1   KEKER & VAN NEST LLP
    STUART L. GASNER - # 164675
2   sgasner@kvn.com
    SIMONA A. AGNOLUCCI - # 246943
3   sagnolucci@kvn.com
    KATHERINE M. LOVETT - # 276256
4   klovett@kvn.com
    633 Battery Street
5   San Francisco, CA 94111-1809
    Telephone: 415 391 5400
6   Facsimile: 415 397 7188

7   Attorneys for WALTER LIEW,
    USA PERFORMANCE TECHNOLOGY, INC.
8
                        UNITED STATES DISTRICT COURT
9
                      NORTHERN DISTRICT OF CALIFORNIA
10
                         SAN FRANCISCO DIVISION
11

UNITED STATES OF AMERICA,	Case No. CR 11-0573-JSW (NC)
Plaintiff,	**DECLARATION OF CHRISTINA M. BLAIS IN SUPPORT OF MOTION TO COMPEL AMENDED BILL OF PARTICULARS**
v.	
WALTER LIEW, CHRISTINA LIEW, USA PERFORMANCE TECHNOLOGY, INC., and ROBERT MAEGERLE,	
Defendants.	Date: October 3, 2013 Time: 2:00 p.m. Place: Courtroom 11, 19th Floor Dept.: Hon. Jeffrey S. White

PUBLIC VERSION (REDACTED)

EXHIBITS C-H FILED UNDER SEAL

DECLARATION OF CHRISTINA M. BLAIS IN SUPPORT
OF MOTION TO COMPEL AMENDED BILL OF PARTICULARS
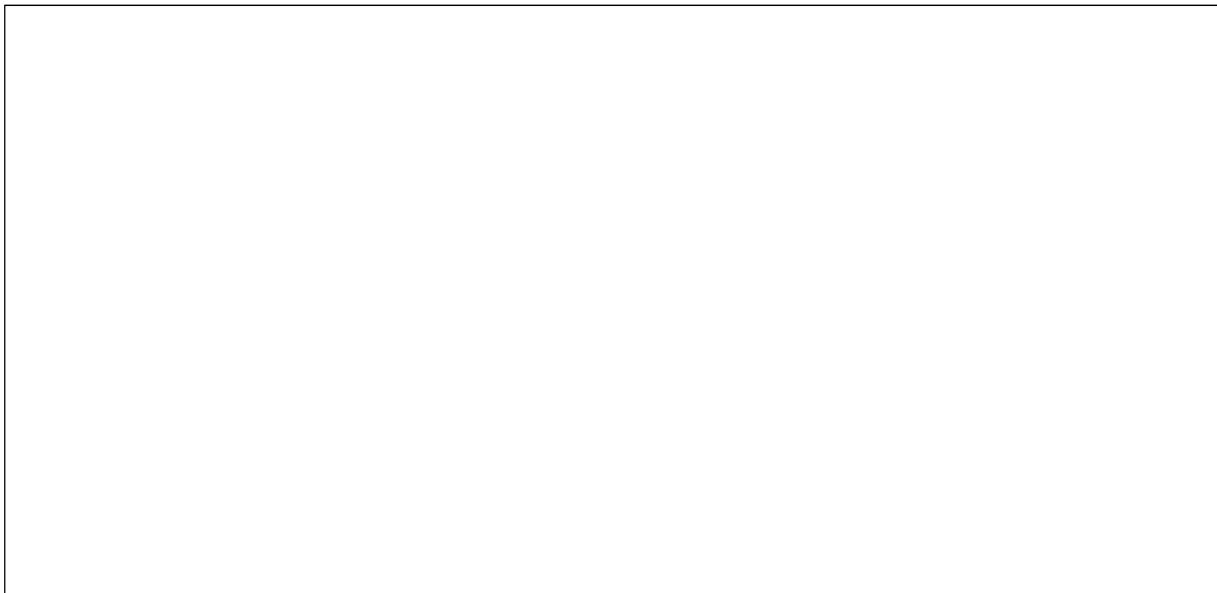Case No. CR 11-0573-JSW (NC)

768427.03

1   I, CHRISTINA M. BLAIS, declare and state that:

2   1.   I am an attorney licensed to practice law in the State of California and am an

3   attorney with the law firm of Keker & Van Nest LLP, located at 633 Battery Street, San

4   Francisco, California 94111, counsel for defendants Walter Liew and USA Performance

5   Technology, Inc. in the above-captioned action. I am not admitted to practice law before this

6   Court. Except where expressly stated, I have knowledge of the facts set forth herein, and if called

7   to testify as a witness thereto, could do so competently under oath.

8   2.   Attached hereto as Exhibit A is a true and correct copy of the August 5, 2013

9   Disclosure Statement of Robert Gibney, bearing the Bates numbers PTI-001269 through PTI-

10   001278.

11   3.   Attached hereto as Exhibit B is a true and correct copy of the August 5, 2013

12   Disclosure Statement of Jim Fisher, bearing the Bates numbers PTI-001247 through PTI-001257.

13   4.   Attached hereto as Exhibit C is a true and correct copy of a document provided by

14   the Government in its May 31, 2013 Rule 16 specification, entitled "361951_Yahoo (Yahoo

15   Mail) Search_entry #266373411_Attached to Email." Pages 24 and 25 of Exhibit C contains the

16   following excerpts:

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DECLARATION OF CHRISTINA M. BLAIS IN SUPPORT OF JOINT REPLY FOR BILL OF
PARTICULARS
Case No. CR 11-0573-JSW (NC)
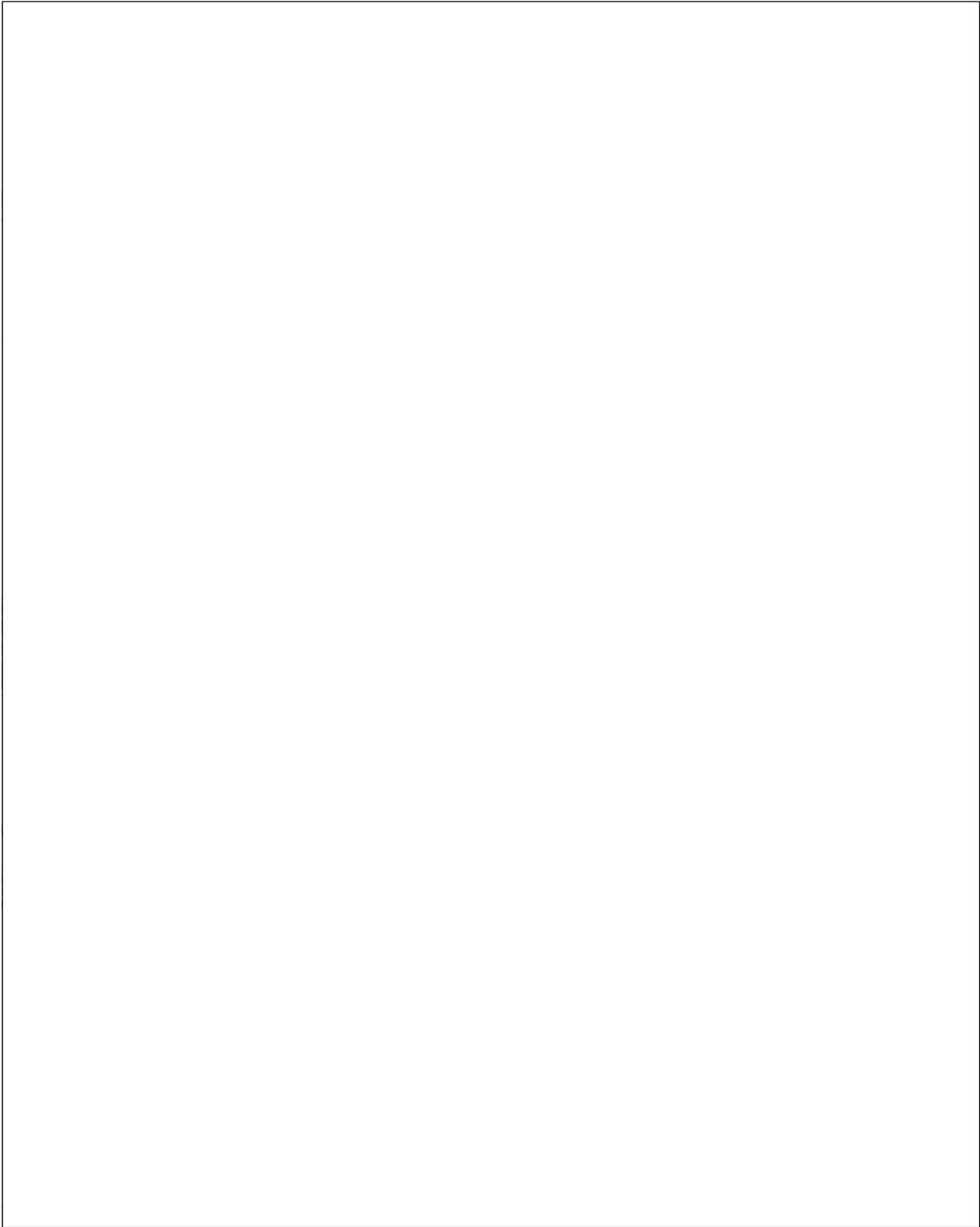
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7   5.   Attached hereto as Exhibit D is a true and correct copy of a document provided by

8   the Government in its May 31, 2013 Rule 16 specification, entitled

9   "O22_PROCESS_VOLUME_1_00006.pdf." Exhibit D contains the following excerpt:

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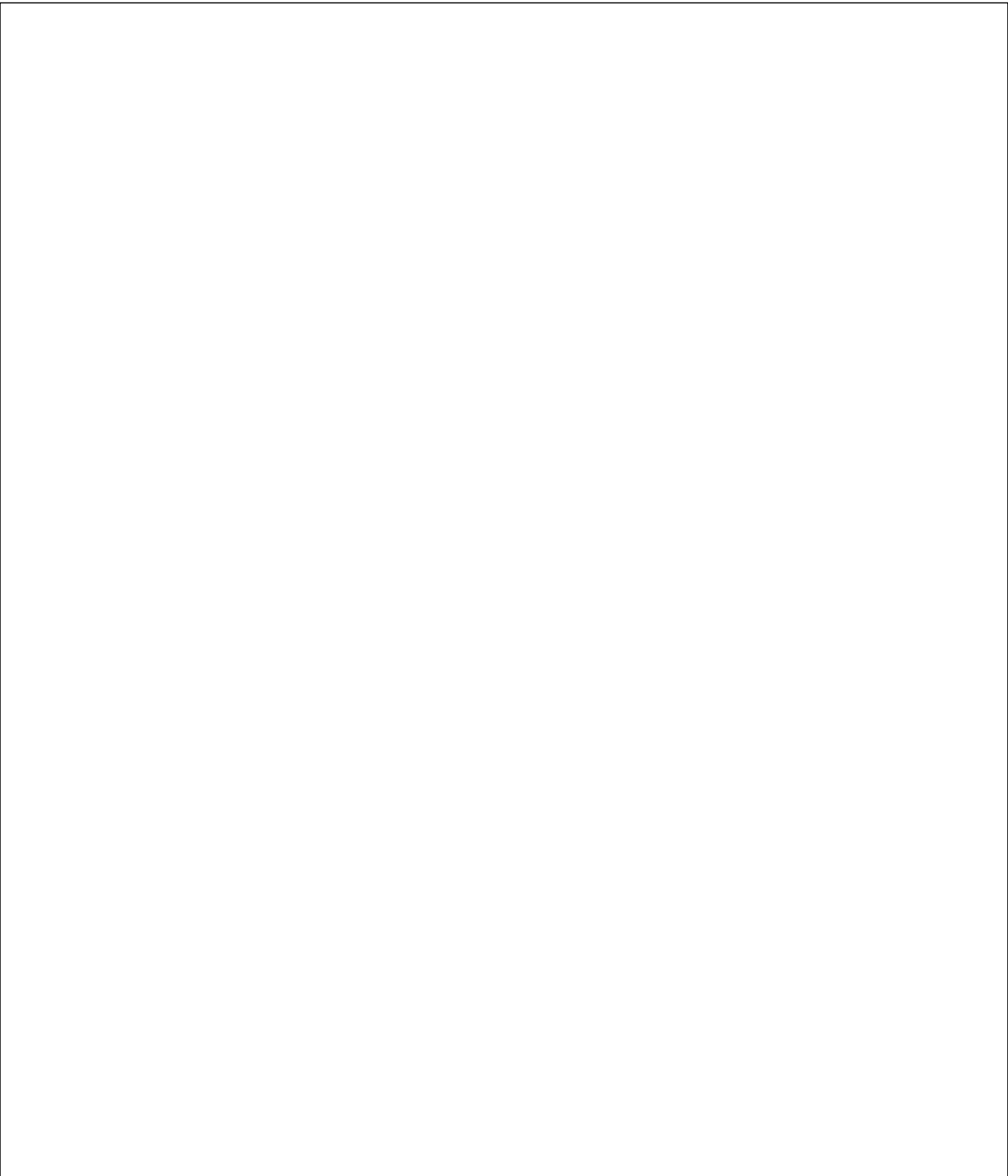14

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22   6.   Attached hereto as Exhibit E is a true and correct copy of a document provided by

23   the Government in its May 31, 2013 Rule 16 specification, entitled

24   "H2_OPERATIONAL_DESC_00002.pdf." Exhibit E contains the following excerpts:

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DECLARATION OF CHRISTINA M. BLAIS IN SUPPORT OF JOINT REPLY FOR BILL OF
PARTICULARS
Case No. CR 11-0573-JSW (NC)

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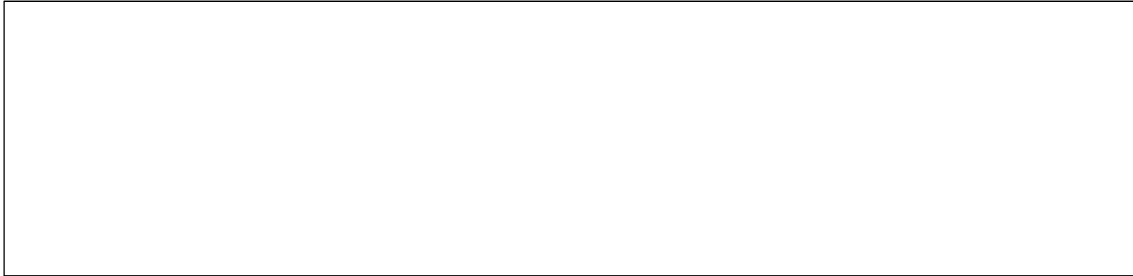
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25   7.   Attached hereto as Exhibit F is a true and correct copy of a document provided by

26 the Government in its May 31, 2013 Rule 16 specification, entitled "100K_PFD[303866].pdf."

27 Exhibit F contains the following excerpts on drawing number PFD-012:

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DECLARATION OF CHRISTINA M. BLAIS IN SUPPORT OF JOINT REPLY FOR BILL OF
PARTICULARS
Case No. CR 11-0573-JSW (NC)

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20   8.   Attached hereto as Exhibit G is a true and correct copy of a document provided by

21   the Government in its May 31, 2013 Rule 16 specification, entitled "OXIDATION[364815].doc".

22   Exhibit G contains the following excerpt:

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1   9.   Attached hereto as Exhibit H is a true and correct copy of a document provided by

2   the Government is its May 31, 2013 Rule 16 specification, entitled

3   "O30_WHITE_BINDER_1_00024.pdf." Exhibit H contains the following excerpts:

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14   10.   I am informed and believe that Keker & Van Nest partner Stuart Gasner met and

15 conferred with Assistant United States Attorney ("AUSA") John Hemann on July 10, 2013

16 regarding the Government's Bill of Particulars.

17   11.   Attached hereto as Exhibit I is a true and correct copy of a July 8, 2013 email from

18 AUSA John Hemann to Stuart Gasner, Peter Axelrod, Doron Weinberg, and Jerry Froelich.

19   12.   Attached hereto as Exhibit J is a true and correct excerpt from *Titanium Its*

20 *Occurrence, Chemistry and Technology*, by Jelks Barksdale, p. 480-508 (2nd ed., 1966).

21   I declare under penalty of perjury under the laws of the United States that the foregoing is

22 true and correct to the best of my knowledge, and that this declaration was executed on August

23 28, 2013 at San Francisco, California.

