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TITANIUM PIGMENTS.  
TITANGESELLSCHAFT, LEVERKUSEN.

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BRITISH INTELLIGENCE OBJECTIVES  
SUB-COMMITTEE

TITANIUM PIGMENTS

TITANGESELLSCHAFT, g.m.b.h. LEVERKUSEN

Reported by

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and

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BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE  
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TABLE OF CONTENTS

<u>Subject</u>					<u>Page No.</u>
Organisation	..	..	..	..	1
General	..	..	..	..	2
Condition of Plant	..	..	..	..	3
Process	..	..	..	..	5
Materials of Construction	..	..	..	..	13
Rutile	..	..	..	..	13
War-Time Distribution	..	..	..	..	14
Copperas	..	..	..	..	15
Titanium Tetrachloride	..	..	..	..	15
Flussmittel - V.26.	..	..	..	..	16

PERSONNEL OF TEAM

W. Woodhall.  
W. A. Cash.

## ORGANISATION

This titanium oxide plant is situated inside the Leverkusen factory of I.G. The company was owned 50% by I.G. and 50% by American interests.

For many of its services such as electricity, water, steam etc., it draws upon the resources of the main factory, but as far as conveniently possible it remains a self-contained unit.

The German directors and chief staff are:-

### Directors

- Dr. Bruggemann - Managing Director.
- Dr. Kuhne - Director (non-executive)
- Dr. Raspe - Technical Director and General Manager.

### Factory Management

- Dr. Weise - Works Manager (reported imprisoned in American Zone).
- Dr. Nespital )
- Dr. Busch ) Section plant managers.
- Dr. Schulz )
- Herr Bekner - Works Engineer.

### Technical Service and Development

- Dr. Werther
- Dr. Mees

Research Staff

Dr. Tillman

Dr. Schaller

Dr. Fischer

GENERAL

In 1939 production was equivalent to 40 tons per day of  $TiO_2$ . During the war this was stepped up to a maximum in 1944 of 50 tons  $TiO_2$  per day. Production ceased completely on October 26th, 1944, due to major damage sustained in a daylight bombing raid by the R.A.F. Production was resumed on a limited scale in December 1945.

The present production was stated to be 10 tons  $TiO_2$  per day and was expected to reach 15 tons per day in 2/3 week's time. Work was being carried out under great difficulties. Large parts of the factory were roofless, many outside walls and practically all windows were missing. In the liquor stages process operations were being carried out amongst tangled debris and the lack of protection from the cold weather was leading to obvious troubles.

The total number of employed was 140 men of whom 25 were skilled tradesmen engaged on repair work. The management estimated that with an additional 20 repair men sufficient work could be done to resume a production of 30 tons  $TiO_2$  per day in about 2/3 month's time.

The main raw materials necessary for increased production would probably be available. Increased supplies of sulphuric acid could be drawn from the I.G. plant. Ample stocks of ilmenite were handy - 35,000 tons in stock on the factory and a further 10,000 tons lying on the far bank of the Rhine immediately opposite. Gas for the calciners was being made in gas producers operating on brown coal. The capacity of these producers was adequate for 30 tons  $TiO_2$  per day. Of course any increased production was dependent on a larger allocation of coal.

CONDITION OF PLANT

Although damage to buildings was extensive the plant equipment did not suffer in proportion. The following table indicates the position of the main items of plant in January, 1946.

Item	No. of Units Installed.	No. fit for use.	Damaged but repairable.	Damaged beyond repair.	Cubic Capacity	Remarks
Ilmenite drier	1	1	-	-	-	5 ton/hour.
Ore	2	1	1	-	-	3 ton/hour each.
Mixers	4	2	2	-	6 M <sup>3</sup>	
Digestors	8	4	3	1	30/35 M <sup>3</sup>	
Clarification tanks	4	4	-	-	-	12 m. diam. x 2½ m.
Crystallising vats	6	2	4	-	20 M <sup>3</sup>	
Centrifugals	2	1	-	1	-	2½ m. diam.
Storage tanks	6	6	-	-	-	One 12 m. diam. x 2½ m. and 5 small.
Concentrators	4	2	2	-	-	

CONDITION OF PLANT (Contd.)

