

EXHIBIT I

TITANIUM

ITS OCCURRENCE, CHEMISTRY, AND TECHNOLOGY

By

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Chapter 17

CHLORIDE PROCESSES OF PIGMENT MANUFACTURE

Processes for the production of pigments from titanic chloride involve thermal hydrolysis of aqueous solutions or the high-temperature splitting (oxidation) of the anhydrous compound. Such solutions may be prepared directly by the action of hydrochloric acid on certain titanium minerals and secondary products, although the more available ores—ilmenite, arizonite, and rutile—are attacked very slowly, if at all, by this reagent, and they are usually treated with chlorine gas at elevated temperature. Anhydrous tetrachloride obtained in this manner is dissolved in water in a separate step to produce solutions of the desired composition.

The earliest investigators fused the ores with alkali metal compounds (sodium carbonate, potassium bisulfate) and dissolved the melt in dilute hydrochloric acid. Many titanates are soluble in hydrochloric acid, but such solutions would necessarily be impure. Similar products may be prepared indirectly by dissolving orthotitanic acid at room temperature, or by adding an alkaline earth chloride to regular sulfate solutions. The resulting alkaline earth sulfate would be insoluble and could be readily removed by settling or filtration.

Hydrochloric Acid Attack

Llewellyn¹ reported a process for decomposing titanium ores with hydrochloric acid in which the ground ore (ilmenite) was digested with the aqueous acid at 50° to 60° C. for a long period of time. After cooling to room temperature, the liquor was filtered to remove any undissolved residue, and the solution containing titanic and iron chlorides was heated at 85° to 90° C. to precipitate the titanic acid. A relatively low temperature was employed during the digestion step to prevent loss of dissolved titanium by hydrolysis. Dissolution was accelerated by introducing gaseous hydrogen chloride continuously or intermittently into the system to maintain the optimum concentration as the reaction proceeded.² According to Riley,³ the whole of the titanium content of titaniferous iron ores

may be dissolved in hydrochloric acid. Solutions containing 100 g. titanic chloride per liter were prepared by dissolving the residue from bauxite after the Bayer process.⁴

By heating finely divided silicate ores of the sphene class,⁵ under controlled conditions with 10 to 20 per cent excess hydrochloric acid of concentration above 15 per cent, the titanium content was converted to chloride and held in solution during the entire extraction process. The acid-ore mixture was first heated under reflux at 40° to 50° C. to avoid loss of hydrogen chloride before the strength of the acid had been reduced by reaction, and to build up a concentration of titanic chloride sufficient to arrest hydrolysis as the temperature was later raised. Losses due to hydrolysis were further reduced by raising the temperature very slowly to the boiling point in 24 hours.

Ores containing iron in the ferric state, such as arizonite,⁶ were first subjected, at 550° to 650° C., to the controlled action of a reducing gas to convert the ferric compounds to ferrous without the formation of metallic iron. The treated ore was then digested with dilute hydrochloric acid under a pressure corresponding to 135° to 180° C. to effect dissolution.

Vigorous and Arrivant⁷ prepared the tetrachloride by the action of hydrochloric acid gas on ferrotitanium. The alloy was heated to a low redness in a porcelain tube, and dry hydrogen chloride was passed through. Reaction proceeded, with the evolution of heat. The ferric chloride formed, condensed in the cooler part of the tube, and tended to clog the passage, while the titanium tetrachloride distilled over and condensed in a receiving vessel. According to a modified procedure, the iron content was selectively dissolved from the alloy with dilute hydrochloric acid, and the residue, containing 80 to 90 per cent titanium, was separated from the oxides and treated with the dry gas as before.

Sulfate solutions of titanium, such as are obtained from ilmenite by commercial methods, were converted to the chloride by treatment with an equivalent amount of calcium, barium, or strontium chloride.⁸ The precipitate of insoluble alkaline earth sulfate was removed by filtration, leaving the solution of titanic chloride.

Chlorination

TITANIUM DIOXIDE. According to Pamfilov and Shtandel,⁹ titanium dioxide chlorinated to the tetrachloride, but carbon should be present in the charge to take up the oxygen and prevent reversal

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of the reaction. Up to 600° C. carbon dioxide was chiefly formed, but above this temperature the monoxide was the main product. Excess chlorine reacted with the carbon monoxide to form phosgene. Ferric oxide and calcium oxide, if present, reacted with titanium tetrachloride to give titanate oxide, ferric chloride, and calcium chloride. Silicates yielded some silicon tetrachloride.

Barton¹⁰ heated a mixture of titanium dioxide and soft coal until the volatile constituents had been driven off, and treated the cinder with chlorine at 650° C. to form the tetrachloride. Similarly, a mixture of crude titanate oxide and carbon was heated with chlorine at 600° C., and the reaction products were led into an expansion chamber maintained at 136° C., where the ferric chloride condensed. The vapor of titanium tetrachloride was then passed through a filter plate, also at 136° C., to a condenser.¹¹ According to another modification, the tetrachloride was prepared by subjecting an ignited mixture of titanium dioxide and lampblack to the action of a stream of chlorine gas.¹² A porous product, which allowed free entry of chlorine,¹³ was obtained by coking at a red heat a briquetted mixture of titanate oxide and sawdust or peat. Once initiated, the heat of reaction was sufficient to maintain the chlorination temperature. In the presence of wood charcoal the reaction went to completion at 500° C.¹⁴ The action of chlorine sufficient to cause at least 1 per cent of the titanate oxide to react per hour started at 800° C.¹⁵ By passing a mixture of carbon monoxide and chlorine over titanium dioxide at a rate of 1 liter per hour for 3.5 hours, 37.4 per cent of the charge was chlorinated at 600° C., and 80.7 per cent at 1050° C.¹⁶ Thus an increase in temperature greatly increased the rate. Employing lampblack instead of carbon monoxide, 67 per cent of the titanium dioxide reacted in 1.5 hours at 600° C., and 79 per cent at 1050° C.