24
25
26   *C. R*

27   CHRISTINA M. BLAIS

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DECLARATION OF CHRISTINA M. BLAIS IN SUPPORT OF JOINT REPLY FOR BILL OF
PARTICULARS
Case No. CR 11-0573-JSW (NC)

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EXHIBIT A

DISCLOSURE STATEMENT
August 5, 2013

Robert Gibney

Background and Qualifications

Mr. Gibney has over 28 years' experience in the titanium dioxide (TiO2) industry, beginning his career with DuPont's national chemical distributor, Van Waters & Rogers (VW&R, now known as Univar) as a paint industry specialist, selling DuPont's TiPure brand of TiO2 throughout the north Texas territory. After 5 years with VW&R, he joined Kerr-McGee as a sales representative selling Kerr-McGee's Tronox brand of TiO2 in the Texas, Oklahoma, Arkansas territories. Mr. Gibney was promoted rapidly to a succession of management positons, eventually becoming Vice President Global Pigment Marketing, responsible for negotiating long-term contracts with the major TiO2 consumers around the world, including Akzo Nobel, PPG and Sherwin Williams, all three of which were and still are major customers of DuPont.

In 2002 Mr. Gibney moved to Canada to become Chief Marketing Officer of Avestor, a high technology lithium battery startup, which was jointly owned by Kerr-McGee and Hydro Quebec. Following his assignment in 2005 he moved back to the TiO2 division as Vice President and General Manager of Paper and Specialties, focusing on Kerr-McGee's German manufacturing operations where the majority of their specialty TiO2 products were produced. Also in 2005, following an activist shareholder run by Carl Icahn, Kerr-McGee decided to evaluate a spin off or sale of the TiO2 business. In the fall of that year, the TiO2 business issued shares under the new company name of Tronox and was eventually spun off to Kerr-McGee shareholders in March of 2006. Mr. Gibney became the Vice President of Investor Relations for the new Tronox and held that position until 2007, when he became VP Corporate Affairs, adding Government Relations and Communications responsibilities. In 2008 he added Human Resources and in 2009 Global Supply Chain, eventually becoming Senior Vice President Global Supply Chain and Chief Administrative Officer. During the company's restructuring between 2009 and 2011, Mr. Gibney also became the acting Managing Director of the Botlek chloride route TiO2 plant.

Following the completion of the Exxaro acquisition by Tronox in August of 2012, Mr. Gibney decided to leave Tronox and is now a full time consultant, specializing in the TiO2 and Mineral Sands industries.

List of Information Reviewed

Attached as Exhibit A to this disclosure is a list of items reviewed by Mr. Gibney in conjunction with this report.

1

DISCLOSURE STATEMENT
August 5, 2013

Subjects of Expert Testimony

1) Mr. Gibney will describe TiO2 as a product – what it is and how it is used. He will provide basic information regarding the types of products in which TiO2 is an ingredient or component, and the different quality levels of TiO2 that are required for different purchasers and products.

2) Mr. Gibney will describe how TiO2 is made. He will describe both the sulfate-route process and the chloride-route process. He will provide information regarding the modern development of these two basic manufacturing processes. Mr. Gibney will explain the costs and benefits of the two processes.

     i. The main benefits of the chloride-route technology are that: (1) it is more efficient; (2) it is cleaner from an environmental standpoint; (3) it has lower fixed costs; and (4) it provides better control of particle size distribution.

3) Mr. Gibney will testify regarding the ways in which major TiO2 manufacturers develop TiO2 production capacity, including by adding on to existing facilities and developing brownfield and greenfield facilities. He will identify the most recent greenfield chloride-route facilities and when they were developed. He will testify that TiO2 manufacturers typically increase production capacity through debottlenecking and by adding new lines alongside existing facilities. Mr. Gibney will explain that greenfield facilities are rare and both difficult and expensive to build.

    a. Kuan Yin is the last ground-up greenfield chloride-route plant to have been constructed. No new chloride-route plant has been built since 1994. This makes information regarding Kuan Yin, including the Basic Data Document, very valuable to a company considering building a new facility.

    b. Kerr-McGee built its most recent chloride route TiO2 plant in 1991, using the same chlorination and oxidation technology in use today at its two other production facilities.

    c. Kronos built their last chloride route facility in 1992, using the same chlorination and oxidation technology in use today.

    d. The rest of the growth in the chloride-route industry has been through debottlenecking and by adding additional lines at existing production facilities. Historically, this is how companies increase their capacity.

DISCLOSURE STATEMENT
August 5, 2013

4) Mr. Gibney will describe the TiO2 manufacturing market. He will provide information regarding the major producers of TiO2 in the market, the types of product they produce, and their customer base.

5) He will testify regarding DuPont's position in the market and the quality and uses of DuPont's product. He will provide information regarding DuPont's TiO2 manufacturing capacity and explain the DuPont is the market leader in TiO2 sales, production capacity, and manufacturing efficiency. He will testify that DuPont's quality is consistently the best in the industry.

   a. Mr. Gibney will explain that DuPont's technology differential explains its success.

6) Mr. Gibney will testify that the major TiO2 manufacturers who utilize the chloride-route method of production closely guard their proprietary technology, including their chlorination and oxidation processes, and that the particulars of that technology are not known to competitors in the market. He will explain that certain information is available through patents and through satellite imagery, but that they key technology that provides a competitive differential is hidden and is not available to competitors in the industry.

7) Mr. Gibney will testify that the major TiO2 manufacturers, including DuPont, rarely license their chloride-route TiO2 manufacturing technology to others in the industry. He will testify that, historically, there are only a few examples of manufacturers licensing their technology. This practice stopped in approximately 1991.

   a. The only example of DuPont licensing its chloride-route technology was in respect of the plant at 2900 Middle Road, Ashtabula, Ohio, which later came to be known as Ashtabula-1. The original operator was Sherwin-Williams, when the plant was commissioned in 1970. Sherwin-Williams designed the chlorination section of the 25,000 t.p.a. plant; DuPont designed the oxidation section. Sherwin-Williams sold this plant to SCM in 1975 and it is nowadays owned by Cristal. This was the last incidence of DuPont licensing its chloride-route technology. Cristal does not license its technology and the design of the Ashtabula oxidation reactor is not available publicly or to competitors in the industry.

   b. Kerr-McGee, which has amongst the least efficient technology with the lowest line rate in the industry, was the most active in licensing its technology. Kerr-McGee stopped in the early 1990s. No other company licenses.

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DISCLOSURE STATEMENT
August 5, 2013

    c. Kerr-McGee licensed to Cristal in the early 1990s. In order to build the plant and teach the new employees the technology and knowledge necessary to run a chloride plant, Kerr-McGee sent several employees to the Cristal Saudi Arabia facility for 2-3 years.

8) Mr. Gibney will testify that the Ashtabula TiO2 plant is not an efficient plant and does not produce the quantity or quality of TiO2 that DuPont's other, more modern, plants produce. He will testify that he does not know how the major components of the Ashtabula plant are designed, because the information regarding that design is not publicly available. The current owner of the Ashtabula facility, Cristal does not license its technology.

9) Mr. Gibney will testify that DuPont's chloride-route process is unique and that aspects of that process are proprietary to DuPont. He will testify that DuPont's competitors are not aware of aspects of DuPont's process that contribute to DuPont's ability to maximize output and efficiency, while maintaining quality. He will testify that the DuPont's ability to keep its process secret gives it a competitive advantage in the market.

10) Mr. Gibney will testify that the major components of the chloride-route process are similar amongst the major manufacturers – that each has chlorination, oxidation, and finishing phases and that the technology used in each phase is similar, but not the same. He will testify that the differences in these components are what provide competitive advantages in output, efficiency, and quality. He will testify that DuPont's technology in the key phases of the process is a "black box" to competitors and competitors spend considerable time and effort attempting to discern, legally, DuPont's designs, methods, and processes.

11) Mr. Gibney will testify that the basic chloride-route technology has not changed much since the 1980s and 1990s, and that company's maintain their competitive advantage by keeping their unique technology secret. The technology at issue in this case, even though it is from the 1980s and 1990s, is still very valuable, particularly to someone designing or building a greenfield facility.

12) Mr. Gibney will testify regarding titanium dioxide production and consumption in the PRC. He will testify regarding the major TiO2 producers in the PRC, the methods of production they use, and the PRC's overall production capacity. He will testify regarding the development of chloride-route manufacturing facilities in the PRC. Mr. Gibney will testify regarding the consumption of TiO2 by PRC customers, including the types and uses of TiO2 prevalent in the PRC. He will testify to the approximate trade balance

between exports and imports, including the types of TiO2 that are imported and exported by the PRC.

13) Mr. Gibney will testify that DuPont's TiO2 process is unique in the chloride-route manufacturing industry. He will testify that that there are portions of the process that are proprietary, including the design of certain key components. He will testify that there are portions of the process that are available on the market from vendors who make components for other TiO2 manufacturers. He will testify that the way in which DuPont integrates and arranges its manufacturing process is unique. There were items in the process that he was not aware of until he saw the materials for this case. He will testify that DuPont's overall process and certain components are confidential and that their confidentiality is valuable, in that it allows DuPont to retain its existing competitive advantage. If this technology was available, others would replicate it and be able to achieve the manufacturing efficiencies and quality that DuPont has achieved.

    a. One aspect of DuPont's technology that is unique is its ability to use any sort of titanium ore in its facilities, including low grade ilmenite ore. This gives DuPont an enormous cost advantage over competitors, who are able to only use highgrade ore, which can cost double the price of lower grade ilmenite.

    b. DuPont's process yields approximately 18 tons/per line hour, utilizing high pressure oxidation. Other manufacturers are not able to come close to approximating this output.

    c. DuPont's proprietary design results in a very low maintenance spend per ton, which gives DuPont a competitive advantage. Trade Secrets 2, 4, and 5 would assist a competitor in designing a facility with low maintenance spend. The unique DuPont design of the chlorinator and oxidation reactor allow DuPont to go for long periods of time, not replicated elsewhere in the industry, between rebuilds.

    d. The flue pond is unique in a variety of respects, including, importantly, the length of the piping that is used, the serpentine pipe configuration. The length of flue pipe is a key component in the cooling process. Manufacturers such as Tronox are limited in their cooling by the length of the flue pipe and have not been able to master the serpentine coiling of the pipes, which allows for dramatically more time in the cooling zone.

    e. The chlorinator design, including ability to handle blow-over in the chlorination process.

DISCLOSURE STATEMENT
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f.   Spray condenser design.

g.   The oxidation reactor design, including the size of the reactor slot. DuPont uses a high pressure oxidizer, versus Tronox which uses ambient pressure. The complexities of operating a high pressure oxidation line are enormous. Tronox attempted to master the high pressure oxidation technology in the late 1990s and spent a considerable amount of time (5-8 years) and in excess of $25 million, but in the end they failed and wrote off the $25 million and closed down the project.

14) Mr. Gibney has reviewed Trade Secret 2, Edgemoor Plant Drawing. He will explain what the drawing depicts. He will testify that TiO2 manufacturers maintain drawings like these for their TiO2 manufacturing facilities. He will explain that manufacturers maintain the confidentiality of drawings like this in order to protect their proprietary technology. He will testify that this diagram and the information it contains is not publicly available, nor is it available to others in the chloride-route industry. He will testify that this information would be valuable to a company that was designing or building a new TiO2 chloride-route facility because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process. Possessing this information would be very valuable to a person attempting to design a new TiO2 facility from scratch.

15) Mr. Gibney reviewed Trade Secret 3, the Accession Report, including the Diemer Correlation. He will explain what the document is. He will explain that the inner workings of the oxidation reactor are one of the most critical components of the TiO2 manufacturing process and that manufacturers keep the details of their reactor designs confidential. He will testify that it is difficult to determine the correct size of the reactor slot to maximize quality output. He will explain that manufacturers maintain the confidentiality of information like this in order to protect their proprietary technology. He will testify that this information is not publicly available, nor is it available to others in the chloride-route industry. He will testify that this information would be valuable to a company that was designing or building an oxidation reactor because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process. Possessing this information would be very valuable to a person attempting to design a new TiO2 facility from scratch, essentially bypassing the decades of trial and error that resulted in the refinement of the technology.

16) Mr. Gibney has reviewed Trade Secret 4, the DuPont Flow Sheet. He will explain what the drawing depicts. He will testify that TiO2 manufacturers maintain drawings like these for their TiO2 manufacturing facilities. He will explain that manufacturers

DISCLOSURE STATEMENT
August 5, 2013

maintain the confidentiality of drawings like this in order to protect their proprietary technology. He will testify that this diagram and the information it contains is not publicly available, nor is it available to others in the chloride-route industry. He will testify that this information would be valuable to a company that was designing or building a new TiO2 chloride-route facility because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process. Possessing this information would be very valuable to a person attempting to design a new TiO2 facility from scratch.

17) Mr. Gibney has reviewed Trade Secret 5, the Kuan Yin Basic Data Document. He will testify as to what the document is. He will explain that manufacturers maintain the confidentiality of documents like this in order to protect their proprietary technology. He will testify that this diagram and the information it contains is not publicly available, nor is it available to others in the chloride-route industry. He will testify that this information would be valuable to a company that was designing or building a new TiO2 chloride-route facility because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process. Possessing this information would be very valuable to a person attempting to design a new TiO2 facility from scratch.

18) Each of trade secrets 2-5 would have been very valuable to Kerr-McGee because each shows parts of the TiO2 process that Kerr-McGee did not have.

19) TiO2 manufacturers do not allow photographs of the inside of their facilities. The configurations used to arrange components are valuable. When Kerr-McGee mothballed its Savannah, George plant, it went in and cut out and removed the key components so that competitors could not come in and look at what they had.

20) Mr. Gibney will testify that large TiO2 facilities are generally designed by engineering firms based on plans provided by the manufacturers. Legitimate engineering firms would not be capable of designing a new TiO2 plant without having obtained plans from the owner of the proprietary technology.

   a. The technology is exceedingly complex. It is said that of all chemical manufacturing, only cyanide is more difficult to manufacture. On a scale of 1-10, if cyanide is a 10, TiO2 is a 9.

21) Mr. Gibney will testify as to the approximate cost per ton of building a greenfield chloride-route TiO2 factory.

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DISCLOSURE STATEMENT
August 5, 2013

22) Mr. Gibney would testify as to what he would do if his corporatation was seeking to build a chloride-route TiO2 factory – how he would go about the process of designing such a factory. He will testify that he would approach an engineering firm with relevant expertise in designing similar factories. Mr. Gibney will testify that the firm would ask him for a set of plans upon which to base the design.

23) If a well-funded corporation like Pangang Group approached a engineering firm and asked if they would design a TiO2 chloride-route facility, what would the engineering firm ask? It would ask for a set of plans for the design. In other words, the plans would be provided by the manufacturer, not the engineering firm.

24) Mr. Gibney has reviewed Walter Liew's credentials and his 2004 letter. He will testify that that in his opinion it would not be possible to master DuPont's chloride-route method and design a DuPont plant without having obtained DuPont's proprietary technology.

25) Mr. Gibney will testify that in his opinion the technology Walter Liew claimed to have acquired is not available on the market and cannot be licensed by or acquired legitimately from the owner of that technology.

26) While he was an executive of Kerr-McGee, Mr. Gibney had responsibilities that included human resources and operations management. Kerr-McGee hired former DuPont employees for various positions because they were well trained and high-quality; they also hired former employees of other TiO2 manufacturers. The DuPont employees were careful not to share detailed information regarding DuPont design and components, particularly with regard to the chlorinator and oxidation reactor. The former DuPont employees hired by Kerr-McGee would not share the type of information Mr. Maegerle shared with Performance Group and USAPTI.

27) Hypothetical Questions:

    a. If, as an executive of a company able to fund the construction of a 100 mtpy, how would you go about retaining an engineering firm? What information would you be required to provide to the firm? What information would the engineering firm provide to you?

        i. If I was working for a company with enough available capital to construct a 100,000 tonne per year chloride route TiO2 plant (approximately $500 million), I would approach a few reputable global engineering firms to assist with the design and construction. Firms such as Kellogg Brown and Root, Jacobs and Bechtel provide the engineering services necessary to

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DISCLOSURE STATEMENT
August 5, 2013

manage a complicated construction project such as a greenfield TiO2 plant. Bids would be evaluated and a final section would occur. The process would then follow the following steps

- Front end design
- Engineering Procurement & Construction (EPC)
- Commissioning Start-up

1. Front end design: (1-2 years)
My firm would then provide detailed specifications for the proprietary sections of the plant along with previous plant drawings to the engineering firm. The firm would integrate these specification and the previous plant drawings into the new plant design schematic. A team of chemical engineers and representatives from R&D from my firm would be involved from day one, interfacing with the third party engineering firm to work day by day on the drawings and plans, making changes to fit the new plant design and incorporating any new design developments from R&D. The engineering firm would provide back a full set of plans, 3D CAD drawings, construction plans, timeline, equipment list and capital cost estimates. The engineering firm would not be responsible for or able to provide the specifications, because such specifications are proprietary and are not available to the market.

