulphate processes.

The ilmenite is oxidized at 750..1200°C (wide temperature range can be explained by the prevailing practice in patent applications), After oxidation, the ore is reduced at 700..1300°C by means of suitable reducing agents until 90 % of total iron is reduced to metallic state. Reduced ilmenite is leached with ferric chloride solution (12 % of  $FeCl_3$  minimum) for 30 min. Metallic iron reacts with ferric chloride as follows:



The solution containing ferrous chloride is separated from the solid product and oxidized by means of air:



Aqueous ferric chloride solution is re-used for leaching.

Normally, the  $\text{TiO}_2$  content of the product is better than 90 % and the byproduct contains at least 99 %  $\text{Fe}_2\text{O}_3$ .

It has been estimated that total investment (in 1971) for a plant producing 100,000 tons/a synthetic rutile would have been 19 million US\$. Operating costs were estimated to amount to 75 US\$/ton product without fuel oil and ilmenite. The amount of carbon needed for reduction is 0.6 ton/ton product. Total energy consumption for the process amounts to 16..18 GJ/ton(synth.rutile+ $\text{Fe}_2\text{O}_3$ ).

If commercialized, this process represents a very strong choice amongst different processes for producing synthetic rutile.

It must be remembered, however, that iron only is leached out from the ilmenite by the ferric chloride solution, practically all other impurities remaining in the product. Hence, the quality of the product in this respect depends on the composition of raw material, ilmenite concentrate. The following figures show the result, if a typical Pulmodai ilmenite is used as raw material, and 2.0 % of FeO remains in the product (as assumed by Tiron Chemical Corp.):

|                         | Ilmenite | Product  |
|-------------------------|----------|----------|
| $\text{TiO}_2$          | 54.58 %  | 91.04 %  |
| FeO                     | 18.11    | 2.00     |
| $\text{Fe}_2\text{O}_3$ | 23.15    | -        |
| $\text{SiO}_2$          | 1.51     | 2.52     |
| $\text{ZrO}_2$          | 0.02     | 0.03     |
| $\text{Al}_2\text{O}_3$ | 1.18     | 1.97     |
| MnO                     | 0.37     | 0.62     |
| $\text{Cr}_2\text{O}_3$ | 0.07     | 0.12     |
| $\text{V}_2\text{O}_5$  | 0.09     | 0.15     |
| MgO                     | 0.85     | 1.42     |
| CaO                     | 0.08     | 0.13     |
|                         | <hr/>    | <hr/>    |
|                         | 100.01 % | 100.00 % |



As can be seen, certain critical contents such as  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MgO}$  increase of course, but still remain within acceptable limits. The situation in this respect is exactly the same in the Western Titanium process. It is evident that the application of these processes is limited to ilmenites containing low amounts of harmful components.

Processes based on selective chlorination.

According to the present writer's knowledge, all these processes are still at bench or pilot plant scale. Du Pont applies direct chlorination of ilmenite successfully in the pigment production, but not for synthetic rutile.

The best known so far is the process developed by Australian Chlorine Technology Ltd, that uses selective chlorination of iron under reducing conditions. The reaction is carried out in a fluidized bed reactor, and the product contains 95 %  $\text{TiO}_2$ . The company has operated a pilot plant producing 10 tons/d.

Although chlorination of the reduced product might appear to be a natural choice, it means a large consumption of chlorine or a great deal of chlorine recovery.

B. The Group of slags

Q I T (Sorel) slag.

The best known process is the Q I T (Quebec Iron and Titanium Corporation) Sorel-slag process with about 900,000 tons/a capacity. It is intended mainly for the sulphate process for making titanium dioxide pigments. It should be noted that this process is successful because of the unique conditions at the site. The Sorel ore is very cheap and in abundant quantity; the hydro-electric power is also low in cost and, because of the demand for the high purity pig iron, the slag can be sold at a very attractive price. It is possible to produce a slag containing a much higher content of  $TiO_2$  but apparently it is not very economic to do so. As the  $TiO_2$  content of the slag rises, the viscosity of the slag in the furnace also increases, leading to many complex problems. The product is not very suitable for chloride  $TiO_2$  pigment.