Item	No. of Units Installed	No. fit for use.	Damaged but repairable.	Damaged beyond repair.	Cubic Capacity	Remarks
Precipitation tanks	6	3	3	-	3 x 45 M <sup>3</sup> 3 x 60 M <sup>3</sup>	
Dorr Settlers	6	2	3	1		16 m. diam. x 2½ m.
Washing Filters	15	4	7	4		Area 20 M <sup>2</sup> each
Repulping Tanks	9	3	3	3	25 M <sup>3</sup>	
Calciners	4	1	2	1		3 x 45 m. long x 2½ m. diam.
Raymond Mills	5	4	1	-		1 x 50 m. long x 2.6 m. dia.
Lodge Cottrell plant	1	-	-	1		5 roll mills.

## PROCESS

### Ilmenite Handling

Ilmenite had been drawn entirely from Norway. A typical analysis of the ore used was:-

	<u>Per cent</u>
TiO <sub>2</sub>	44.40
FeO	34.00
Fe <sub>2</sub> O <sub>3</sub>	12.44
FeS	0.63
SiO <sub>2</sub>	2.79
MgO	3.55
MnO	0.37
V <sub>2</sub> O <sub>3</sub>	0.175
NiO	0.085
CuO	0.015
P <sub>2</sub> O <sub>5</sub>	0.015
Cr <sub>2</sub> O <sub>3</sub>	less than 0.01

The ilmenite was stored in large piles in the open. As protection against wind losses it was covered with tarred paper. Light rails were laid among the ilmenite piles and the ore was transported on bogies into the grinding house. It was discharged through a grating down to an elevator system which raised it to storage bins. From here it fed into a drier. This was a simple gas fired rotary. The dry ilmenite fell through a screen - about



5 mm. spacing - into another bucket elevator system discharging into storage bins.

The ore was then ground in continuous ball mills (one Pfeiffer, one Hardinge) to a fineness corresponding to 0.5% residue on 180 mesh Tyler screen. Large hoppers were provided for storage of ground ilmenite which was conveyed from here by screw conveyors to the next stage - acid digestion.

### Digestion

Acid - 96% H<sub>2</sub>SO<sub>4</sub> - was drawn from the I.G. sulphuric acid plant and stored in large mild steel tanks. These tanks were fitted with cooling coils because, on occasions, it was necessary to cool the acid.

Ilmenite was mixed with acid in brick lined mild steel vessels - about 6 cub. metres capacity - fitted with gate type stirrers. Each batch consisted of 10 tons ilmenite and 15.4 tons sulphuric acid. About two-thirds of the acid was first mixed with the ore. The charge was run down to the digester vessels, and the remainder of the acid used to wash out the mixers. In very warm weather the attack was liable to start in the mixers - hence necessity for cooling the acid.

The digestors were steel vessels, lead lined, with a double acid resisting brick lining of capacity 30/35 cub. metres. The bricks were jointed with Hoechst cement, and after this cement had been given the usual acid pickling and washed, the joints were pointed with Asplit cement. The digestors had conical bottoms, with large lead run-offs and hard-rubber lined cocks. Arrangements were made for blowing in steam and air through the bottom of the digestors. To break the steam and air into small bubbles a lead distributing plate with small holes (7.5 m.m.) was set in the conical bottom of each vessel. The digestors had heavy wooden lids and wooden stacks carried away fumes. The latest had a fume stack built of heavy mild steel pipe, brick-lined.