2. EPC: (2-3 years)
A EPC team,would then be put in place to oversee the project, including the engineering firm and members of the R&D and company's engineering team.

3. Commisioning Start-up
A start-up of a chloride route plant can take up to 3-4 years to reach full production capacity. When Kerr-McGee commissioned its last chloride plant in Kwinana, Western Australia, it took from 1991 to 1995 for the plant to be able to produce in specification product at designed production capacity rates. Kerr-McGee provided 10-15 highly experienced plant engineers to the commissioning phase to assist in training the new operators.

b. Would a 10-employee engineering company that does not employ a chemical engineer be capable of designing a 100 mtpy TiO2 factory? Why not? No. In order to construct a state of the art, world-class chloride route TiO2 plant, you

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August 5, 2013

would need the expertise of one of the global engineering firms. DuPont has
traditionally used Bechtel for their plant construction projects. The complexities
of a modern chloride TiO2 plant require a variety of engineering disciplines,
including chemical, electrical, fluid dynamics, mechanical, and pyro metallurgy.
In addition, the TiO2 company would need to provide a large number of experts
to work hand in hand with the global engineering firm in order to design,
construct and commission such a plant.

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EXHIBIT B

DISCLOSURE STATEMENT
August 5, 2013

<u>Jim Fisher</u>

<u>Background and Qualifications</u>

1990 – 2013 CEO and President, IBMA, Inc.
- IBMA, International Business Management Associates, Inc. is an international knowledge based consulting firm, providing specialized consulting services to the TiO2 pigments and minerals industries.
- Founded IBMA, January 1, 1990

Prior Work Experience

1967–1978: Union Carbide Corporation in a number of technical (i.e. R & D Project Scientist) positions and commercial (i.e. Marketing Manager, Silicones) positions.
1978–1989 with NL Industries, V.P. Planning and Technology for Kronos and Rheox for eight years.

Education

- The University of Michigan: B.S.E. (ME) 1966, M.S.E. (ME) 1967.
- Union Carbide Program with Columbia Business School (M.B.A. Equivalent)
- Stevens Institute of Technology (Ph.D. program) – Course Work Only, No Dissertation.

IBMA

- IBMA formed January 1, 1990, in Princeton Junction, New Jersey.
  - Grew to 5 full time employees in 1992.
  - Shrunk to 3 in 1996 as operations became more efficient.
- Focused on two areas:
  1. TiO_2 pigments and minerals – primary focus since 1993
  2. Project finance, mergers and acquisitions.
- IBMA presently operates with two full time employees and numerous associates as needed.
- IBMA has performed work for approximately 100 multinational clients and annually does consulting work for 20 different clients.
  - All of IBMA's clients are large multinational firms, most of whom are located outside the United States.
- IBMA is best known for its specialized work in the TiO_2 pigments and minerals industries.
  - Annually prepares cash production costs for every major TiO_2 pigment plant and major TiO_2 mineral operation.

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- Compiles producer profitability (pre-tax operating income) for major TiO_2 pigment producers.
- Developed TiO_2 pigments and minerals integrated supply/demand forecasting model.
- Prepares biannual TiO_2 pigments and minerals market research, supply, production and selling price forecasts.
- Constructed a chlorination model for converting TiO_2 containing minerals to $TiCl_4$.
- Prepared in depth market research for TiO_2 pigment usage in all major global regions.
- Conducted bench-marking studies for all major TiO_2 pigment producers and major TiO_2 mineral suppliers, focusing on technical issues.
- Co-founder and editorial consultant for bimonthly newsletter, "TiO_2 Worldwide Update".
- Recently updated 466 page Multiclient Report: "TiO_2 Worldwide Review and Outlook"

Information Reviewed by Mr. Fisher

Attached as Exhibit A to this disclosure is a list of items reviewed by Mr. Fisher in conjunction with this report.

Subjects of Expert Testimony

1) Mr. Fisher will describe TiO_2 as a product – what it is and how it is used. He will provide:
   a. Basic information regarding the types of products in which TiO_2 is an ingredient or component in its end uses.
   b. The different quality levels of TiO_2 which are required for different end uses.

2) Mr. Fisher will describe how TiO_2 is made:
   a. In both the sulfate-route process (SP) and the chloride-route process (CP).
   b. Information regarding the modern development of these two basic manufacturing processes.
   c. Benefits of the SP processes.
      i. Readily available technology
      ii. Relatively easy to operate as this is a batch process.
      iii. Produces anatase as well as rutile pigment products. Anatase is preferred in about 10% of end use applications.
   d. Benefits of the CP technology are
      i. Lower costs
      ii. Cleaner
      iii. Produces better rutile type pigment products.

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3) Mr. Fisher will testify regarding the ways in which major TiO_2 manufacturers develop TiO_2 production capacity, including:

   a. Adding on to existing facilities. TiO_2 manufacturers typically increase production capacity through
      i. Debottlenecking existing production lines
      ii. Brownfield facilities: adding new lines alongside existing facilities.

   b. Greenfield facilities: Building new pigment plants at a new site. He will identify the most recent green field chloride-route facilities and when they were developed.
      i. Kuan Yin is the last ground-up green field chloride-route plant to have been constructed. No new chloride-route plant has been built since 1994. This makes information regarding Kuan Yin, including the Basic Data Document, very valuable to a company considering building a new facility.
      ii. Tronox (Kerr-McGee) built its most recent chloride route TiO_2 plant in 1991 at West Australia, using the same chlorination and oxidation technology in use today at its other CP production facilities.
      iii. Kronos built their last chloride route facility in 1992 at Lake Charles, LA, using the same chlorination and oxidation technology they use today.

   c. The rest of the growth in the chloride-route industry has been through debottlenecking and by adding additional lines at existing production facilities. Historically, this is how companies increase their capacity.

4) Mr. Fisher will describe the TiO2 manufacturing industry. He will provide information on
   a. The major producers of TiO_2 in the industry
   b. Types of product they produce and,
   c. Their customer base.

5) He will testify regarding DuPont's position in the industry and end markets, and the quality and uses of DuPont's product. He will provide information regarding
   a. DuPont's TiO_2 manufacturing capacity
   b. DuPont is the market leader in TiO_2 sales, production capacity, and manufacturing efficiency.
   c. DuPont's quality is consistently the best in the industry.
   d. DuPont's superior technology differential advantage explains its success.

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6) Mr. Fisher will testify that the major TiO_2 manufacturers who utilize the chloride-route method of production closely guard their proprietary technology.
   a. Including their chlorination and oxidation processes.
      i. The particulars of that technology are not known to competitors in the market.
      ii. Some information is available through patents and through satellite imagery, but that the key technology that provides a competitive differential is hidden and is not available to competitors in the industry.

7) Mr. Fisher will testify that the major TiO_2 manufacturers, including DuPont do not presently license their chloride-route TiO_2 manufacturing technology to others in the industry. He will testify that, historically, there are only a few examples of manufacturers' licensing their technology. This practice stopped in approximately 1991 when Kerr McGee (now Tronox) last licensed their CP technology to the National Titanium Dioxide Company in Saudi Arabia in a JV called Cristal Pigments, and to the Tiwest JV in West Australia at the same time.
   a. The only example of DuPont licensing its chloride-route technology was with respect to the plant at 2900 Middle Road, Ashtabula, Ohio, which later came to be known as Ashtabula-1. Sherwin-Williams was the original operator of the plant when it was commissioned in 1970. Sherwin-Williams designed the chlorination section of the 25,000 tonne per year plant; DuPont designed the oxidation section. Sherwin-Williams sold this plant to SCM in 1975 and it is nowadays owned by Cristal. This was the last incidence of DuPont licensing its technology. Cristal does not license its technology and the design of the Ashtabula oxidation reactor is not available publicly or to competitors in the industry.

8) Mr. Fisher will testify that the Ashtabula TiO_2 plant is not a state of the art CP plant. It is considered to use first generation CP technology.
   a. It is not an efficient plant and does not produce the quantity or quality of TiO_2 that DuPont's other, more modern, plants produce.
   b. He does not know how the major components of the Ashtabula plant are designed, because the information regarding that design is not publicly available. The current owner of the Ashtabula facility, Cristal does not license its technology.

9) Mr. Fisher will testify that DuPont's chloride-route process is unique and that aspects of that process are proprietary to DuPont.
   a. DuPont's competitors are not aware of aspects of DuPont's process that contribute to DuPont's ability to maximize output and efficiency, while maintaining quality.

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      b. DuPont's ability to keep its process secret gives it a significant competitive advantage in the market.

10) Mr. Fisher will testify that all CP pigment producers utilize the same major components of the chloride-route process
      a. Each CP producer has chlorination, oxidation, and finishing operations and that the technology used in each phase is conceptually similar, but not the same.
      b. Even though DuPont's CP pigment competitors have similar operations, they differ greatly in design, operation and integration into the entire chloride process.
      c. The differences in these operations are what provide DuPont competitive advantages in output, efficiency, and quality.
      d. DuPont's superior technology in these key operations of the CP is a "black box" to its competitors and competitors spend considerable time and effort attempting to discern, legally, DuPont's designs, methods, and processes.

11) Mr. Fisher will testify that the basic chloride-route technology has not changed much since the 1980s and 1990s
      a. CP pigment producers maintain their competitive advantage by keeping their unique technology secret.
      b. The basic CP technology at issue in this case, even though it is from the 1980s and 1990s has been modified and improved since then.
      c. It is still very valuable, particularly to someone designing or building a green field facility.

12) Mr. Fisher will testify regarding titanium dioxide production and consumption in the PRC.
      a. The major TiO_2 producers in the PRC, the methods of production they use, and the PRC's overall production capacity.
      b. The development of the PRC's TiO_2 pigment manufacturing industry.
      c. Its global status today and its competitive position.
      d. The development of chloride-route manufacturing facilities in the PRC.
      e. The consumption of TiO_2 by PRC customers, including the types and uses of TiO2 prevalent in the PRC.
      f. The approximate trade balance between exports and imports, including the types of TiO_2 that are imported and exported by the PRC.

13) Mr. Fisher will testify that DuPont's TiO_2 process is unique in the chloride-route manufacturing industry.
      a. There are many portions of the process that are proprietary, including the design of certain key components.

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b. There are some portions of the CP that are available on the market from vendors who make components for other TiO_2 CP manufacturers.

c. However the way in which DuPont integrates and arranges its manufacturing process is unique and is organized in such a way as to protect its proprietary technology.

d. There were items in the process that he was not aware of until he saw the materials for this case.

e. DuPont's overall CP and certain components are confidential and that their confidentiality is valuable, in that it allows DuPont to retain its existing competitive advantage. If this technology was available, others would replicate it and be able to achieve the manufacturing efficiencies and quality that DuPont has achieved.

    i. One key aspect of DuPont's CP technology that is unique is its ability to use any sort of titanium containing ore in its facilities, including lower cost ilmenite ore. This gives DuPont an enormous cost advantage over competitors, who are able to only use high-grade ore, which can cost double or triple the price of ilmenite.

    ii. DuPont's unique CP technology operates with large line sizes and yields approximately 21 tonnes/per line hour per year (175,000 tonnes per year per line at 8,760 hours per year at a 95% operating rate), utilizing high pressure oxidation. Other manufacturers are not able to come close to approximating this output as the next most efficient CP plant is the Kronos plant in Louisiana with 9.4 tonnes/line hour per year (75,000 tonnes per year per line at 8,760 hours per year at 91% operating rate). This line size advantage enables DuPont to realize significant economies of scale with their very large CP pigment plants.

    iii. The difference in operating rates between DuPont (95%) and Kronos (91%) is due to:

        1) DuPont's greater experience operating CP technology in their large plants. The chemical industry operates with the "Experience Curve" which was prepared by a group of McKinsey consultants with chemical industry companies in the 1970s. The principal conclusion is that with every cumulative doubling in a chemical producer's production of a specific product, the cash cost of production in real (un-inflated) terms is reduced by ~20%. This 20% figure varies with different chemical products, and generally explains the rationale for DuPont consistently enjoying a 20% to 30% cost advantage compared to their pigment competitors. Mr. Fisher was exposed to the Experience Curve while at Union Carbide and has applied it to pigment producers while at Kronos

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and IBMA and found that raw material conversion efficiencies and operating rates are good metrics for demonstrating the advantages of DuPont who has the largest cumulative production experience in the pigment industry.

2) DuPont is recognized in the pigment industry as having the best trained personnel and the most sophisticated operating and control systems.

3) The DuPont 95% figure was communicated to Mr. Fisher by a senior DuPont executive during a consulting assignment. While the Kronos 91% figure is from Mr. Fishers experience with Kronos.

iv. This large DuPont CP line size provides them with another cost advantage in that it is a much more efficient consumer of manpower which averaged 12% of the cash cost of production for all CP plants in 2012. Because of DuPont's larger line size they experience 992 tonnes per man year per line. Conversely Kronos experiences 346 tonnes per man year per line at their efficient Louisiana CP plant. Adjustment to each pigment plant's manpower is made annually by IBMA and includes considerations for the plant's location (hours worked per year per man), complexity of the plants equipment and control systems, and plant equipment sizes, and skill of maintenance and contract personnel.

f. DuPont's proprietary design results in a very low maintenance spend per ton, which gives DuPont a competitive advantage. Trade Secrets 2, 4, and 5 would assist a competitor in designing a facility having a low maintenance spend. The unique DuPont design of the chlorinator and oxidation reactor allow DuPont to go for long periods of time before a shut down between re builds. This is not replicated elsewhere in the industry.

g. The DuPont flue pond is unique in a variety of respects, including, importantly, the length of the piping that is used, the serpentine pipe configuration. The length of flue pipe is a key component in the cooling process. Manufacturers such as Tronox are limited in their cooling by the length of the flue pipe and have not been able to master the serpentine coiling of the pipes, which allows for dramatically more time in the cooling zone.

h. The chlorinator design, including its ability to handle blow-over in the chlorination process and long operating times between shut downs for re bricking.

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    i. Spray condenser design. This has a material impact on the reliability of the chlorination system consisting of the chlorinator, top duct and solids removal system.

    j. The oxidation reactor design, including the size of the reactor slot. DuPont uses a high pressure oxidizer, versus Tronox which uses ambient pressure requiring chlorine gas compression. The complexities of operating a high pressure oxidation line are significant and have material implications on other integrated operations. Tronox attempted to master the high pressure oxidation technology in the late 1990s and spent a considerable amount of time (5-8 years) and in excess of $25 million, but in the end they failed and wrote off the $25 million and closed down the project.

14) Mr. Fisher has reviewed Trade Secret 2, Edgemoor Plant Drawing. He will explain what the drawing depicts:

    a. TiO2 manufacturers maintain drawings like these for their TiO_2 manufacturing facilities.

    b. They scrupulously maintain the confidentiality of drawings like this in order to protect their proprietary technology.

    c. This diagram and the information it contains is not publicly available, nor is it available to others in the chloride-route industry.

    d. This information would be valuable to a company that was designing or building a new TiO_2 chloride-route facility because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process.

    e. Therefore possessing this information would be very valuable to a person attempting to design a new TiO2 facility from scratch.

15) Mr. Fisher reviewed Secret 3, the Accession Report, including the Diemer Correlation. He will explain what the document is:

    a. The inner workings of the oxidation reactor are one of the most critical components of the TiO_2 manufacturing process and that manufacturers keep the details of their reactor designs confidential.

    b. Mr. Fisher is not aware of any other TiO_2 pigment producer having the analytical expertise and competence to develop the very valuable and useful Diemer Correlation.

    c. It is difficult to determine the correct size of the reactor slot to maximize quality output and reliability of this operation.

        i. Manufacturers maintain the confidentiality of information like this in order to protect their proprietary technology.

