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THE R. & H. CHEMICALS DEPARTMENT
E.I. du Pont de Nemours & Co., Inc.
Chemical Division--Niagara Falls
June 5, 1933.

Preparation of Titanium Pigments from Titanium Ores (N3349)

By: A. A. Levine
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Summary of Work to Date

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OBJECTIVES

1. To briefly summarize methods found in making a literature study of the preparation of titanium tetrachloride.

2. To summarize laboratory work covered to date on the preparation of titanium tetrachloride.

INTRODUCTION

In recent years titanium pigments have increased in use for the reason that they have a better covering power than the ordinary pigments. The subject of titanium pigments became of interest to the R. & H. Chemicals Department on account of findings of the Experimental Station who were working on the problem for the Krebs Pigment Co. They found that the titanium oxide made by way of hydrolysis of the tetrachloride gave a pigment in the rutile form which as far as is now known is the only way to obtain that particular form.

Successful development of a process for producing a satisfactory titanium pigment by way of the chlorides of titanium will provide an outlet for 25 to 38 tons of chlorine per day according to a statement by Dr. Keats of the Experimental Station.

The methods used by the Titanium Pigment Co. and the Commercial Pigments Corporation are very similar in nature and are carried out essentially as follows: The "ilmenite" ore is digested in 70.0% sulfuric acid until the greater per cent of the titanium oxide and ferric oxide are dissolved. This produces a cake low in residual acid. The cake is leached with water and the residue reworked with subsequent batches. Scrap iron is added to the solution to reduce all iron to the ferrous state. About 80.0% of the iron is removed as crystallized sulfate by cooling. The solution is clarified and the hydrolysis step carried out to produce the titanium dioxide.

The titanium dioxide formed in this way is prepared for use by calcining at 850°C. The pigment formed in this way is the anatase form which is not the best form of the pigment.

It has been found at the Experimental Station that the titanium oxide obtained from the hydrolysis of titanium tetrachloride gives the desired form upon calcining. Their preliminary cost estimates show that the most economical place of producing titanium tetrachloride is at the Niagara Falls Plant.

A literature search has been made to determine the present known methods for preparing titanium tetrachloride. A process was next laid out on paper which appeared to be the simplest and most economical to apply on a commercial scale. The various steps were then tried out on a laboratory scale in order to determine the feasibility of the process and if possible to obtain weighed yields in the various steps.

CONCLUSIONS

1. The preparation of titanium tetrachloride by the process outlined is chemically feasible.

2. A form of titanium carbonitride has been prepared in a laboratory scale arc furnace in 1500 - 2000 gram lots. The analysis does not differentiate between titanium as metal, carbide, nitride or oxide, hence it is not known to what extent the titanium oxide was reduced. The material produced was iridescent, brittle and gave a smooth fracture upon breaking. It conformed to descriptions of the material by Moissan in his book "The Electric Furnace".

3. The electric furnace product was readily chlorinated at 200 - 600°C. Preparation of titanium tetrachloride was rapid at first but tapered off after a few hours of operation.

A yield of 50 - 55% on titanium tetrachloride was obtained based on the titanium content of the carbide and the titanium tetrachloride found in the chlorination product.

Since chlorination was carried out as high as 500°C for several hours and titanium carbide chlorinates readily at 200°C it is quite probable that the electric furnace reduction was not more than 60 - 70% complete.

RECOMMENDATIONS

It is recommended that:-

1. The Experimental Station and the Krebs Pigment and Color Corporation make an economic study of the problem in line with the proposed method of manufacturing titanium tetrachloride.

2. Further laboratory work be held up on the problem until a decision has been reached on the basis of the above recommendation.