Richards Bay slag.

At the mineral sands operations of Richards Bay Minerals in South Africa 1979 was the first full year of production. The projected capacity is 460,000 tons/a slag, 115,000 tons/a zircon, and 56,000 tons/a rutile. R B slag with its 25 % of  $TiO_2$  is the only titania slag available in Western markets in addition to the Sorel. R B Minerals produces slags suitable for both chloride and sulphate processes. According to recent information "five out of ten" groups that operate chloride route plants have ordered substantial tonnages for use in 1980. The company apparently is optimistic about selling all its 1980 production, which is planned to be 399,000 tons of slag, 217,000 tons of pig iron, 115,000 tons of zircon, and 56,000 tons of rutile. The owners of the enterprise are Quebec Iron and Titanium Corp. (40 %), Union Corp. Ltd (30 %), The South African Industrial Development Corp. (20 %), and South African Mutual Life Assurance Society (10 %) (I.M. 1978: 125, 13). The prices are highly competitive: end 1979 the R B slag US\$ 135/ton FOB compared with natural rutile in Australia US\$ 330/ton FOB. The ore reserves of Richards Bay are estimated to 41 m ton of ilmenite, 1.5 m ton of rutile, and 3.4 m ton of zircon.

### VIII. ACKNOWLEDGEMENTS

Mr. F.B.P. de Silva, Chairman & Managing Director of the Ceylon Mineral Sands Corporation, has followed the consultant's work with great interest, and supported him in many ways during his appointment.

Mr. S.A. Mendadeva, Plant Manager, and the consultant's counterpart, has contributed significantly to the present work by giving valuable local information, and arranging various practical facilities.

Mr. A.A. Paul, Chief Chemist, has provided the consultant with water analyses, and other useful information.

The consultant has had many useful discussions with Mr. Keith I. Litt UNIDO Team Leader and Expert in Mineral Processing, which have greatly facilitated his work.

The consultant wishes to extend his sincere thanks to all persons mentioned, and acknowledges gratefully the friendly and co-operative attitude of all the staff members of CMSC and UNIDO he met during his appointment.



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ESTABLISHED UNDER THE STATE INDUSTRIAL CORPORATIONS ACT NO. 49 OF 1957)

ANNEX

Yen Ref.:-

Our Ref.:-

## TYPICAL ANALYSIS - ILMENITE

### 1. CHEMICAL ANALYSIS

#### Constituents - determined

#### Percentage

|                                |     |                  |
|--------------------------------|-----|------------------|
| TiO <sub>2</sub>               | ... | 54.58            |
| Fe <sub>2</sub> O <sub>3</sub> | ... | 23.15            |
| FeO                            | ... | 18.11            |
| SiO <sub>2</sub>               | ... | 1.51             |
| ZrO <sub>2</sub>               | ... | 0.02             |
| Al <sub>2</sub> O <sub>3</sub> | ... | 1.18             |
| MnO                            | ... | 0.37             |
| Cr <sub>2</sub> O <sub>3</sub> | ... | 0.07             |
| V <sub>2</sub> O <sub>5</sub>  | ... | 0.09             |
| HgO                            | ... | 0.85             |
| CaO                            | ... | 0.08             |
| P <sub>2</sub> O <sub>5</sub>  | ... | Traces ( / .01%) |

Total 100.01%

### 2. SCREEN ANALYSIS (BSS)

|   |     |    |        |
|---|-----|----|--------|
| + | 60  | .. | 0.30%  |
| + | 72  | .. | 0.32%  |
| + | 100 | .. | 12.72% |
| + | 150 | .. | 40.82% |
| + | 200 | .. | 33.82% |
| - | 200 | .. | 11.90% |

#### USUAL GUARANTEES

|                  |     |                     |
|------------------|-----|---------------------|
| TiO <sub>2</sub> | ... | 53% Minimum         |
| Moisture         | ... | Less than 2 percent |

16.3.80

MINES LOCATION: PULMOODAI

PHONE: 9 PULMOODAI

TELEX: SANDSCOMIN-1