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        ii.   This information is not publicly available, nor is it available to others in the chloride-route industry.

    d. This information would be extremely valuable to a company that was designing or building an oxidation reactor because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process. Possessing this information would be very valuable to a person attempting to design a new TiO2 facility from scratch, essentially bypassing the decades of trial and error that resulted in the refinement of the technology.

16) Mr. Fisher has reviewed Trade Secret 4, the DuPont Flow Sheet. He will explain what the drawing depicts:

    a. The DuPont Flow Sheet is the first part of the pigment plant design process and is essential to successfully replicating the DuPont CP technology.

    b. TiO_2 manufacturers maintain drawings like these for their TiO_2 manufacturing facilities and that manufacturers maintain the confidentiality of drawings like this in order to protect their proprietary technology.

    c. This diagram and the information it contains is not publicly available, nor is it available to others in the chloride-route industry and this information would be valuable to a company that was designing or building a new TiO_2 chloride-route facility because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process.

    d. Possessing this information would be very valuable to a person attempting to design a new TiO_2 facility from scratch.

17) Mr. Fisher has reviewed Trade Secret 5, the Kuan Yin Basic Data Document. He will testify as to what the document is:

    a. TiO_2 pigment manufacturers maintain the confidentiality of documents like this in order to protect their proprietary technology.

    b. This diagram and the information it contains is not publicly available, nor is it available to others in the chloride-route industry.

    c. This information would be valuable to a company that was designing or building a new TiO_2 chloride-route facility because it provides design information that is not publicly available, especially if the company's goal is to replicate the DuPont process.

    d. Possessing this information would be very valuable to a person attempting to design a new TiO_2 facility from scratch, particularly since the Kuan Yin plant is DuPont's newest CP pigment plant and contains all the current upgrades to their CP technology. It is considered as using third generation CP technology, while. Ashtabula 1 utilizes first generation CP technology.

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18) Each of trade secrets 2-5 would have been very valuable to Kronos or other competitors because each shows parts of the TiO_2 process that they did not have.

19) TiO_2 manufacturers do not allow comprehensive photographs of the inside of their facilities as these photographs verify the design data and provide a good view of the practical aspects of plant layout, equipment sizing and configuration. The configurations used to arrange components are valuable.

20) Mr. Fisher will testify that large TiO_2 facilities are generally designed by engineering firms based on plans (but not calculations) provided by the manufacturers. Legitimate engineering firms would not be capable of designing a new TiO_2 plant without having obtained plans from the owner of the proprietary technology.

  a. The technology is exceedingly complex. It is said that of all chemical manufacturing, only cyanide is more difficult to manufacture. On a scale of 1-10, if cyanide is a 10, TiO_2 is a 9.
  b. This technology is well beyond the capabilities of a contractor to design and build a CP pigment plant without these trade secrets and proprietary pigment producer technology.

21) Mr. Fisher will testify as to the approximate cost per ton of building a green field chloride-route TiO_2 factory:
  a. A green field 175,000 tonnes per year CP pigment plant requiring significant infrastructure is estimated at $700 million ($4,000 per tonne of capacity).

22) Mr. Fisher will offer his opinion that based on the information he reviewed, USAPTI was taking information directly from proprietary DuPont documents.
  a. This opinion is based on Mr. Fisher having 35 years (1978 – 2013) experience in this industry.
  b. During his tenure at NL Chemicals (now Kronos) and later detailed technical work on CP process technology while at IBMA with clients Huntsman Tioxide and Kerr McGee (now Tronox), Mr. Fisher has been exposed to three of the four types of CP technology practiced by these IBMA clients. From information reviewed during his work on this litigation as an expert witness, he has concluded that the DuPont CP technology has unit operations which are very different from the three CP technologies he is intimately familiar with. Since DuPont carefully guards their CP technology, he therefore concludes that the USAPTI information had to have come directly from proprietary DuPont documents.

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23) Mr. Fisher will offer his opinion that the information he reviewed that was prepared by USAPTI and its employees could not have been derived from general knowledge regarding the TiO_2 manufacturing process.

    a. This opinion is based on Mr. Fisher having 35 years (1978 – 2013) experience in this industry and never having seen this level of detailed information on any CP technology, other than the Kronos CP technology he was exposed to while at Kronos (NL Chemicals).

    b. This information is much too detailed and specific to DuPont to have been seen in the public domain.

24) The detailed information prepared by USAPTI, such as line-sizes, equipment sizes, and detailed designs demonstrate that the information was copied from an existing, operating CP plant or plants.

    a. This level of detailed information on the DuPont CP technology has never been seen by Mr. Fisher in the public domain.

    b. Consequently he concludes that this detailed information must have been copied from an operating DuPont CP plant.

    c. Flow charts and material balances including handwritten notes must be from DuPont and personnel intimately familiar with DuPont's CP pigment plant operations..

    d. These P&IDs (Piping and Instrumentation Drawings) are unique to DuPont and have to have come from DuPont with handwritten notes prepared by a (former) DuPont employee.

    e. Some equipment drawings may have come from vendors but the handwritten notes had to have been provided by a (former) DuPont employee having access to proprietary technology and experience operating such equipment.

25) Mr. Fisher will offer his opinion that the USAPTI oxidation reactor and chlorinator – the two key parts of the process – were copied from current DuPont designs, but not from the Ashtabula plant.

    a. The Ashtabula 1 plant uses a first generation DuPont design while the USAPTI designs are clearly from a third generation CP design.

    b. This is even more obvious as the Ashtabula 1 plant uses a modified Sherwin Williams designed chlorination technology which is very different than the DuPont chlorination technology which USAPTI has.

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EXHIBIT C
FILED UNDER SEAL

EXHIBIT D
FILED UNDER SEAL

EXHIBIT E
FILED UNDER SEAL

EXHIBIT F
FILED UNDER SEAL

EXHIBIT G

FILED UNDER SEAL

EXHIBIT H
FILED UNDER SEAL

EXHIBIT I

From: Hemann, John (USACAN) [mailto:John.Hemann@usdoj.gov]
Sent: Monday, July 08, 2013 07:32 PM
To: Stuart L. Gasner
Cc: Axelrod, Peter (USACAN) <Peter.Axelrod@usdoj.gov>; Doron Weinberg; 'JerryFroelich' <jerryfroelich@comcast.net>
Subject: RE: US v. Liew/Bill of Particulars

Stuart –

I'm weighing how I feel about disappointing you. In the meanwhile, I will put you in touch with my mother, with whom I'm sure you will have a nice chat.

Each of the items listed in the bill of particulars is based on one or more specific pieces of evidence seized from defendants, each of which will be admissible at trial.   The terms used in the bill of particulars are terms used by the defendants in the course of their illegal conduct; they are not our terms and are not taken from DuPont documents (though, of course, these also are terms used by DuPont).

We believe that the evidence will show that defendants believed that each of these items was a DuPont design that had been misappropriated. I would note that Judge White held that we do not need to describe a trade secret for Counts Three and Five, we need to describe an item that defendants believed was a trade secret. This we have done.

We have a number of things in the queue before we will have time to sit down with you and discuss in more detail, which I'm sure you appreciate. We'd be happy to talk more about this after we get a few of the other things off our plates.

John

From: Stuart L. Gasner [mailto:SGasner@KVN.com]
Sent: Monday, July 08, 2013 4:45 PM
To: Hemann, John (USACAN)
Cc: Axelrod, Peter (USACAN); Doron Weinberg; 'JerryFroelich'
Subject: US v. Liew/Bill of Particulars

John –   2

Received the Bill of Particulars, and was disappointed to say the least. While the government has now recited virtually every area of a titanium dioxide plant and listed some components, nothing in your submission describes the alleged trade secrets in sufficient detail. If you believe that your Bill of Particulars complies with the Court's order and do not intend to do more, I guess I need to file a motion. Would you please advise ASAP as to whether it makes sense to meet and confer further on this, or whether we should proceed with our motion?

Best regards,

STUART

Stuart L. Gasner
Attorney at Law

KEKER & VAN NEST LLP

415 676 2209 direct | vCard | sgasner@kvn.com
633 Battery Street, San Francisco, CA 94111-1809 | 415 391 5400 main | kvn.com

EXHIBIT J

JELKS BARKSDALE, Ph.D., Columbia University, is Associate Professor of Chemistry, Auburn University, and a consultant on titanium dioxide pigments. He has previously been a research chemist with the National Lead Company, Titanium Division. Dr. Barksdale has written widely on chemistry in general, including college textbooks, and titanium in particular, and holds a number of patents pertaining to titanium dioxide pigments.

JELKS BARKSDALE, Ph.D., Columbia University, is Associate Professor of Chemistry, Auburn University, and a consultant on titanium dioxide pigments. He has previously been a research chemist with the National Lead Company, Titanium Division. Dr. Barksdale has written widely on chemistry in general, including college textbooks, and titanium in particular, and holds a number of patents pertaining to titanium dioxide pigments.

TITANIUM

Its Occurrence, Chemistry, and Technology

JELKS BARKSDALE

Auburn University

Consultant on Titanium

SECOND EDITION

To
Robbie Barksdale
and
William Jelks Barksdale

Preface

The purpose of this book is to provide a comprehensive working reference on titanium for all those interested in the sources, chemistry, and technology of the element.

Since this book first appeared, many significant developments have been made in the field of titanium, and the literature has increased at an accelerated rate. Largely as a result of national defense demands coupled with government subsidies, titanium metal has been developed to the stage where many commercial plants have been built for its production. Civilian uses for titanium metal are increasing steadily.

Improved titanium dioxide pigments having the rutile crystal form and produced by modifications of the original sulfate process, which at the time of the First Edition had just been introduced commercially, have now largely replaced the older anatase-type pigments. During this period the commercial production of titanium dioxide pigments of the rutile type by the vapor phase oxidation of anhydrous titanium tetrachloride at a high temperature was accomplished. A number of plants now employ this process on a large scale.

This Second Edition emphasizes the more important recent pigment and metal developments, together with new occurrences and studies of ore deposits and advances in the chemistry of titanium.

JELKS BARKSDALE

Auburn, Alabama
  September, 1966

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TITANIUM

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Vapor Phase Oxidation
of Titanium Tetrachloride
to Produce Pigment

THERMAL SPLITTING

A soft finely divided titanium dioxide of excellent pigment properties is produced from vaporized titanium tetrachloride by a process in which the splitting reaction is brought about by reaction with oxygen or air at temperatures above 1000° C.[1] In carrying out the process, a saturation vessel, constructed and operated on the lines of a wash bottle, is charged with titanium tetrachloride and heated at 120° C. Nitrogen is passed through to produce a gaseous product consisting of approximately equal parts of the two constituents, and this mixture is passed simultaneously with preheated air into an upright cylindrical reaction tube heated by external means to 1100° C. The proportions and quantities of the agents are so regulated that for each liter of reaction space there is introduced, per minute, 1000 ml of the tetrachloride-nitrogen mixture (500 ml titanium tetrachloride vapor), and 1000 ml air. In passing through the reaction vessel in a downward direction, the gases react to form titanium dioxide and chlorine, and the products are discharged into a dust chamber where separation is brought about. Titanium dioxide produced in this manner possesses excellent pigmentary properties and does not require subsequent processing.

To minimize coarsening and undesirable crystallization of the particles during the splitting reaction, the gaseous mixture of tetrachloride and air is raised rapidly to the reaction temperature. The gases are preheated, but to minimize premature reaction they are not mixed before reaching the splitting chamber, which is already heated to the required tempera-

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ture. The choice of splitting temperature above 1000° C, and the gas velocity, may be regulated within wide limits.

This process has the advantage over the various types of hydrolytic decomposition in that the chloride component is recovered not as hydrochloric acid but as elemental chlorine gas which is used directly for attacking more ilmenite or other titanium raw material.

The various steps of the process are shown in Fig. 21–1.

By subjecting vaporized titanium tetrachloride to thermal decomposition in the presence of oxygen, titanium dioxide of pigment grade is produced without the formation of large crystals by keeping the vapors out of contact with hot surfaces within the chamber during the splitting reaction.[2] Apparently titanic oxide formed adjacent to the hot walls of the reaction vessel, deposits on the surface, and serves as seed which grows to form large crystal agglomerates, and these reduce the average tinting strength of the product.

In carrying out this improved process, oxygen and titanium tetrachloride vapor, in the proportion of 3.3 moles of the former to 1 mole of the latter, are introduced continuously into a reaction chamber of sufficient size to permit thermal decomposition of the tetrachloride but to prevent a significant proportion from reaching the walls of the chamber. The reactants are preheated separately to the reaction temperature of 1500° to 1800° F before bringing them together in the splitting chamber, where a temperature of 1500° to 1800° F is also maintained. The collected titanium dioxide, in powder form, is further calcined to remove the last traces of chlorine. Pechukas and Atkinson[3] employed a special calcination chamber to heat titanium tetrachloride vapor with oxygen at 400° to 800° C to produce a pigment of improved properties. Schornstein[4] introduced parallel streams of the vaporized tetrachloride diluted with an inert gas, and of air mixed with 2 to 70 per cent water vapor based on the oxygen component, both preheated at 800° to 900° C, into a chamber so that an oxidation reaction took place out of contact with the walls. In a similar process, titanic chloride and air are preheated separately to 1000° to 1100° C and passed into a reaction chamber maintained at 750° C by means of a cooling jacket.[5] The proportion of chloride to oxygen is 1 to 4. During the reaction a yellow-green flame burns at the outlet of the preheating tube and a pigment smoke issues from the other side of the reaction vessel. The pigment is very voluminous and possesses excellent whiteness.

To minimize crystal growth and produce titanium dioxide of pigment grade, the chloride vapor is not allowed to come in contact with hot surfaces of the reaction chamber. This is effected by maintaining an atmosphere of nitrogen around the tetrachloride inlet.[6] A temperature of 1000° C is employed. The same result is attained by causing the titanium
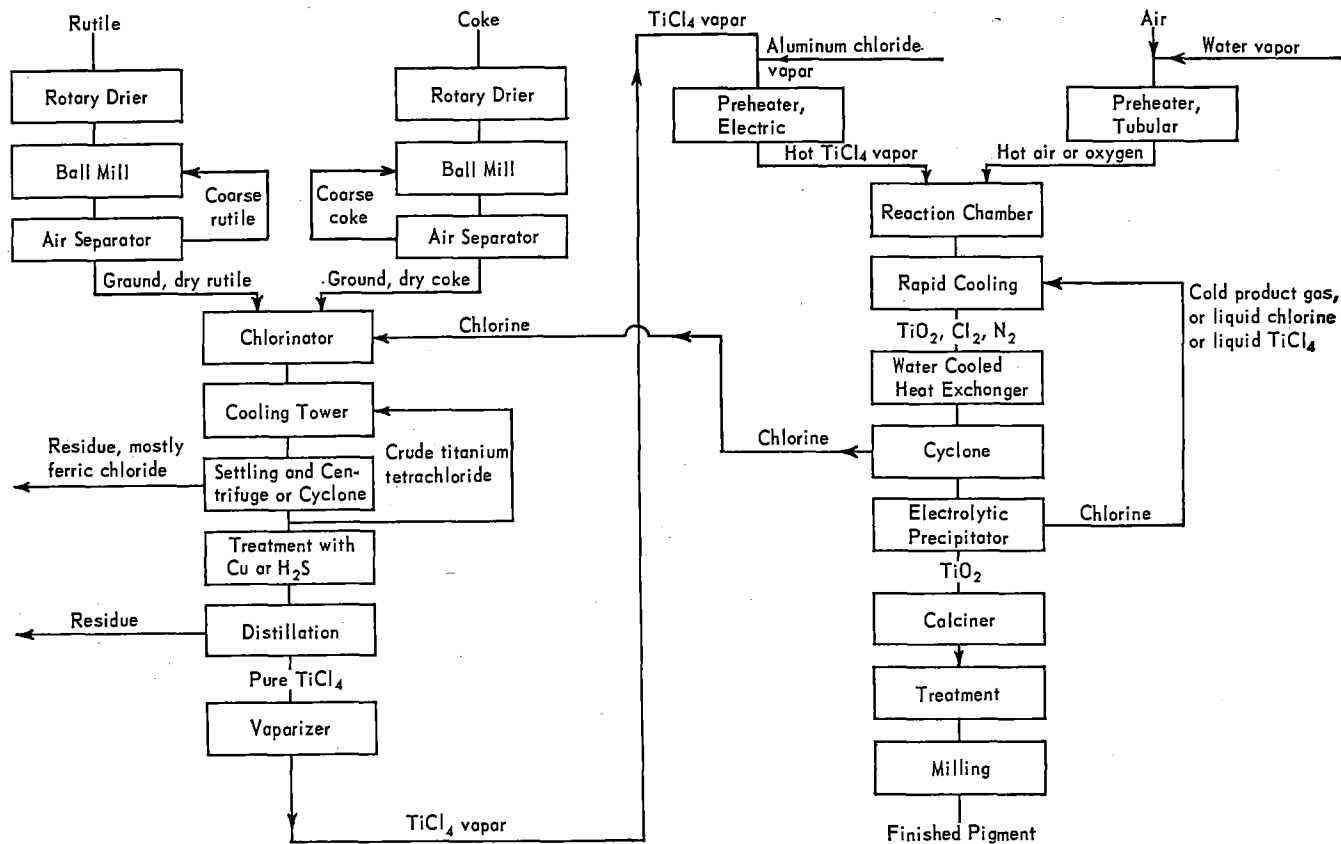
Fig. 21–1. Flow sheet of the chloride process for the manufacture of titanium dioxide pigment.

tetrachloride vapor to react with an oxygen countercurrent in a vertical cylindrical furnace, and withdrawing the evolved chlorine so that it surrounds the area of introduction (inlet) of the tetrachloride.[7] This procedure prevents reaction from taking place at the hot surfaces.