SUMMARY

Methods of preparing titanium tetrachloride from ilmenite ore were reviewed as recorded in the patent literature and R. & H. reports. The methods recorded involved briquetting of the ore with carbon and chlorinating at 800°C., first by reduction of iron oxide at 800 - 900°C with subsequent leaching with ferric chloride to remove the iron and final briquetting with carbon and chlorinating at 800°C and also selective chlorination of the iron and titanium at different temperatures after reduction of the iron with carbon at 800 - 900°C. Other records were found to show that the electric furnace product, titanium carbonitride, could be chlorinated at 200 - 500°C. After a review of these methods a process was laid out as follows:-

SUMMARY (Cont'd.)

1. Electric furnace fusions of ilmenite and carbon to form the carbonitride which is a reduced concentrate of titanium carbide and titanium nitride.

2. Crushing and sizing of the product.

3. Chlorination of sized product at 200 to 500°C.

4. Purification of the crude titanium tetrachloride by redistillation.

This lay-out seemed to involve the least amount of mechanical handling and the least number of steps in going from the crude ore to the finished product. All four steps were carried out successfully on the laboratory scale. Weighed yields were taken on the chlorination step but exact data on these yields are in doubt since difficulties were experienced with methods of analysis which have not been ironed out as yet.

DISCUSSION OF KNOWN METHODS FOR PREPARING TITANIUM TETRACHLORIDE

(See "Literature and Patent References Relative to the Chloride Processes for Preparing Titanium Oxide", Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, April 24, 1933.)

Various methods have been suggested for the chlorination of ilmenite ore to form titanium tetrachloride. A few of these methods are recorded briefly in the following:

The ore has been finely ground, mixed with soft coal, coked, crushed and sized, dried and chlorinated at temperatures around 650 - 750°C. The crude product was then purified by distillation.

In other processes the ore is briquetted with carbon using a starch paste as a binder, drying and chlorinating as suggested in the first case.

One process was mentioned in which the ore was briquetted with carbon and heated to around 800 - 900°C to reduce the iron. The reduced product was then chlorinated at 350°C to remove the iron. The temperature was then raised to 550 - 600°C and chlorine fed in the opposite direction to prepare the titanium tetrachloride.

Another variation is mentioned in which the ore is reduced at 800 - 900°C with carbon and the iron next extracted with iron chloride leaving the concentrated titanium oxide. This oxide was then briquetted with carbon, dried, and chlorinated at 550 - 600°C and the product purified by distillation.

In this plant in 1924 titanium tetrachloride was made by direct chlorination of titanium carbide or carbonitride. See report

DISCUSSION (Cont'd.)

"Preparation of Titanium Tetrachloride from Titanium Carbide", D. O. Notman, May 8, 1924. Mr. P. S. Brallier of the Niagara Smelting Corporation also described this method in Volume 49 "Transactions of the American Electro Chemical Society" for 1926. It is our understanding that the carbide is a product of the electric furnace fusion of a titanium ore with an excess of carbon.

It may be noted that the earlier processes involve briquetting, extractions, high temperatures, endothermic reactions with difficult conditions for applying heat and other mechanical steps that would contribute towards high cost.

After a review of these various methods a process was laid out on paper as shown in the following section:-

PROPOSED PROCESS FOR THE PREPARATION OF TITANIUM TETRACHLORIDE

See attached flow sheet, blue print No. 1.

In the electric furnace the oxides of iron and titanium should be reduced to the carbide or nitride formed and should be recovered in the form of a dense, brittle mass which could be easily crushed and sized for convenient chlorination. By this method handling should be simplified since there is no briquetting involved.

The chlorination step is exothermic and on a large scale should require cooling instead of the application of outside heat as in the case of the briquetted ores. The chlorination reaction should occur between 200 - 400°C, a much lower temperature than required for direct chlorination of the ores, hence as a result there should be much less wear and tear on the equipment. The crude product should be readily purified by fractional distillation of such materials as dissolved chlorine and ferric chloride.

EXPERIMENTAL WORK

A. Electric Furnace Fusion - See blue print No. 2.

1. Power Source

200 K.V.A. transformers tapped for 20, 40, 60 and 80 volts to supply 10,000, 5,000, 2,500 and 2,500 volts respectively. A volt meter and ammeter were available for proper control.