When the ilmenite-acid mixture was in the vessel air was blown

through from the bottom. The reaction was started by running in, from the top, about 17/1800 litres of water. This took about two minutes. Over the next ten minutes the temperature was rising and then a very violent reaction set in. Clouds of steam and acid fume were given off and the digestion vessel rocked considerably. This reaction was complete in about two minutes. The maximum temperature attained during the reaction was 180°C. The charge had set to a dry brown mass with many large cracks running through the cake. Steam was not used during the attack we saw, but we were informed that it was used if the reaction seemed slow to start.

Water for dissolving was then run in, and the air blow continued. Addition of water was spread over two hours, but the total dissolving time was 6/8 hours. After about two hours a large lead basket, loaded with iron scrap, was lowered into the liquor. This served to reduce all ferric ion to ferrous and to form a slight excess of titanous ion.

When dissolving and reduction were complete the liquor was run down over one hour to the next stage - clarification. The average cycle in each digester vessel was 16 hours, though this time could be reduced if necessary. The reaction efficiency was 97% based on amount of TiO<sub>2</sub> from ilmenite entering solution. The final liquor run down to clarification was :-

S.G.	1.52	±	0.02
TiO <sub>2</sub>	130	gn.	per litre
Fe	120	"	" "
Total H <sub>2</sub> SO <sub>4</sub>	440	"	" "
Tempr.	60°C.		

#### Liquor Clarification

The clarification tanks were of concrete, lead lined. They

had shallow conical bottoms and were 12 metres diam. by  $2\frac{1}{2}$  metres deep. They had no stirrers. Generally 4 digester batches were run down into each clarifier which normally contained a good deal of liquor left from previous clarification. As the liquor was running down over a period of one hour a solution of Nekal was led into the liquor stream to act as clarifying agent. Nekal is manufactured by I.G. as a wetting agent, mainly for the textile trade, and is a sodium salt of di-butyl naphthalene sulphonic acid. The Nekal was added as a 1% solution and 6 kgm. was used to each digester batch.

When the clarification vessel was full the temperature should have been  $50^{\circ}\text{C}$ . When we inspected the plant they were working under difficulties and the liquor was much cooler, so that crystallisation of ferrous sulphate was taking place. The liquor was allowed to stand and the coagulated slimes settled. After about 4 hours they could commence drawing off liquor from the top, by syphoning, using a decanting pipe attached to a float. Float and pipe were constructed of staybrite alloy and were connected to a rubber hose. The clear liquor was pumped away to crystallising vessels.

When sufficient clear liquor was drawn off, the clarification cycle was repeated. At intervals of 2 to 3 weeks the accumulated slimes were washed out by a hose pipe and the slurry pumped away to settling tanks outside. The heavier fraction (unattacked ilmenite) was collected here and taken away to a dump. The overflow passed through a coarse gravel filter to the river Rhine.

### Crystallisation

The crystallisers were steel tanks with the usual lead and brick lining - capacity 28 cub. metres - fitted with large lead covered copper cooling coils and gate type wooden stirrers. When a crystalliser was full of liquor steam was passed through the coils to remove crystal formed in previous run. Cooling water was then passed and temperature reduced to  $20^{\circ}\text{C}$ . About 60% of the iron sulphate in solution was crystallised out here.

The crystal slurry was dropped to a centrifuge feed tank where it was kept constantly stirred. From here it fed through a hydraulically controlled feed valve to an Escher-Wyss continuous running batch centrifuge of the horizontal spindle type. The feed valve was controlled by the automatic timing gear of the Escher-Wyss machine. In addition, near to the machine, was a hand operated rubber lined cock on the feed line. This was used by the workman to check the feed if the running was not satisfactory.

The Escher-Wyss centrifuge had a diameter of  $2\frac{1}{2}$  metres and ran at about 400 r.p.m. The timing of each cycle - feed, drain, wash, drain, skim - was done by the Escher-Wyss automatic gear operating through a hydraulic system. Each cycle lasted  $12\frac{1}{2}$  minutes and during this time dealt with one ton ferrous sulphate crystal. The crystal was skimmed out by a knife which removed all but the last 5 mm. of crystal. The ferrous sulphate discharged down a chute through breaker arms to a rubber belt conveyor, and so to a gas fired rotary drier. This drier served to remove all superficial moisture, but not any water of crystallisation. The wash water followed the main liquor stream.