Shchegrov [8] calculated the free energy of the reaction of titanium tetrachloride with oxygen and the thermodynamically possible degree of conversion of the tetrachloride to the dioxide, and compared the results with experimental data. The reaction begins slowly at 500 to 600° C. Above this range the conversion increases sharply with temperature and with the increase in oxygen concentration. The products of the reaction between titanium tetrachloride vapor and dry oxygen are only titanium dioxide and chlorine. The free energy values for the reaction at 1073 and 1573° K are calculated to be −30.28 and −23.06 kilogram calories per mole, respectively.[9] Corresponding equilibrium values are 1.35×10^6 and 1.44×10^3, respectively. Oxidation begins at 700° C and accelerates sharply with increased temperature. At 1100 to 1150° C almost complete burning of the titanium tetrachloride delivered into the reaction zone is effected. Formation and growth of the titanium dioxide crystals up to 3 to 4 mm in size take place in the upper relatively cold part of the reactor. The proportion of particles of titanium dioxide smaller than 1 micron gradually increases to a maximum at 1150° C. A similar study indicates that at 1100 to 1150° C almost all of the titanium tetrachloride vapor is oxidized.[10] The oxidation probably consists of two simpler processes; oxidation of titanium tetrachloride in the vapor phase, and the oxidation of titanium tetrachloride on the surface of the solid phase. Titanium dioxide is in the gaseous phase at the moment of its formation but is immediately deposited in a crystalline form. Obtained in this manner, the titanium dioxide contains some absorbed chlorine and consists of a mixture of anatase with rutile possibly as a solid solution. After heating for 1 hour at 900° C the chlorine is driven off and the titanium dioxide is 100 per cent of the rutile crystal form.

Titanium tetrachloride before oxidation to produce titanium dioxide pigment is heated up to 2000° C by passing through electrically heated resistor elements of dense mixtures of graphite and amorphous carbon located in the heating conduit or zone.[11] For example, a vaporized mixture of titanium tetrachloride containing 1 per cent aluminum chloride at 300° C was passed at a rate of 64 pounds an hour through an electrically heated graphite resistor tube unit enclosed in a nickel shell. The resistor tubes are maintained at a temperature of 1800° C by the resistance to a 60 cycle electrical current passing through the walls of the tube. On discharge from the unit the mixture of titanium tetrachloride, aluminum chloride, and chlorine vapor at 860° C was passed directly and continuously into an associated vapor phase oxidation reactor unit for

producing high grade rutile titanium dioxide pigment by reaction with air. The proportion of chlorine in the gas mixture was up to 5 per cent.

Pigments are produced by the vapor phase oxidation of the tetrachloride by a process which permits the use of metal heat exchangers for preheating the oxygen.[12] Undesirable metal compounds picked up from the heat exchangers and carried as solid particles in suspension are removed by passing the gas through a ceramic filter medium. The porous refractory filter is preferably constructed of alumina but may be of silica, boron carbide, or clay. These filters have an average pore diameter of 0.1 mm and are constructed in the form of a thimble or a flat disc. A brick-lined shell filled with silica wool filters is also satisfactory. The filter may be cleaned by passing hot concentrated hydrochloric acid through it, followed by a water wash. In a specific operation, the air preheater consisted of coiled, stainless steel tubing. The filter was a porous fused alumina thimble with average pore diameter of 0.09 mm. A silica outer container housed the filter. The metal preheater tube was heated in a gas fired furnace to 970 to 1070° C. After 5 hours service the filter was cleaned.

An organic chloride as carbon tetrachloride is added to the vaporized titanium tetrachloride to react with and remove the oxygen from the air present as a contaminant [13] before preheating to decrease the corrosion of the equipment. The most useful refractory from the standpoint of corrosion is fused silica, but it is fragile and subject to progressive deterioration at elevated temperatures. Furthermore, silica has a low heat conductivity and it is not practical at temperatures above 1000° C. Heat exchange apparatus may be designed using electrical heaters of carbon or graphite shapes. However, oxygen in the vapors derived from air dissolved in the tetrachloride or from oxychlorides present attacks the heated surfaces of the carbon units. To overcome this difficulty the oxygen is removed from the titanium tetrachloride vapor by heating with it an organic chloride to furnish a carbon content sufficient to react with the oxygen present in the vapor. Suitable organic chlorides are carbon tetrachloride and tetrachloroethane. In an example, a vaporized mixture of titanium tetrachloride containing 1 per cent by weight of aluminum chloride at 300° C was passed at a rate of 60 pounds per hour into an electrically heated carbon resistor tube unit. This titanium tetrachloride contained 120 ppm oxygen just prior to entrance of the vapor into the heating unit. An amount of tetrachloroethane vapor was added to react with the oxygen to form carbon monoxide and chlorine. Allowing for a slight excess, 11.3 ml of tetrachloroethane was added per hour. The mixed titanium tetrachloride-aluminum chloride gases were then passed through the interior of the electrically heated resistor tube maintained at 1800° C by the passage of a 60 cycle electric current through the walls of the

tube where they were heated to 850° C and passed directly into an associated vapor phase cooxidation unit for the production of high-grade rutile pigment.

Preheated titanium tetrachloride vapor and water-enriched air are rapidly mixed in the reaction zone at 800 to 1400° C by charging the vapor through a restricted peripheral slotted inlet into the reaction zone in the form of a thin sheeted stream directly into the humidified air in a direction at right angles to its direction of flow.[14] Various mixing devices have been proposed. These include fuel and jet turbine types of burners; jet mixers and injectors wherein one reactant passes separately through a main conduit while the other reactant flows through auxiliary or separate tributary conduits; for example, a concentric jet type of mixer. Such mixing is not instantaneous and becomes complete at a point considerably removed from the discharge. Counter currents and eddies are set up along the internal walls of the reactor vessel which create dead spots where objectional titanium dioxide crystal growth takes place. This mixing device is constructed of silica.

Pigment is produced by admitting titanium tetrachloride vapor and oxygen to a reaction chamber at 850° to 950° C through separate feed ports in the same direction in such a way that the titanium tetrachloride stream flows within the oxygen stream.[15] The gases are preheated so that on mixing the resultant temperature before reaction is above 300° C. A molar ratio of titanium tetrachloride to oxygen of 1 to 1, to 1 to 6 is maintained. The velocity ratio of the oxygen to the titanium tetrachloride is less than one. Nonturbulent flow is maintained. By this procedure the reaction takes place out of contact with the hot surfaces including the surrounding walls of the reaction chamber and the tips of the conduits through which the gases are admitted. For example, the ratio of oxygen to titanium tetrachloride was 4 to 1 and the furnace temperature was maintained at 850 to 950° C. The titanium tetrachloride was preheated to 830° C and the oxygen to 850° C so that the temperature attained on mixing, irrespective of the heat of reaction, was 820° C. Water vapor to the extent of 2.3 per cent was introduced by bubbling the air through water at 35° C.

Vaporized titanium tetrachloride preheated to 1050° C and oxygen preheated to the same temperature are blown into a reaction chamber in which the pressure is reduced to less than 30 mm of water to produce finely divided rutile type pigment.[16] The titanium dioxide is collected immediately in a low temperature chamber, and the chlorine is drawn off. Thus, from titanium tetrachloride of 99.98 per cent purity and oxygen of 99.98 per cent purity, titanium dioxide of 99.9 per cent purity with a particle size of 0.3 to 0.5 micron and having a rutile content of 99.5 per cent was obtained in a 95.5 per cent yield. Titanium tetrachloride is

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introduced into the bottom of a reaction zone through a pipe, the end of which is covered by a porous cup of unglazed porcelain or aluminum carrying an orifice.[17] About 90 per cent of the titanium tetrachloride issues through the orifice, where it meets a counter-current of air or oxygen preheated to 1100° C and reacts on contact. The remaining 10 per cent diffuses through the porous cup walls and surrounds the hot surfaces with a fluid envelope containing no oxygen, thus preventing reaction at the inlet boundaries and crystal growth thereon. Titanium tetrachloride is decomposed to form the finely divided dioxide in a special burner fed with a stoichiometric mixture of oxygen with the vapor uniformly dispersed in the gas stream.[18]

Vapors of titanium tetrachloride and oxygen or air are admitted into a reaction chamber separately or mixed so that the heat of the reaction is used to heat the incoming stream without decreasing the temperature inside the reactor.[19] The titanium dioxide has a particle size of 2 to 5 microns. The oxidation reaction proceeds at 1050 to 1100° C. Wilson[20] injected an annular stream of titanium tetrachloride vapor into a central stream of oxygen. To produce pigmentary titanium dioxide the reactor is designed so that the titanium tetrachloride and oxygen injection tips are cooled to maintain their surface temperature above the vaporization temperature of the tetrachloride but below the oxidation temperature.[21] A surface temperature of 700 to 800° C is suitable to prevent buildup of objectionable scale deposits on the injection tips. Scale if allowed to form causes plugging and decreases the conversion efficiency of the reactor. Titanium dioxide of extremely fine particle size is produced by concentric impingement of an oxygen containing gas on titanium tetrachloride vapor so that contact of the oxide product with the walls of the reactor is prevented.[22] Crystal growth is further impeded by rapidly withdrawing the product from the high temperature reaction zone.

Pigmentary titanium dioxide is obtained by decomposing the tetrachloride in the vapor phase with an oxidizing gas in a reaction zone having porous walls.[23] To prevent contact of the reactants with the internal surfaces of the zone, an inert gas is diffused through the porous walls from an external source maintained under pressure. Titanium tetrachloride and air heated to 700° C are introduced separately into a reaction chamber to form a turbulent gas stream so that the oxide is precipitated in the finely divided form.[24] Simultaneously, finely divided refractory particles are directed against the walls near the gas inlets to prevent the accumulation of pigment particles. During the oxidation step, oxygen or nitrogen heated by induction or by an arc to 2000° C is added to supply auxiliary heat to achieve 950 to 1100° C in the reaction zone.[25] Additives to the inert gas to induce the formation of rutile are 0.1 to 10

parts aluminum chloride, 0.1 to 10 parts of zirconium chloride, and 0.01 to 5 parts of silicon tetrachloride per 100 parts of titanium dioxide. Titanium dioxide is added for nucleation.

Vapors of titanium tetrachloride may be superheated by entraining hot quartz sand particles in the vapors and causing the mixture to flow in a confined elongated stream as a fluidized suspension until the desired heat exchange is effected.[26] The sand is then separated from the superheated vapors. For example, the addition of 500 pounds per hour of sand at 1000° C to 250 pounds per hour of titanium tetrachloride at 138° C superheated the vapor to 800° C. The vapor phase oxidation of titanium tetrachloride containing 0.1 to 20 per cent of an organic diluent produces finely divided particles of the dioxide.[27] Air is fed into a reaction zone so that its linear speed is greater than the speed of the stream of titanium tetrachloride vapor.[28] This air stream sucks the titanium tetrachloride into the reaction zone and provides fast and intimate mixing. An inert gas may be introduced between the streams of air and vapor to prevent premature reaction, thereby eliminating crust formation on the surfaces of the feed orifices. The addition of aluminum chloride or zinc chloride increases the rutile content of the pigment to 99 per cent. Silicon tetrachloride favors anatase formation. Compounds of potassium limit the particle size growth of the titanium dioxide.

The heat transfer for the decomposition of titanium tetrachloride with oxygen is provided mainly by heating an auxiliary inert gas with an electric arc and mixing it with the reaction gases.[29] This heat transfer involves also the ionization energy as the inert gas, nitrogen, attains temperatures up to 30,000° C and reaches the reaction zone at temperatures of 5000 to 15,000° C. Reaction temperatures for the decomposition of titanium tetrachloride are 1100 to 1200° C. To obtain oxide of high purity, titanium tetrachloride is purified by distillation and then oxidized with an excess of oxygen.[30] After separating the suspended oxide, the gaseous mixture of oxygen and liberated chlorine is treated with the original chloride under pressure so that chlorine is absorbed. The chloride is treated under reduced pressure to liberate the chlorine.

In the production of pigment from titanium tetrachloride and oxygen at 800 to 1450° C, the formation of coarse dendrites on the reactor walls is prevented by passing chlorine through a porous wall to convert it to the tetrachloride.[31] A mixture of titanium tetrachloride 0.088 and oxygen containing 2.4 per cent water 0.105 mole per hour, heated to 1020° C, is passed through a porous graphite tube surrounded by a quartz jacket through which dry chlorine 0.118 mole per hour at 30° C is introduced. The tube remains free of deposits and pigment grade titanium dioxide is produced. Titanium dioxide having a rutile content of more than 40 per

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cent is obtained by oxidizing titanium tetrachloride in an oxygen containing gas at 1200 to 1400° C.[32] The gas burner is designed so that the gas layers are 1 mm to 1 cm in thickness.

Strong titanium dioxide granules for ceramics are obtained by passing gaseous titanium tetrachloride through titanium dioxide containing from 0.05 to 0.3 per cent water.[33] During the operation, particles of 0.2 to 0.5 micron grow to 10 microns in diameter.

FLAME OXIDATION

Finely divided titanium dioxide is obtained by bringing vapors of the tetrachloride into the direct flame of a combustible gas or vapor.[34] For example, purified gas loaded with titanic chloride vapors is ignited in air. Highly dispersed titanium dioxide results, and owing to its high specific volume it is carried along with the gas currents and separated in a chamber provided with several filtering materials or in precipitators of the Cottrell type.

Titanium dioxide pigments of the anatase and rutile form are manufactured by the combustion in full displacement flow of a stream of carbon tetrachloride and oxygen with carbon monoxide and additional oxygen present to supply supplemental heat.[35] The mixture is supplied at a temperature of 650° C through an aluminum tube to a refractory combustion tube. En route, it passes in full displacement flow, streamlined or turbulent, into a stationary, self-sustaining flame, formed by the combustion of fuel gas within the tube. In this tube the mixture is burned, thereby oxidizing the titanium tetrachloride to the dioxide. The combustion mixture has an average flow rate of from 0.67 to 1.33 of its axial flow rate in the center of the conduit. As shown in electron photomicrographs the particles of the pigment are well-formed, compact, approximately spherical in form, and very uniform in size. Krchma[36] heated the tetrachloride vapor by direct contact with the combustion of carbon monoxide with oxygen. If one mole of carbon monoxide at 18° C is burned in an insulated chamber with 0.5 mole of oxygen preheated to 900° C, sufficient heat is evolved that the mole of carbon dioxide produced is heated to 900° C with 61,600 calories left over. This amount of heat is sufficient to raise the temperature of 3.6 moles of titanium tetrachloride vapors from 200 to 900° C and will produce a gas mixture at 900° C of 78.3 per cent titanium tetrachloride and 21.7 per cent of carbon dioxide. Powdered coke, carbon black, or petroleum coke may be used in place of the carbon monoxide. In an example, liquid titanium tetrachloride was quickly volatilized and superheated to 250° C in a conventionel electrically heated tube or coil preheater constructed of silica. The tetrachloride vapor was conducted to a mixing chamber also constructed of

silica. Carbon monoxide was burned with air in a separate ceramic chamber. Air was introduced and combustion was initiated by a spark. The hot carbon dioxide product gases were immediately conducted to the silica mixing chamber where the tetrachloride vapor was introduced and rapidly preheated to 950° C. This resulting hot mixture of titanium tetrachloride and carbon dioxide was at once passed to an oxidation chamber where it was reacted with air preheated to 975° C to produce titanium dioxide pigment.