2. Electrodes

The electrodes were 1-1/2 inch carbon or graphite, movable so that the arc could be readily controlled.

3. Fusion Crucible

Although in the earlier fusions a graphite crucible was mounted below the electrodes, in the final method of operation developed a square box was made of 1/2 inch graphite plates. The dimensions

EXPERIMENTAL WORK (Cont'd.)

A. Electric Furnace Fusion

3. Fusion Crucible (Cont'd.)

of the box were approximately 8" x 8" x 8". The electrodes met in the top of the box after passing through holes in the side. The box was insulated by Sil-O-Cel brick to give the highest efficiency possible from the arc.

4. Operation of the Furnace

a. Charge:- Although no analyses were furnished with the ilmenite ore supplied by the Krebs Pigment and Color Corporation a typical analysis was given in the patent literature as follows:-

Titanium oxide	53.66%
Ferrous oxide	17.09%
Ferric oxide	18.68%
Zirconia	0.94%
Alumina	1.12%
Silica	3.80%
Calcium oxide	0.72%
Manganese oxide	1.36%
Phosphorus anhydride	0.84%
Loss on ignition	0.70%
Total	98.91%

In the first 5 runs ilmenite ore and carbon (approximately 100 mesh coke or charcoal) were mixed in the ratio of 1000 grams ore to 330 grams carbon. In the last fusion made the carbon was increased to 660 grams.

In the earlier runs the charge was placed in a 4" by 5" graphite crucible in small amounts but in later runs the crucible consisted of the graphite box as shown and the charge made up of 8 - 10 lbs. of material. The charge was placed in the lower part of the furnace with the electrodes converging about 2" above and in the center of the charge. The furnace was then covered to prevent the circulation of air as much as possible.

b. Fusion:- Various voltages were tried. 60 volt operation proved to be too severe as the arc could not be well controlled. In one run at this voltage the Sil-O-Cel brick was volatilized during 5 minutes operation. The following run was made at 20 volts without satisfactory results since the arc could not be maintained without holding the electrodes together by hand. 40 volts operation proved to be quite satisfactory since the arc was easily maintained and a constant load of 1600 amperes could be held with frequent adjustment of the electrode spacing. The best runs were made at 40 volts and 1600 amperes for 25 minutes. Two good batches were made under these conditions in which 1800 and 2000 grams of the fusion product were obtained.

EXPERIMENTAL WORK (Cont'd.)

A. Electric Furnace Fusion (Cont'd.)

5. Description of the Fusion Product

Since the heat was applied above the charge, the product appeared on top in the form of a lump approximately 1" thick in the center tapering to the edges, 6" wide and 8" long.

The best product was readily crushed in a crusher and sized to 4 - 8 mesh which made a very convenient form for chlorination. The material was hard and brittle, and had a slight iridescent appearance. The best part was free from blow holes while that near the edges of the lump often contained blow holes and grains of unreduced ilmenite.

The samples for best chlorination runs were selected from the crushed and sized material, care being taken to select the most dense material with no oxide coating on the surface.

6. Discussion of Fusion Product

This laboratory was inexperienced in the appearance of a good form of the carbonitride. It was recognized that our methods of analyses, which were not thoroughly worked out, would not differentiate between the metal, carbide, nitride or oxide since it was expected that if all oxide was not converted to the reduction product, complete chlorination would be difficult in subsequent chlorination steps. There are difficulties to overcome in the higher temperature fusion on the small scale that may be readily overcome on large scale operation. This point may be checked by obtaining the carbonitride from the Titanium Alloys Co. which is made in their regular electric furnace reduction of titanium ores and then making a comparative chlorination run.

B. Chlorination Furnace Operation - See blue print No. 3.

1. Furnace Charge and Chlorine Supply

A sample of carbonitride was selected from the 4 to 8 mesh material. This sample was so selected that it would be as free as possible from blow holes and oxide film. 210 grams was used in Run No. 3, while 125 grams was used in Runs No. 4 and 5.