The centrifuge basket and screen were built of V4A alloy and the outside casing was steel, lead lined. The liquor leaving the centrifuge contained 145 g/l  $TiO_2$ . It passed to a large storage tank which was similar to, and could be interchanged with, the clarifiers. Some froth was present on top of the liquor. The liquor was being drawn from the bottom of this tank and pumped away to the evaporators.

### Evaporation

These were of the Kestner climbing film type, operating under atmospheric pressure, and working with pre-heater tubes. The vapour from the evaporators passed round the pre-heater tubes. All tubes in contact with liquor were copper. The concentration here was increased to 220/230 g/l and the hot liquor fed direct to precipitation tanks.

## Precipitation

The precipitation tanks were steel vessels, lead lined, with a double layer of acid resisting brickwork. There were two sizes handling liquor batches of about 35 or 50 cub. metres and yielding either 7 or 9 tons  $TiO_2$ . Heating was carried out with live steam fed in at two points by lead pipes. Propeller type agitators were fitted with two propellers on one spindle.

The method of precipitation was as follows. Liquor batch was raised to the boil ( $109^{\circ}C$ ) over one hour, and maintained there for 6 hours. Water equivalent to 20% of the original batch volume was then added quickly and the whole raised to boil again, and maintained for 2 hours. The same volume of water was again added. Temperature was again raised to boil and maintained for one hour, when precipitation was finished.

The efficiency of precipitation was 97%. The settling rate of the precipitated  $TiO_2$  could be checked by diluting one part of pulp from finished precipitation with five parts of water. Precipitate should then settle at rate of 80 mms. in 30 mins.

## Washing

From these tanks the precipitated  $TiO_2$  was pumped away to large Dorr settlers. These were of concrete, lead lined, though one later settler had been rubber lined and finished with a layer of acid resisting brick. These settlers were 16 m. diameter and  $2\frac{1}{2}$  m. deep. As the  $TiO_2$  batch was pumped in it was diluted with filtrate liquor from the later rotary filters. The overflow from the primary settler contained 100 g/l  $H_2SO_4$ .

The underflow pulp of  $TiO_2$  was transferred through a Dorr pump to a second similar Dorr settler where it was again diluted with filtrate liquor to 20/30 g/l  $H_2SO_4$ . The waste liquor overflow from these settlers ran away direct to the river.

The underflow from the second Dorr passed to a series of rotary vacuum filters. Each filter had a filter area of about 20 sq. metres. The filters were designed to wash in series. After washing on three filters the  $TiO_2$  pulp passed to a repulper tank. This was a steel vessel, lead and brick-lined, of about

25 cub. metres capacity, and fitted with an agitator. The S.G. of the pulp was adjusted here and kept constant and any additions of salts was normally made here. The  $TiO_2$  was pumped from this tank to the final filter. Calcium phosphate ( $CaHPO_4$ ) was being added to the  $TiO_2$  in amount corresponding to 0.35% P205 on the pigment. The final de-watered pulp was pushed into the calciner by a bronze screw acting inside a silicon-iron tube.

The filters in use were normal rotary vacuum filters, of wooden construction, with automatic valves feeding a compressed air blow just prior to discharge. One filter was using a rubber roller discharge device which did not seem very satisfactory, the others used simple knife scrapers. Some filters, not in use, were fitted with string dischargers. Among the filters not in use was a Wolf filter, with a steel, rubber lined body and trough, and cast lead gratings for carrying filter-cloth. Cotton cloths were used and successful experiments had been made with cloth woven from poly vinyl chloride.