The exothermic heat of the reaction of titanium tetrachloride with oxygen is not adequate to reach the required temperature of 950 to 1100° C or even to maintain this temperature so that auxiliary heat must be supplied in the reaction chamber.[37] The preheated oxygen-titanium tetrachloride mixture is introduced through a rotating center jet. Auxiliary fuel such as carbon monoxide and hydrogen with the oxygen required for combustion are injected through ring-shaped outlets surrounding the center jet. A rotating motion in a direction opposite to that of the reaction mixture is imparted to the auxiliary combustion zone by vanes in the ring-shaped outlets. The particle size of the titanium dioxide is controlled by variations in the gas flow rate, temperature, and component reactions. In a typical operation, a mixture of 1 volume titanium tetrachloride vapor and 1.5 volumes of oxygen at 250° C was injected through the center jet at a velocity of 20 meters per second. At the same time 0.8 volume of carbon monoxide was introduced through the inner nozzle and 0.4 volume of oxygen through the outer ring nozzle. The mixture ignited at a distance of 5 to 10 cm from the nozzle. A titanium dioxide pigment with a particle size of 0.5 micron was obtained at a yield of 99 per cent.

A suitable unit for the oxidation of titanium tetrachloride with oxygen in an auxiliary flame comprises three concentric tubes connected to a reaction chamber.[38] The titanium tetrachloride vapor passes through the innermost tube. Oxygen with controlled water vapor content (0.005 volume per cent for titanium tetrachloride) passes through the intermediate tube. Gases for the auxiliary flame such as hydrogen, carbon monoxide, illuminating gas, gasoline vapor, oil vapor, or mixtures pass through the outside tube. The temperature of the reaction chamber may vary from 500 to 1200° C, and the amount of material produced ranges from 0.5 to 50 kg per hour with a particle size less than 0.1 micron.

Mixed vapors of titanium tetrachloride and oxygen are sent through a burner tube having one or two outer concentric tubes carrying carbon monoxide and oxygen.[39] To mix the flammable gases thoroughly with the charge vapors, the ends of the tubes are constricted. The auxiliary flame from these gases aids the reaction and titanium dioxide of 0.2 to 0.4 micron particle size is obtained. By the reaction of a dispersion of

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titanium tetrachloride in oxygen or air at 1200° C in a vertical reactor into which carbon monoxide and acetylene or carbon monoxide and hydrogen are also admitted the finely divided oxide is obtained.[40] The pigment powders obtained in the process have an average particle size of 0.5 to 2.0 microns. The properly proportioned mixture is ignited in the reaction furnace.[41]

Titanium dioxide of exceptional fineness and high purity is produced by introducing the vaporized tetrachloride in a stream of preheated air into an insulated, tubular reactor so that the vapor is surrounded by an annular blanket of flame.[42] The flame is maintained by burning a gaseous mixture of hydrocarbon with oxygen. Sufficient hydrocarbon is present to ensure on combustion complete hydrolysis of the tetrachloride. Sufficient oxygen is present for complete combustion. One per cent carbon dioxide vapor is added to the hydrogen auxiliary fuel in the oxidation of titanium tetrachloride to produce a pigment containing more than 50 per cent rutile.[43] Titanium dioxide pigments containing at least 60 per cent rutile are made by passing a mixture of titanium tetrachloride vapor and an oxygen-containing gas into a reactor in the form of a layer 1 to 10 mm thick.[44] The reaction is kindled by a flame surrounding the reactant gas mixture which is preheated to 135° C.

Pigment is produced by thermally decomposing a gaseous mixture of titanium tetrachloride containing free oxygen under flame conditions in the presence of 0.01 to 10.0 per cent of a volatile silicon compound.[45] To avoid premature oxidation a maximum preheating temperature of 500° C is employed. The process is carried out by utilizing an auxiliary flame and maintaining a temperature of 750 to 1200° C of the atmosphere immediately ambient to the auxiliary flame. By this process titanium dioxide containing more than 90 per cent anatase is produced. To eliminate the stoppages caused by titanium dioxide deposits on exit orifices and reactor walls, the hot gases from the oxidation of the tetrachloride are evacuated from the chamber center by cooled aluminum-magnesium alloy tubes without deforming the flame pattern.[46] Recycled cold gas is brought to the center by the suction created by the flow of hot gases in the tubes.

By the reaction of titanium tetrachloride, carbon monoxide, and oxygen in a cylindrical chamber preheated to 1000° C, spherical titanium dioxide particles are obtained.[47] The gas ignites spontaneously, producing 80 per cent anatase having a particle size of 0.2 micron, and chlorine. This titanium dioxide product is separated from the chlorine in a cyclone separator and in a Cottrell precipitator. The hot gases from the combustion of low hydrogen content carbonaceous material are passed into a flowing stream of titanium tetrachloride to produce titanium dioxide and chlorine.[48] Fuels include carbon black, coke, charcoal, and coal. A com-

bustion temperature between 1400 and 2200° F is produced. Between 1 and 5 mole per cent aluminum or a compound may be added with the carbonaceous material to deposit alumina on the pigment particles.

A mixture of titanium tetrachloride and air preheated to 200 to 600° C is heated rapidly in a closed refractory lined reactor by a flame of sulfur vapor to 800 to 1200° C to produce titanium dioxide.[49] The reaction products are cooled, titanium tetrachloride is removed, and the gases are led through a catalyst chamber with added oxygen to form sulfuric acid. This sulfur vapor can be mixed with the titanium tetrachloride and oxygen, separately injected through nozzles or through a fluidized bed of sand or rutile. Titanium dioxide of pigment grade is produced by introducing titanium tetrachloride vapor into a free oxygen containing hot reaction zone and at the same time introducing into the reactor tangent to the flow of the tetrachloride separate streams of a burning fuel and an auxiliary gas which is inert to the pigment particles.[50] Suitable gases are chlorine, nitrogen and carbon dioxide.

During the vapor phase oxidation of titanium tetrachloride in a fluidized bed of titanium dioxide, carbon monoxide is burned in the bed to maintain the operating temperature at 950 to 1250° C.[51] Blocking of the bed by partial fusion near the carbon monoxide inlet is prevented by dilution with nitrogen, chlorine, or carbon dioxide to lower the temperature. Additional chlorine is added to the vapor of purified titanium tetrachloride before heating with oxygen to produce the dioxide of the proper particle size and reduce the loss of chlorine.[52] The excess oxygen in the final gas mixture from the oxidation step is removed by burning a carbonaceous material. This also serves to heat the chlorine recovered in the process for reaction with more ore.

FLUIDIZED BED OXIDATION

Titanium tetrachloride and air preheated to 1000° C are passed into a fluidized bed of an inert material, as rutile or zircon, where they react to form pigment-grade titanium dioxide, which is carried away by the product gases.[53] The material comprising the fluidized bed has a particle size of 40 to 1000 microns. A velocity is maintained at five times the minimum fluidizing velocity. Materials suitable for the bed are rutile, alumina, silica, and zircon which have been treated to remove any objectionable impurities. The reaction chamber consists of a shaft furnace having as a base a perforated plate with porous diaphragms above to allow the gas to pass upward but to prevent passage of solid particles through the plate. Temperatures of 800 to 1100° C are maintained in the furnace. As an alternative the titanium tetrachloride and air may be premixed at temperatures below 500° C before they are passed into the

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fluidizing bed. Crystals of titanium dioxide formed are deposited on the bed solids rather than on the walls of the reactor.

In an example, a silica tube 5 inches in diameter and 36 inches long mounted vertically was heated in an electrically wound furnace. A porous silica disc was cemented in the base of the tube to support the fluidized bed. The lower part of the tube was sealed with two inlet tubes. One supplied the air into the chamber below the disc; the other supplied the titanium tetrachloride and passed through the disc. Silica sand having a grain size of 250 to 350 microns to a static height of 7 inches constituted the fluidized bed. The bed was heated to 920° C while maintained in a fluidized state by the admission of air at the rate of 12 liters a minute. Titanium tetrachloride was admitted at a rate of 0.18 mole per minute and the air was adjusted so that the ratio of the tetrachloride to oxygen was 1 to 3. The reaction was practically instantaneous and the time of contact in the fluidized bed zone was approximately 2 seconds. At least 99.9 per cent of the titanium tetrachloride was converted.

Gaseous titanium tetrachloride is passed with oxygen through a hot bed of granular silica or rutile to effect reaction.[54] The very fine titanium dioxide particles are carried out by the gas stream. The reaction may be carried out in the presence of 0.5 to 7 weight per cent, calculated as the oxides, of zirconium chloride as a modifying agent.[55] By preheating the reactants, the rate of the reaction in a fluidized bed is increased.[56] Deposition of titanium dioxide on the fluidizing particles is inhibited by the preheating. The yield of pigment recovered from the effluent gases from the fluidized bed oxidation of the tetrachloride is improved by introducing metallic aluminum into the bed.[57] Less titanium dioxide is left in the bed. This effect is caused by alumina deposition replacing titanium dioxide on preferred sites on the bed particles. A similar effect is obtained by introducing chlorine and carbon monoxide or carbon into the bed at a location shielded from the oxygen.[58]

The vapor phase oxidation of titanium tetrachloride is carried out at 750 to 1500° C in a bed of fluidized refractory particles under conditions that at least part of the titanium dioxide formed remains within the bed.[59] By gradual withdrawal of particles from the bed, accompanied by gradual addition of fluidizable particles of alumina, silica, zirconium oxide, or titanium dioxide, the size distribution of the particles is controlled. Particles withdrawn from the bed have a larger mean size than that of the particles added. The finely divided titanium dioxide which escapes from the reaction bed with the fluidizing gases may be used as a pigment or may be returned to the bed to control the particle size of a later product. Titanium dioxide of larger particle size withdrawn from the bed is especially suitable for the manufacture of vitreous enamels.

Pigment-grade titanium dioxide is produced by the reaction of the tetrachloride vapor with an oxygen-containing gas and a chloride vapor conditioning agent in a fluidized bed composed of 0.001 to 0.1 inch particles of a heat resistant material such as titanium dioxide, alumina, or silica at 750 to 1250° C.[60] Small amounts of water in the gas mixture accelerate the reaction. A gas velocity is maintained high enough to keep the bed fluid and to remove most of the titanium dioxide formed. This is recovered in cyclone separators. Effective conditioning agents are titanium trichloride, aluminum chloride, and silicon tetrachloride. Titanous chloride and aluminum chloride promote rutile formation. The bed is heated by introducing carbon monoxide or other fuel gas.

As an illustration, in a fluidized bed of 40 to 60 mesh titanium dioxide 16 cm deep and 5.1 cm diameter in an externally heated silica tube, a temperature of 1080° C was maintained with an upward flow of a gas mixture providing purified titanium tetrachloride at a rate of 12.4 ml per minute, aluminum chloride 0.21 g per minute, oxygen containing 4.53 mg of water per liter 15 liters per minute, and nitrogen 6.1 liters per minute. Twenty per cent of the titanium dioxide formed remained in the bed. The remainder separated from the effluent gas in a cyclone was 100 per cent rutile pigment having a Reynolds tinting strength of 1625.

The larger particle sizes of titanium dioxide are withdrawn from the fluidized bed and chlorinated.[61] A gas stream carries off the fine pigment particles and the larger particles fall to the bottom. The reactor is a refractory lined vertical cylinder arranged for gravity charging of titanium dioxide and with four angled pipes for feed of titanium tetrachloride, oxygen, chlorine, methane, carbon monoxide, and nitrogen.

NUCLEI

Pigment-quality titanium dioxide of the rutile crystal form is produced by reacting at 900 to 1200° C in the vapor phase over a period of 0.1 to 1 second purified titanium tetrachloride with air in the presence of 0.1 to 5 per cent water vapor based on the total volume of gases to continuously form within the reacting gases small amounts of titanium dioxide nucleating agent which promotes and insures the production of a high quality product.[62] Titanium tetrachloride vapor and air enriched with 0.1 to 3 per cent water vapor are separately and continuously introduced into an oxidation zone where they are rapidly and thoroughly mixed. These reactants are preheated before introduction into the reaction chamber and the reaction is carried out at a constant temperature of from 900 to 1200° C. The product is cooled by mixing with cold gases from a previous reaction to below 600° C. This should be effected in 1 second

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and does not exceed 10 seconds. The rutile titanium dioxide is separated
from the gaseous mixture by a cyclone, electrostatic separator, filtration
through a porous medium, or any conventional means.

As an illustration, titanium tetrachloride vapor preheated to 800° C
was admitted to the reaction chamber at a continuous rate of 100 parts
by weight per hour into the upper portion of a reaction chamber main-
tained at 1050° C. Simultaneously, air preheated to 800° C and contain-
ing 0.95 per cent water vapor by volume was continuously admitted
through a separate inlet adjacent to the titanium tetrachloride inlet. The
air flow was 20 parts by weight of oxygen per hour. Inside the reactor
the gas streams converged immediately to become rapidly mixed. Flow
rates were adjusted to get a retention time of 0.5 second. The reaction
products at 1000° C were cooled quickly by introducing sufficient cold
chlorine gas to drop the temperature to 300° C in less than 2 seconds.
The titanium dioxide particles were separated in filter containers. In the
production of the seeding agent titanium tetrachloride reacted with water
to form very finely divided titanium dioxide and hydrochloric acid.

To prepare finely divided titanium dioxide, 1 volume of the tetrachlo-
ride vapor and at least 3 volumes of air or oxygen containing a small
proportion of water vapor are separately preheated in concentric tubes
so that on mixing a temperature of at least 600° C is attained.[62a] The gases
are mixed in a chamber large enough to permit complete reaction to take
place before the mixture strikes the chamber walls. Dilution of the chlo-
ride with nitrogen or carbon dioxide and high gas velocities during the
mixing favor small particle size.

Titanium dioxide pigment having the rutile crystal form is prepared
by feeding a stream of the tetrachloride into the center of a slowly moving
stream of oxygen in a concentric burner.[63] Both gases are preheated and
both move in streamline flow. Addition of up to 5 per cent water vapor
in the oxygen and of up to 0.25 per cent silicon tetrachloride in the tita-
nium tetrachloride yields a better pigment. The mean particle size of
the pigment is between 0.1 and 0.35 micron. Oxygen and titanium tetra-
chloride preheated to 850° C are fed to the reactor in a mole ratio of 4 to
1. With the addition of 2.3 per cent water vapor to the oxygen and 0.07
per cent silicon tetrachloride to the titanium tetrachloride, the pigment
has a rutile content of 91.5 per cent and a tinting strength of 1800.

Further improvement in pigment properties is obtained if the water for
forming the nucleating agent is produced in situ by the oxidation of hy-
drogen present during the reaction.[64] Also, more efficient control over
the reaction results. Pure anhydrous titanium tetrachloride vapor, air,
and from 0.0062 to 0.186 mole of hydrogen per mole of the tetrachloride
to form from 0.1 to 3 per cent water vapor by volume are separately and
continuously introduced into a reaction vessel at a constant temperature

of 900 to 1200° C. The reactants are preheated before introducing into the furnace. Retention time in the furnace is from 0.1 to 1 second to allow time for complete reaction but not enough time to result in undesired particle growth of the titanium dioxide. In an example, 5330 g of vaporized titanium tetrachloride preheated to 1050° C was introduced per hour into the reaction vessel. Through separate openings air preheated to 1050° C was introduced at a rate of 3400 liters per hour. Through a third opening methane preheated to 1050° C was admitted at a rate of 52.6 liters per hour, equivalent to 9.4 liters of hydrogen per hour. Within the reaction chamber the temperature was 1080° C. The collected titanium dioxide after removal of absorbed chlorine was of the rutile crystal form, had a particle size of 0.17 micron, and possessed excellent pigment properties. To produce rutile rather than anatase, the conditions are: a minimum water content, minimum preheating temperature, minimum retention time, and quick cooling.