Chlorine was supplied from a small weighed chlorine cylinder. The chlorine rate was controlled by its movement through a sulfuric acid bubbler.

2. Chlorination Temperature

In the second run it was noted that chlorination started a little above 200°C and titanium tetrachloride collected in the balloon flask. In subsequent runs the furnace was operated at 400 - 500°C

EXPERIMENTAL WORK (Cont'd.)

B. Chlorination Furnace Operation (Cont'd.)

2. Chlorination Temperature (Cont'd.)

since yields of titanium tetrachloride were the chief interest and not the chlorination temperature or the selective effect of chlorine on iron and titanium at varying temperatures.

3. Operation of the Furnace

The furnace was raised to the desired temperature and the chlorine feed started. The rate of 40 - 60 grams of chlorine per hour was maintained for the first 2 or 3 hours after which the rate was gradually reduced to 15 - 20 grams per hour. The runs were continued for 10 to 20 hours.

The titanium tetrachloride was collected in the balloon flask throughout the run. Ferric chloride collected in a cold part of the furnace tube and at times caused a restriction. At such times this part of the tube was heated with a free flame to drive the iron on through to the balloon flask.

A record was maintained of the chlorine used and 50 - 100% excess of chlorine was added before the run was stopped. The run was usually stopped when the feed rate was between 5 and 10 grams of chlorine per hour and a large percentage of the chlorine was carried on through the furnace. When chlorination was stopped the titanium tetrachloride was distilled over into the receiving flask and weighed. This product contained small amounts of chlorine and ferric chloride in suspension.

4. Purification of Crude Titanium Tetrachloride

The material obtained from the chlorination was purified by distillation in a long necked flask with a Kjeldahl distilling head. The product boiled at a constant temperature around 135°C.

It was noted in the distillation that free chlorine was first refluxed off. This was followed by the collection of amber colored crystals along the neck of the distilling flask and walls of the condenser. These crystals collected sometime before the titanium tetrachloride begain to distill over. The first fractions of titanium tetrachloride were colored by this material but the product gradually became whiter in color until it was almost water-white near the end of the distillation.

The product showed only traces of iron when dissolved in acid and tested with thiocyanate. No quantitative test was made. It is thought that the amber color in the product is probably due to an oxychloride or partial hydrolysis product of the titanium tetrachloride.

EXPERIMENTAL WORK (Cont'd.)

C. Yield Data

Due to the high temperatures, dusting losses, and small scale on which fusions were made it was not possible to obtain weighed yields.

1. Chlorination Runs

Five chlorination runs were made. Runs No. 1, 2 and 4 were not satisfactory due to accidents during operation. Methods of analysis at this time were not thoroughly checked to the point where a yield could be taken as 100% reliable. However, the figures are given for Runs No. 3 and 5 and should show definitely the trends in the experimental work.

Run No. 3

Wt. of carbonitride chlorinated	219 g.
Wt. of titanium tetrachloride recovered	189 g.
Titanium carbide equivalent in the carbonitride used	55%
Titanium carbide equivalent accounted for in furnace residue, condenser system and converted to recovered titanium tetrachloride	101.32 g.
Titanium carbide equivalent accounted for in the system	84.0%
Titanium carbide equivalent recovered as titanium tetrachloride	49.3%
Titanium carbide equivalent found in the condenser system	2.75%
Titanium carbide equivalent remaining in the chlorinating furnace residue	31.4%

Run No. 5

Wt. of carbonitride chlorinated	125 g.
Wt. of titanium tetrachloride recovered	117.3 g.
Titanium carbide equivalent in the carbonitride used	55.58%
Titanium carbide equivalent recovered as titanium tetrachloride	54%

Further analyses were not made.

Reference:- Notebook N.F. 365, pp. 1-39.

MLR:MCH

Copies to: Vault
Exec.
Chem.
Levine
M.L.Ross
N3349
~~H.K.~~
L.M.Wilson
Kratz - Experiments

MES
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