### Calcination

These were four rotary calcination furnaces, but only one was in use. This was 45 m. long by 2.5 m. external diameter (1.8 m. internal). It had a 5% inclination and was doing one revolution per 40 minutes. It was heated with producer gas from brown coal - calorific value equivalent to 1400 Cal. per cub. metre. This gas was considered very poor and in normal times gas from the Ruhr coke-oven grid was used at 4000 Cal.

The temperature reached in the calciner was about 900°C. The gas flame projected through a short furnace head - no combustion box was fitted. The flame was dull red and 10/12 feet long. With richer gas it was said to be 3/4 feet long. At the burner end was a control platform and here was mounted the indicating instruments of two pyrometers - a thermo-couple placed in the gas stream at the feed end, and a Fery optical pyrometer focussed on to the pigment just prior to discharge. The feed end temperature for good conditions was said to be 350°C. and discharge end about 890°C. Poor gas and irregular feed were disturbing conditions and the feed end temperature was observed between 450-500°C.

The furnace gases discharged downwards into a dust collecting box where about 1 ton  $TiO_2$  was collected each 2 weeks. In normal times the furnace gases passed through a water spray cooling tower and finally to a Lodge-Cottrell mist precipitator for  $SO_3$  fume. This part of the plant was completely destroyed and the gases were passing direct to a Zeta stack.

Of the remaining calciners, which were not in use, two were of similar dimensions, though one was fitted with a combustion box. This combustion box had not been considered a success. The other, and latest, calciner was 50 m. long and 2.6 m. external diameter. This was fitted with a short furnace head, but a combustion box was standing nearby. This furnace had not been in use. The intention had been to operate both with and without combustion box to determine best conditions. These furnaces were lined with two types of brick, "Maxial II" for the feed zones, and "Maxial V" for the hot zones.

From the calciners the pigment discharged into rotary coolers, then into bucket elevators which transferred it to silos.

#### Grinding & Packing

From the unground pigment bins the material was fed to Raymond 5 roller mills. The ground pigment was picked up on a system of rubber belt conveyors and taken away to a separate building for storage, blending and packing. For storage of ground oxide large steel silos were used, with sloping bottoms, capable of holding about 100 tons each. The ground pigment gave sticking trouble in the silos. To overcome this, one silo had four porous tiles installed at the bottom and compressed air was blown at the back and through these. These tiles had been built up from graded coke bonded with cement.

A number of drum type mixers were installed and used for making reduced blends. The only blended pigment developed during the war had been a mixture with ground natural calcite. This corresponded to 25%  $TiO_2$ , 70% calc spar, and 5%  $ZnO$ . This was intended mainly for water paints.

## Quality

The quality of the titanium oxide pigment being produced was not very good. Compared with typical British standards the product had a yellow tone, and lacked brightness. The tinting strength, measured by reduction with ultramarine blue, was about 450 as against a typical British standard of 480. The fineness of grinding and texture was quite satisfactory.

## MATERIALS OF CONSTRUCTION

No outstanding development seemed to have taken place.

For process vessels lead lining protected by one or two layers of acid resisting brickwork was standard. The brickwork was jointed with Hoechst cement, pickled, and then the joints pointed with Asplit cement. In only one case was a large vessel rubber lined in place of lead - a Dorr settler. The rubber lining was again protected by acid resisting bricks. There was reason to believe that this settler was intended for solutions containing traces of hydrochloric acid - as might be the case if rutile was prepared from tetrachloride seed.

The only staybrite type alloy used was an early Krupps grade V4A.

During the war some use had been made of a high chromium-iron alloy GS2 (said to contain 28% Cr, with no Me). This had been used for centrifugal pumps handling liquor from settlers to evaporators, and filtrate liquor from the rotary vacuum filters. These pumps had been very satisfactory.

## MANUFACTURE OF RUTILE TITANIUM OXIDE

During the war a considerable amount of rutile type titanium oxide had been made for use in welding rods, metallurgy, and electrical ceramics. This was important owing to the shortage of natural rutile in Germany. It was made very simply by calcining at higher temperatures than the normal pigment quality. Two grades were manufactured. The first by running the usual calcination about 50°C higher. This yielded a harsh titanium oxide which was not completely rutilised.