By the oxidation of the tetrachloride with atomic oxygen in the gas phase or in a fluidized bed titanium dioxide in a finely divided state is prepared.[65] Water vapor is present during the reaction.

In the vapor phase oxidation process preheated titanium tetrachloride vapor is rapidly mixed with preheated air containing 0.5 to 20 per cent of an oxide of nitrogen.[66] The oxides of nitrogen react rapidly with titanium tetrachloride to form nuclei which act as growth centers for the pigment particles. Effective oxides are nitrous oxide, nitric oxide, and nitrogen dioxide. The oxidation reaction is carried out at a temperature of 900 to 1350° C which requires preheating of the reactants to temperatures above 600° C. The oxide of nitrogen is added to the air before or after preheating. For example, titanium tetrachloride vapor preheated to 750° C was admitted through one inlet to a reaction chamber maintained at 1000° C. An amount of air 5.1 times the volume of the tetrachloride vapor preheated to 770° C was admitted through a second inlet so arranged that mixing took place rapidly. Nitrogen dioxide was added to the air just prior to introduction into the mixing zone in an amount sufficient to give 0.2 per cent of the oxide of nitrogen. After a retention time in the furnace of 0.25 second the reaction product was removed from the reaction zone and cooled quickly to prevent particle growth. From the cooled mixture the titanium dioxide was recovered as pigment grade.

The particle size of titanium dioxide pigments produced by the vapor phase oxidation of titanium tetrachloride is controlled through the use of nucleating agents.[67] For this high temperature oxidation fragile nonmetallic equipment such as fused quartz is required to withstand the high corrosive gases. Ordinarily water vapor is added to the air used to develop the desired particle size and aluminum chloride is added to the titanium tetrachloride to prevent discoloration of white paints and enamels

caused by the titanium dioxide. By adding a suitable nucleating agent the preheating temperature of the titanium tetrachloride may be lowered thereby simplifying the process and at the same time pigment of excellent properties is obtained. A portion of the titanium tetrachloride vapor is preheated with a reducing agent to form a small proportion of lower valent chlorides such as titanium trichloride and dichloride in the vapor or as finely divided solids prior to or at the point of the introduction of the vapor into the oxidation reactor. The resulting vaporized mixture of titanium tetrachloride and lower valent chlorides is continuously oxidized to titanium dioxide of pigment grade by reaction with air at 800 to 1350° C. The titanium tetrachloride is reduced to form the lower valent chloride by heating with a granular metal as titanium, with hydrogen, or with a hydride at 136 to 400° C. After discharge from the reactor the reaction products are cooled quickly and the titanium dioxide is separated from the gaseous medium, calcined at 500 to 700° C, and milled in a fluid energy mill. Metals for reducing the titanium tetrachloride are sodium, magnesium, aluminum, titanium, and zinc. Hydrides of titanium, sodium, aluminum, and zinc may be used.

In an example, 100 parts by weight of titanium tetrachloride vapor were preheated to 765° C in silica equipment. A portion of this stream was continuously admitted at a rate equivalent to 10 parts by weight per hour to a lower chlorides generator where 10 per cent of the diverted titanium tetrachloride was passed over titanium sponge granules to form titanium trichloride in the vapor as a nucleator. This mixture was united with the main tetrachloride stream, and the nucleated vapor was charged immediately and continuously into the reaction chamber of a tubular form of vertical reactor of corrosion resistant construction. Simultaneously, 17 parts by weight of oxygen as air preheated to 750° C were continuously charged from a separate inlet into the reactor and mixed with the titanium tetrachloride. Reaction took place at a temperature maintained at 1000° C. The low rate provided an average retention time of the reactant and product gases within the reactor of 0.15 second. Titanium trichloride made up 2.5 parts by weight of the mixed vapor. After cooling the titanium dioxide product rapidly to below 600° C, the titanium dioxide was separated, calcined at 650° C for 2 hours, and ground in a fluid energy mill.

Titanium dioxide of small, uniform particle size and improved tinting strength is made by the vapor phase oxidation of the tetrachloride with air or oxygen at 700 to 1500° C in the presence of 0.01 to 20 mole per cent of an aromatic organic compound.[68] The mole ratio of titanium tetrachloride to oxygen is from 1 to 1 to a value of 1 to 10. Nucleating centers that control the titanium dioxide particle size are formed by the decom-

position of the organic compound in the reaction zone. Benzene, phenyl chloride, trichlorobenzene, biphenyl, and naphthalene are preferred organic compounds. An orifice-annulus burner is used in the process.

To decrease the abrasive effect titanium dioxide of spherical form is produced by the vapor phase oxidation of titanium tetrachloride at a temperature of 900 to 1200° C in the presence of a small amount, 2 to 10 per cent by weight, of a sulfur chloride or phosphorus chloride.[69] In paint production, iron particles are ground off the mills and discolor the paint film. In the pigment process the reacting vapors and oxygen or air remain in the heated chamber for 0.1 to 5 seconds. During the reaction the titanium tetrachloride and sulfur or phosphorus chlorides are converted to their respective oxides with chlorine being formed as a by-product. The products withdrawn from the reaction chamber are cooled rapidly to prevent further growth of the titanium dioxide particles. From the gas stream titanium dioxide can be separated and recovered by cyclone separators, settling chambers, glass cloth filters, or other suitable means. As an illustration, a mixture of 2 parts by weight of sulfur monochloride and 98 parts of titanium tetrachloride was vaporized, preheated to 1000° C, and then introduced through a central orifice of a concentric type nozzle to the reaction chamber maintained at 1000° C. Dry oxygen similarly preheated to 1000° C was concurrently admitted through the outer annulus of the concentric nozzle into the reaction chamber at a rate such that 38 parts by weight of oxygen were admitted for each 100 parts of the chloride mixture. The gases were allowed to remain in the furnace for 3 seconds, after which they were rapidly cooled. Titanium dioxide recovered from the product by passage through a glass cloth filter consisted predominantly of spherical particles.

Anatase of particle size 0.1 to 0.5 micron is obtained by combustion at 900° C of a mixture containing titanium tetrachloride 25, silicon tetrachloride 0.25, oxygen 44.75, and nitrogen 30 per cent.[70] A particle size of 0.1 micron results from the combustion of a mixture of titanium tetrachloride 1, oxygen 1.5, nitrogen 1.6, and silicon tetrachloride 0.05 parts. The products with 2 to 10 per cent silica have limited use as pigments.

Specified vapor mixtures are formed by transferring liquid mixtures of the components to a surface heated to a temperature above the boiling point of the highest boiling constituent.[71] Thus 99 parts of liquid titanium tetrachloride mixed with 1 part of liquid silicon tetrachloride was agitated rapidly and dropped at a rate of 2 parts per minute onto a surface heated to 250° C to effect vaporization. The vaporized mixture is oxidized to give titanium dioxide pigments. Likewise small amounts of chlorides of aluminum, phosphorus, tin, and antimony can be added to the titanium tetrachloride.

ALUMINA

Pigment-grade titanium dioxide is produced by heating vaporized anhydrous titanium tetrachloride containing 1 to 2 per cent anhydrous aluminum chloride and up to 5 per cent anhydrous chlorine at 136 to 1000° C with oxygen.[72] The vapor mixture is heated to 350° C in contact with an electrically heated tubular resistor composed of amorphous carbon. From the heater the vapors are passed through a second resistor furnace consisting of elecrically heated solid graphite and then into a reaction chamber for interaction with oxygen. Titanium dioxide having a particle size of 0.75 micron and a rutile content of 95 per cent is obtained by the reaction at 1200° C of the vapors of titanium tetrachloride and aluminum chloride with an oxygen containing gas.[73] The mixed vapors are produced by passing a mixture of oxygen and nitrogen through an evaporator containing the two components at 95° C. A mixture obtained by treating 4.5 volumes of bromine and 10 volumes of nitrogen with pure aluminum at 600° C together with titanium tetrachloride 100, silicon tetrachloride 0.5, oxygen 180, and nitrogen 140 volumes yields on oxidation particles of 0.5 micron diameter comprising 95 per cent rutile. Rutile titanium dioxide pigment is prepared by the thermal decomposition of a gaseous reaction mixture of titanium tetrachloride and oxygen in the presence of 0.01 to 10 per cent of a volatile aluminum compound which is converted to the oxide in the process.[74] Between 0.1 and 1 per cent ferric chloride based on the weight of the titanium tetrachloride is included to avoid discoloration.

Finely divided titanium dioxide of pigment grade is produced by the decomposition of vaporized titanium tetrachloride with gases containing free oxygen at a temperature above 600° C in the presence of aluminum chloride and silicon tetrachloride.[75] For instance, a reaction gas mixture consisting of titanium tetrachloride, aluminum chloride, silicon tetrachloride, oxygen, and nitrogen is ignited at 1200° C to produce a pigment containing 0.9 per cent aluminum oxide and 0.35 per cent silica. Pigment-grade titanium dioxide admixed with alumina and nonpigment-grade titanium dioxide is prepared by oxidizing titanium tetrachloride in a fluidized bed at 900° C.[76] Carbon monoxide is introduced to supply heat. Aluminum chloride vapor is added through ports above the fluidized bed. Fine particles of pigment-grade titanium dioxide are carried from the bed with the gas stream. Air or oxygen preheated to 500 to 1200° C is mixed with similarly preheated aluminum chloride within 0.1 to 3 seconds before reaction with titanium tetrachloride vapor at 500 to 1200° C to give a pigment of uniformly fine particle size.[77] The aluminum chloride, 0.1 to 10 mole per cent of the titanium tetrachloride, forms alumina nuclei be-

tween 0.05 and 0.5 micron suspended in the air stream which serve as centers of growth for the titanium dioxide.

Pigmentary-grade titanium dioxide is produced by the vapor phase oxidation of the tetrachloride in the presence of salts or oxides of calcium, strontium, barium, or cerium at 900 to 1400° C by means of air containing water vapor.[78] The reaction products leaving the furnace at 1150° C are quickly quenched to 600° C to prevent increase in particle size.

METHODS OF PREVENTING THE FORMATION OF TITANIUM DIOXIDE SCALE ON THE WALLS OF THE REACTORS AND CONDUITS

The high-temperature vapor phase oxidation of purified titanium tetrachloride with air is carried out under conditions which suppress the deposition of titanium dioxide particles on the walls of the reacting chamber and the conduits.[79] Titanium tetrachloride vapor reacts with oxygen at 900 to 1600° C to produce titanium dioxide and the resulting suspension is cooled quickly to 600° C at which temperature the particles lose their tendency to grow in size. This cooling may be effected by injecting cold reaction product gases, cold titanium tetrachloride or liquid chlorine. The suspension may be cooled below 600° C by indirect means and passed through a cyclone and Cottrell precipitator to remove the titanium dioxide. A principal difficulty arises from the tendency of the titanium dioxide particles to adhere to the walls of the equipment. Coarse particles are formed on the hot surfaces of the reaction chamber.

If the titanium tetrachloride reacts with oxygen in a combustion chamber having walls of a porous refractory material and carbon monoxide passes transversely through the porous walls into the chamber, formation of the coarse material and of the deposit is prevented. The porous walls of the apparatus are surrounded by a gas-tight steel jacket with space between through which the gas is admitted at a slight pressure. Alundum is a suitable material for the porous refractory walls. In addition to repelling the preformed particles of titanium dioxide the carbon monoxide reacts chemically with any free oxygen adjacent to the surface of the combustion zone to prevent its reaction with titanium tetrachloride. By supplying the reducing agent, the carbon monoxide favors the reaction of chlorine with any titanium dioxide that may have plated on the walls of the reactor.

Objectionable titanium dioxide scale deposition and buildup on the internal surface of the reactor used in the vapor phase oxidation of titanium tetrachloride with air is prevented by periodically removing the scale during the reaction by passing a rotating, reciprocally movable, internally

cooled scraping device over the surface.[80] By internally cooling the scraping unit it is maintained at a temperature low enough to avoid corrosion by the chlorine gas. Consequently the pigment is not discolored.

As an application of the process, a vertical cylindrical reactor constructed of nickel and having a 9 inch internal diameter was utilized in the cooxidation of titanium tetrachloride and aluminum chloride. The water cooled scraper was provided with an open ring type of cutting head, the internal diameter of which was slightly less than the internal diameter of the reactor so that it could be moved up and down in the reactor. An electric motor attached to the shaft outside the reactor rotated the scraper. Purified titanium tetrachloride at the rate of 1250 pounds per hour was separately preheated to 950° C and aluminum chloride vapor equivalent to 5 per cent per hour of alumina was mixed with it. The combined vapors were charged continuously into the reactor. Dry air at a rate of 1050 pounds per hour was preheated to 1030° C and water amounting to 6.2 pounds per hour was added by combustion of an equivalent quantity of acetylene in the preheated air and charged into the reactor. The two streams, the chloride vapor and the moist air, became quickly mixed in the reaction zone where they reacted to form titanium dioxide, alumina, and chlorine.

The reactor for the production of pigmentary titanium dioxide is designed so that the titanium tetrachloride and oxygen injection tips are cooled to maintain their surface temperature above the vaporization temperature of the tetrachloride but below the oxidation temperature.[81] A surface temperature of 700 to 800° C is suitable and prevents buildup of objectionable scale deposits on the injection tubes.

In the continuous vapor phase oxidation of titanium tetrachloride to produce pigments, to prevent scale formation on the internal surfaces of the reactor, a wall of rigid, porous, refractory material is used.[82] The wall is kept below 300° C. A shielding gas is maintained over the surface by charging an inert normally gaseous fluid in the liquid state through the pores of the reactor walls for vaporization on the surfaces within the oxidation zone. To avoid incrustations with titanium dioxide the gaseous mixture of titanium tetrachloride and oxygen at 500° C is directed upwards into the center of the reactor.[83] Here it encounters the cascade-like descending, coarse titanium dioxide which has been obtained by separation from the finer particles produced in the oxidation reaction. It is cooled to 250° C before re-entry.

Vaporized titanium tetrachloride is reacted with humidified air at 1000 to 1350° C in a porous carbon tube with chlorine gas diffusing through the walls of the porous tube.[84] This gas shields the surface from contact with the reactants so that undesirable titanium dioxide scale or film does not collect on the surface of the reactor. In the former processes a por-

tion of the titanium dioxide formed deposits on and tenaciously adheres to the internal surfaces of the reactor. A portion of the product is lost since it cannot be recovered in useful form. Even if the titanium dioxide forms in a desirable state, the conditions at the surface of the reactor cause an undesirable particle size growth which renders the product unfit for pigment use. Even where loss of material can be tolerated, segments of the scale frequently dislodge from the surface to contaminate the product. A wide variety of proposals for removing deposits of this type have been suggested, including mechanical scraping, chemical removal, and inert gas shielding.

In an example, employing a reactor provided with a porous carbon reaction zone tube having an internal diameter of 12 inches, a length of 24 inches, and an average pore radius of 48 microns, titanium tetrachloride vapor heated to 850° C was supplied at a rate of 41,000 pounds per hour where it was oxidized upon admixture with a stream of oxygen heated to 1150° C. Twenty-five per cent excess oxygen or 8300 pounds per hour was admitted. The oxygen contained 7.5 pounds of water per 100 pounds of oxygen. Chlorine at room temperature was supplied to the exterior walls of the porous carbon reactor tube at a rate of 3060 pounds, the equivalent of 3.38 pounds per square foot of wall area, per hour. The oxidation reaction proceeded over an extended period of time without serious deterioration of the porous carbon reactor wall and without buildup of titanium dioxide scale.

In decomposing volatile halides of titanium with humidified air at high temperature, some of the oxide remains in the apparatus and interferes with the full flow of gases. These oxides can be removed by reaction at 800 to 1300° C with a mixture of equal parts by volume of chlorine and carbon monoxide.[85] In this process the vapor phase oxidation of titanium tetrachloride with air at 900 to 1200° C is continued until the accumulation of scale on the walls begins to seriously impair the operation of the furnace. At this stage the introduction of reactants is interrupted and a mixture of equal parts by volume of carbon monoxide and chlorine is introduced to convert the titanium dioxide scale to the gaseous tetrachloride which leaves the furnace with the carbon dioxide formed.