For the second quality, which was particularly dense, the first grade was given a second calcination in another small rotary calciner to a temperature of 1300°C. Both these grades could be ground, with difficulty, in the Raymond mills. For welding rod manufacture a mixture of about equal proportions of each grade had been used.

The ordinary treatment with calcium phosphate was not normally given when these grades were being made. However, batches of poor, off colour pigment were always passed on for further calcination to rutile quality, so that some contamination with calcium phosphate did occur.

It should be made clear that neither of these grades represented a pigment quality rutile. Pre-war research had been carried on in the laboratories here on pigment rutile production from titanium tetrachloride seed. There was no evidence that this research had progressed during the war, and certainly no sign of any manufacture of pigment rutile.

#### WAR-TIME DISTRIBUTION OF PRODUCTION

Based on a monthly production figure of 1200 tons TiO<sub>2</sub> the war-time distribution had been:-

	<u>Tons TiO<sub>2</sub></u>
General pigmentary purposes including paints, distempers etc.	300
Rutile grades for welding rods and metallurgy, etc.	300
Vitreous enamelling, mainly as "Flussmittel"	100
Paper manufacture	100
Silk delustring	100

	<u>Tons TiO<sub>2</sub></u>
Electrical Ceramics	50
Manufacture of TiCl <sub>4</sub>	50
General export to European countries	200

#### COPPERAS DISPOSAL

The copperas produced here as a by-product found a ready market mainly in the manufacture of the catalyst used in synthetic oil industry. The balance was easily absorbed for agricultural needs.

#### MANUFACTURE OF TITANIUM TETRACHLORIDE

This had been made here during the war by chlorination of titanium oxide, and used for smoke screen work. The plant was not operating.

Titanium oxide, made on the plant, was mixed with ground coke (2 parts TiO<sub>2</sub> and 1 part C). This was briquetted, using waste sulphite-cellulose liquor. An ordinary coal briquetting machine was used, forming egg shaped briquettes about 10 cms. by 5 cms. These were dried by calcining in a small gas fired rotary furnace. No precautions were taken to maintain a reducing atmosphere and the briquettes showed signs of combustion on the surface. This furnace was about 12 m. long and 1 m. diameter.

The hot briquettes were fed intermittently into the chlorination tower. This was a brick lined steel vessel, about 4 m. high and 1.5 m. diameter. No external heating was needed, the reaction being exothermic. Ash was removed periodically from the bottom of the tower. Titanium tetrachloride vapour passed out at the top of the tower, first through a cyclone dust collecting chamber, then

through a filter of glass wool. It was condensed in iron coils, sprayed outside with water.

The reaction was adjusted so that practically all the chlorine was absorbed. The gases after condensing  $TiCl_4$  were sprayed with water and discharged to atmosphere.

#### MANUFACTURE OF FLUSSMITTEL - V.26.

About 100 tons per month of titanium oxide went to the vitreous enamel industry. The bulk of this went to I.G. to be made up by them into a pre-smelt of sodium titanium silicate, and marketed by them as V.26. This was made at Leverkusen under the direction of Dr. Heimsoeth.

The plant consisted of a number of small drum type mixers, two batch rotary frit furnaces, gas fired, and a small mill for frit grinding.

The raw material mix was :-

Quartz flour	27.5 Kg.
Titanium Oxide	39.8 "
Soda	49.6 "
Sodium nitrate	2.9 "
Sodium silicofluoride	2.5 "
Fluorspar	3.7 "

The mixed batch was heated to about  $1100^{\circ}C$ . and the fluid melt poured out into water. This frit was then dried, ground and packed.

Its approximate composition was :-

TiO <sub>2</sub>	39%
Na <sub>2</sub> O	28/50%
SiO <sub>2</sub>	23/30%
CaF	Balance

49182/1350/23.4.46./PSC/27.59.2.