An inert gas is injected as a separator between the preheated titanium tetrachloride vapor and oxygen-containing gas forced into the reaction chamber to prevent clogging of the concentric nozzle openings by the titanium dioxide.[86] A spinning or spiral motion is given to the gas components to assure complete mixing. The concentric injection tubes for the gas components are provided with spiral separating strips in such a manner that a clockwise tangential motion is given to the gases from the central and the outer tubes, while the gas from the middle tube has a counter-clockwise motion. Pigmentary titanium dioxide is obtained by

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the vapor phase oxidation of the tetrachloride in a porous, tubular type reaction furnace.[87] To prevent contact of the reactants with the internal surface of the reactor, an inert gas is diffused through the porous walls from an external source maintained under pressure. In the vapor phase oxidation of titanium tetrachloride, incrustation of the burner nozzle is prevented by using hydrogen instead of air as the scavenging gas.[88]

COOLING AND SEPARATING TITANIUM DIOXIDE FROM CHLORINE AND OTHER PRODUCT GASES

The products formed in the vapor phase oxidation of titanium tetrachloride are cooled quickly from 1000° C to 600° C or lower by adding cold gases from a previous reaction, and the titanium dioxide is recovered from the cooled mixture.[89] Final cooling is effected against the aluminum walls of the apparatus which have a high thermal conductivity. The metallic walls may be cooled with water. After cooling the chlorine has little action on the aluminum of the container, primarily a result of the aluminum oxide coating which forms on the surface. Although dry dust-free air, inert gases, or liquefied inert gases may be employed, cooled gas from a previous reaction is more suitable.

In an example, 20 kg per hour of titanium tetrachloride are decomposed with 9 kg per hour of air, 3 kg per hour of carbon dioxide, and 1.7 kg per hour of oxygen of 98 per cent purity in a reaction furnace. The reaction products with titanium dioxide suspended leave the furnace at the bottom at 1000° C. The gases are composed of 41 per cent chlorine, 20.5 per cent carbon dioxide, 29.5 per cent nitrogen, and 9 per cent oxygen, and carry in suspension 750 g per cubic meter (S.T.P.) of titanium dioxide. Immediately after leaving the reaction furnace double the quantity of the reaction gas formed in the process of oxidation but free from titanium dioxide and having a temperature of 20° C is admitted at the exit of the furnace with the hot reaction gases through a nozzle. This decreases the temperature of the mixture to 400° C and decreases the concentration of the titanium dioxide to 250 g per cubic meter. The gas composition is cooled to 150° C in water cooled aluminum tubes. The titanium dioxide is recovered from the gas by a water cooled cyclone and a water cooled electric filter made of aluminum. After removal of the titanium dioxide, the gas current is divided in two parts; two-thirds is cooled to 20° C and reused, while the other one-third is used to chlorinate more ore.

The hot product gases containing titanium dioxide are fed with regulated amounts of cold particles of silica sand or agglomerated titanium dioxide particles into the water jacketed cooling conduit to prevent accumulation of titanium dioxide on the inside of the cooling conduits.[90]

In this process from 5 to 15 per cent of coarse particles are added. The suspension of produced and added titanium dioxide particles is maintained at a high enough velocity through the heat exchangers that the particles remain in suspension. The coarse particles abrasively scour the internal walls of the conduit and prevent deposition of titanium dioxide particles. First the larger abrading particles are removed in the settling chamber, cyclone, or other means and recycled. Thereafter the finer pigment particles are separated in cyclones, precipitators, or filters.

For example, titanium tetrachloride and aluminum chloride were mixed in proportion to yield 99 parts of titanium dioxide to 1 part of alumina and heated to 895° C at a rate equivalent to 2500 pounds per hour of titanium dioxide. Air containing 1 per cent water vapor by volume was heated to 1060° C and quickly mixed with the chloride vapors under 9 psi gauge in an oxidation reactor provided with a scraper for removing oxide scale deposit from the inner walls. The reaction products were continuously fed into a 1500 foot length of water cooled aluminum pipe, the first one-third of which was 12 inches in diameter and the remaining portion was 10 inches in diameter, and then into the collection apparatus. Simultaneously 1100 pounds per hour of cool, recycled gas from a previous reaction was introduced into the system before passing through the water cooled coil. At 2.5 minute intervals 10 pounds of titanium dioxide pigment in the form of aggregates below 0.25 inch in diameter were added to the reaction product at the entrance to the cooling coil.

The hot titanium dioxide suspended in gases produced in the vapor phase oxidation of the tetrachloride is cooled by passing the suspension through a conduit surrounded by water.[91] A pressure is maintained on the water less than the pressure of the gases so that in case of leaks the gas escapes into the water. The water in each compartment is continuously checked for pH to locate any leaks in the system. Water jackets of the first 14 legs are constructed to give a 5 foot head of water; the last five legs are equipped with 3 foot jackets because of the lower gas pressure toward the discharge end. Water exerts a pressure of 0.45 psi per foot of head. The cooling water is supplied at 35° C. The reaction product consisting of 3500 pounds of titanium dioxide, 6230 pounds of chlorine, 1050 pounds of nitrogen, 317 pounds of oxygen, and 170 pounds of hydrochloric acid per hour were at a temperature of 1300° C. Cooled recycled product gases were continuously fed at 3500 pounds per hour to cool the products to 1000 to 1200° C before entering the first leg of the heat exchanger. In operation 3900 pounds per hour of titanium dioxide were separated from the product gases and sent to the calciner.

A hot suspension of titanium dioxide in the gaseous products at 900 to 1350° C obtained from the vapor phase oxidation of the tetrachloride is cooled quickly to 100° C by direct contact with liquid chlorine or with

liquid titanium tetrachloride within 10 seconds to insure titanium dioxide particles of 0.1 to 0.25 micron.[92] In a specific operation, a gaseous suspension at 1000° C comprising the reaction products from the vapor phase oxidation of titanium tetrachloride with air was continuously fed at a rate of 82 cubic feet per minute directly into a conventional spray cooler for passage upward. By volume the suspension was composed of 30 per cent chlorine, 68.5 per cent nitrogen, 1.4 per cent oxygen, 0.09 per cent hydrochloric acid, and 0.29 pound of solid titanium dioxide suspension per pound of gases. The spray cooler was constructed of refractory bricks and the spraying equipment was made of nickel. Concurrently liquid titanium tetrachloride at a feed rate of 2.6 tons a day or 215 pounds per hour was continuously discharged from a spray nozzle into the upper part of the cooler for passage downward for direct contact with the hot gaseous suspension. As a result, the suspension was quenched to 300° C within 10 seconds. After cooling, the suspension was passed through a conventional cyclone separator and thence into a Cottrell precipitator to separate the pigment particles. To condense out and recover the titanium tetrachloride for reuse, the gases were passed through a condenser which cooled them to 25° C. In another example, liquid chlorine was used instead of the titanium tetrachloride.

The separation of titanium dioxide, obtained by the decomposition of the tetrachloride with an oxygen containing gas, from the gaseous products is facilitated by diluting the reaction mixture with a cold inert gas to decrease the temperature rapidly to 400° C.[93] This is followed by further cooling in a water cooled aluminum tube to 150° C. The titanium dioxide is then separated in a cyclone separator and an aluminum electrofilter, both of which are water cooled.

Walmsley[94] cooled the reaction product by passing the suspension through a fluidized bed of coarse titanium dioxide granules which are cooled by contact with tubes around which a cold liquid circulates. The coarse granules in motion prevent the fine suspended particles from adhering to the walls of the bed. Granules of the cooling bed have a diameter at least 100 times that of the suspended titanium dioxide particles, and the gas velocity is at least 1.5 times the critical velocity for fluidizing. Cooling is better effected in stages in several beds. In an example in which 75 pounds of titanium tetrachloride vapor was oxidized per hour at 1040° C in a fluidized bed of 14 to 36 mesh titanium dioxide, 40 per cent of the pigment passed out in the effluent gases which contained per hour 56 pounds of chlorine and 12.8 pounds of titanium dioxide of 0.86 micron average grain size. This gaseous suspension at a velocity of 1.7 feet per second passed upward through a water cooled 8 inch diameter aluminum tube containing a bed of 39 pounds of 44 to 60 mesh titanium dioxide which was fluidized to a 10.5 inch height. The bed weight in-

creased to 39.2 pounds in 2 hours by deposition of fine titanium dioxide, but the remainder of the fines passed out with the gases at 226° C.

A hot suspension of titanium dioxide in the product gases is cooled to 300 to 400° C by blowing into it a cold suspension from a previous reaction having the same particle size.[95] Similarly the hot gaseous suspension is evacuated continuously from the combustion chamber through a cooled tube which opens into the central part of the chamber.[96] After removal of the titanium dioxide the gas is recycled into the reactor by another cooled tube opposite the first. Booge [97] cooled the pigment suspension in a cyclic process outside the reaction vessel. The hot suspension is brought in contact with cool chlorine-containing gas from a previous reaction from which the solid titanium dioxide has been removed. After cooling, the titanium dioxide is separated from the mixture and a part of the gas is recycled for cooling further quantities of the hot reaction product.

Titanium dioxide obtained by the vapor phase oxidation of the tetrachloride is recovered from the hot gases by cooling first by dilution with a chilled gas and then passing the suspension over cooled aluminum surfaces coated with aluminum oxide.[98] From the cooled suspension the titanium dioxide is removed by cyclones or by electric precipitators. The dust-free gas is cooled and recycled to the process as a cooling agent. In an example, titanium tetrachloride is oxidized at 1000° C with an oxygen-nitrogen-carbon monoxide mixture to give a suspension of titanium dioxide in a gas containing chlorine, carbon dioxide, nitrogen, and oxygen. The mixture is cooled to 400° C by adding recycle gas at 20° C and further cooled in water cooled aluminum tubes. Solid titanium dioxide is recovered first in a water-cooled cyclone and then in a water-cooled electric precipitator. Two-thirds of the exit gas is cooled and recycled; the remainder is used to chlorinate more titanium ore.

Rapid cooling below 600° C to reduce corrosion is effected before separating the titanium dioxide pigment.[99] To eliminate clogging by the particles the hot gases are evacuated from the chamber center by cooled aluminum-magnesium alloy tubes without deforming the flame pattern. By another process the titanium dioxide is separated from the vehicular gas in a vertical cylindrical chamber having a high velocity, longitudinal paddle stirrer.[100] Separation is also effected in a fluidized bed of titanium dioxide of the same origin.[101]

In the process of cooling a suspension of titanium dioxide particles in the gaseous products of reaction, primarily chlorine and nitrogen, the inner surfaces of the heat exchangers are kept free of titanium dioxide particles by introducing particulate solid carbon dioxide which sublimes in the cooling zone.[102] The reaction product at 1150° C containing finely divided pigmentary titanium dioxide, chlorine, nitrogen, and a small

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amount of hydrogen chloride is continuously discharged into an elongated, water cooled, tubular, corrosion-resistant metal (aluminum, nickel, or stainless steel) heat exchanger consisting of several vertical sections connected in series by 180-degree bends. The product is cooled to below 600° C in not more than 5 to 10 seconds and discharged to a cyclone, filter, or Cottrell precipitator. At the point of introduction of the reaction products to the chamber a stream of solid carbon dioxide particles 0.3 to 0.4 inch in diameter in an amount of 1 to 10 per cent by weight of the titanium dioxide is introduced. These solid particles of carbon dioxide completely evaporate during passage with the suspension through the cooler within 20 seconds. As a result of the concurrent abrading and cooling functions of the solid carbon dioxide, the heat transfer surfaces of the cooler are kept free of compacted titanium dioxide particles.

REMOVAL OF CHLORINE AND HYDROCHLORIC ACID FROM TITANIUM DIOXIDE

According to Kitamura [103] chlorine is completely removed from titanium dioxide produced by the vapor phase oxidation of the tetrachloride by treating the product with steam at 300° C. To remove adsorbed chlorine, Werner [104] mixed 100 parts of titanium dioxide prepared by the vapor phase oxidation of the tetrachloride with 1.8 parts by weight of boric acid and heated it for 1 hour at 600° C. The pigment obtained was very fine grained and soft. It had a pH of 7.6, an oil absorption of 21.9 and high resistance to discoloration in baked enamels. Similar results were obtained by passing steam containing 0.1 per cent boric acid through the stirred, dry pigment powder at 150° C.[105] The residual acid content of titanium dioxide prepared by the vapor phase oxidation of titanium tetrachloride is neutralized by treating the reaction products with boron chloride at 300 to 900° C.[106] After treatment the solid titanium dioxide is separated from the gas stream and heated at 100 to 200° C in air or in air-containing steam. The boron trichloride calculated as boric oxide is 0.87 per cent of the titanium dioxide.

To avoid the residual acidity of titanium dioxide pigments, from 0.1 to 2.0 per cent by weight of the tetrachloride of molten aluminum is sprayed into the furnace and oxidized to aluminum oxide at the same time.[107] From 0.1 to 5 per cent by volume of water vapor is added to the air admitted. The air enriched with water vapor is preheated to 1350° C, and the oxidation reaction takes place at 900 to 1300° C. A slot jet type of mixing apparatus is employed. For best results the retention time of the reactants in the furnace is from 0.05 to 1 second. The product gases with the suspended solids are cooled to below 600° C by introducing chilled gas from a previous run or by introducing chilled sand. A cyclone, a

porous filter medium or an electrostatic separator is used to remove the titanium dioxide particles.

For example, titanium tetrachloride vapor at 300° C was continuously admitted at a rate equivalent to 100 parts by weight per hour to the upper portion of a vertical reaction chamber constructed of nickel and cooled by means of a circulating molten salt mixture. Simultaneously air containing 1 per cent moisture by volume, preheated to 1050° C, was admitted continuously to the furnace at a rate equivalent to 19 parts by volume of oxygen per hour through a separate inlet. At the same time molten aluminum at 775° C was sprayed into the converging streams of air and titanium tetrachloride in the reaction zone through a ceramic lined nozzle by means of an annular stream of air. Aluminum was introduced at a rate of 0.95 parts by weight per hour. The three reactant streams were rapidly mixed in the upper part of the reactor where the heat of reaction maintained a temperature of 1260° C in the reaction zone. The flow rates provided a retention time of reactants and products within the reaction chamber of 0.15 second. The gaseous suspension of titanium dioxide and alumina was discharged at the lower end of the furnace at 1180° C and cooled quickly by quenching at the reactor outlet by mixing with it cooled product gases in a ratio of 30 parts by weight per hour. After initial cooling the gaseous suspension was passed through a water-jacketed cooling conduit. The pigment of titanium dioxide and alumina was separated from the gaseous products by filtration, calcined to 650° C for 2 hours, and dry ground in a fluid energy mill.

Since the titanium tetrachloride was preheated only to 400° C corrosion problems did not exist. Conversion of titanium tetrachloride was 100 per cent. The finished pigment containing 95.7 per cent titanium dioxide and 4.3 per cent alumina had an excellent resistance to yellowing in enamel finishes.

Titanium dioxide obtained by the vapor phase oxidation of the tetrachloride is neutralized by mixing in the dry state with an oxide or hydroxide of an alkaline earth metal followed by moistening with a limited amount of water and finally drying.[108] Titanium dioxide recovered from the product gases contains 0.1 to 0.3 per cent by weight of hydrochloric acid along with chlorine. The chlorine may be removed by aeration but the hydrochloric acid adheres firmly to the many small particles. Although this closely held hydrochloric acid may be removed by calcination at 600° C, an agglomeration of the particles results, so that the product must be milled. About 0.1 per cent of the alkaline earth compound is mixed with the pigment dry at 100° C to avoid lump formation. From 1 to 3 per cent of water is then added as a spray or as steam to the agitated mixture. After neutralization the pigment is dried without further treatment.

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In an example, titanium tetrachloride is decomposed with an excess of oxygen in a flame of carbon monoxide and oxygen, and the titanium dioxide formed is separated by an electrostatic filter at a temperature of 200° C. The titanium dioxide is passed into a rotating mixing drum fitted with a jacket for heating and for cooling. A vacuum is applied to free the material from chlorine held in the voids. To the resulting product, which contains 0.1 per cent hydrochloric acid, 0.15 per cent screened calcium hydroxide is added and mixed in the rotating drum for 30 minutes. During the mixing operation the temperature drops from 100 to 80° C. By blowing in steam or a spray of water with the drum rotating the mixture is adjusted to a moisture content of 1 per cent. The drum is rotated for 30 minutes more, after which it is evacuated and filled with carbon dioxide. After 30 minutes the drum is heated to 100° C and a suction is applied to remove the moisture and unreacted carbon dioxide.