The equilibrium gas mixture,¹⁷ formed on treating titanate oxide and carbon with chlorine at 400° to 1000° C., contained from 30 to 50 per cent by volume of titanium tetrachloride. The other gases were carbon monoxide and carbon dioxide, and as the temperature rose the proportion of monoxide increased at the expense of the dioxide.

In a pilot-plant study of chlorination of briquets, made by heating a mixture of 3 parts rutile, 1 part charcoal, and 1.75 parts thin tar binder, unground rutile was as effective as ground and more effective than titanium dioxide pigment.¹⁸ The chlorine efficiency was 94 per cent with 70 per cent conversion of the charge, but decreased if all the charge was consumed. The condensed liquid, after separation

from ferric chloride by decantation, was clear and yellow, and contained 99 per cent titanium tetrachloride with 0.02 per cent iron. Redistillation from copper gave a colorless product.

The optimum temperature of chlorination of titanium dioxide-carbon mixtures was reported to be much lowered in the presence of manganese dioxide catalyst.¹⁹ In an actual operation, the temperature at which the tetrachloride formed was reduced from 500° to 480° C. by including 0.2 per cent manganese dioxide in the charge. Titanomagnetite concentrates gave a high yield only above 600° C., and the process was complicated by the sublimation of ferric chloride. Spheerite reacted rapidly only above 800° C. Titanic oxide was attacked faster than silica, but slower than calcium oxide.

Most of the iron of ilmenite or titaniferous iron ores was selectively dissolved by leaching with hydrochloric acid, leaving a residue of crude titanous oxide. Such a product, obtained by digesting the finely ground ore with hot hydrochloric acid in a closed vessel, was elutriated from heavy sand, mixed with soft coal, and heated in a stream of chlorine gas at 600° to 700° C. to produce the tetrachloride,²⁰ which, after purification by fractional distillation, was dissolved in water, and the solution was subjected to thermal hydrolysis. The precipitate was washed and calcined to yield titanium dioxide of pigment grade, while the liquor containing the liberated hydrochloric acid was employed to leach the iron from another batch of ilmenite.

ILMENITE. Titanium tetrachloride was formed by subjecting a briquetted mixture of ilmenite and coal to the action of chlorine at a temperature sufficient to volatilize the compounds formed, but not above 750° C.²¹ The products were purified by redistillation. Donaldson²² heated ilmenite or similar ores with charcoal at a temperature below 1000° C., but sufficiently high to reduce all iron compounds to the metallic state without much reduction of titanium. The iron was selectively converted to ferric chloride and volatilized by the action of chlorine at a temperature between 350° and 1000° C. and the residue of titanium dioxide was chlorinated according to normal procedure. A tough granular mass having very desirable form for chlorination was obtained by drying a mixture of 20 to 25 parts powdered coke with 50 to 60 parts ilmenite and 20 parts titania in colloid suspension.²³ The suspension was prepared by agitating 100 parts of sulfuric acid-free hydrous titanous oxide (40 per cent solids) with 15 parts of concentrated hydrochloric acid. Briquettes formed by heating a mixture of titanium ore, ground to 0.5

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mm., and coal, with a starch paste as binder, out of contact with air proved quite satisfactory.²⁴

In a study²⁵ of chlorination of titanomagnetite concentrate containing 44 per cent titanium dioxide, 31.4 per cent ferrous oxide, 16.9 per cent ferric oxide, 1.84 per cent silica, 0.05 per cent chromium oxide, 0.72 per cent manganous oxide, 0.6 per cent copper, 2.76 per cent magnesium oxide, 0.15 per cent phosphorus pentoxide, and 0.16 per cent water, at temperatures up to 600° to 650° C., in a porcelain tube in the presence of solid carbon with a gas velocity of 3 liters per hour for 6 hours, a yield of 98 per cent was obtained. The concentrate was treated in the powdered form and in briquettes of various sizes. Optimum temperature of chlorination of titanium dioxide in the presence of manganese dioxide was found to be 450° to 480° C., and above 500° C. without the catalyst, with a yield of about 90 per cent.

Separation of iron from ilmenite or similar ore was effected by subjecting the finely-ground material, (300 mesh) without previous reduction, to selective chlorination in the absence of a reducing agent at 800° C.²⁶ At this temperature the iron only was attacked, and the resulting ferric chloride was removed from the reaction chamber by sublimation as formed, leaving a residue of titanium dioxide together with a small amount of silica and other impurities. Chlorination of the titanium component began at 815° C., and this temperature should not be exceeded during the initial stage of the process. Best results were obtained above 800° C. The ferric chloride was deposited in cooling chambers and later decomposed by heat to regenerate chlorine for use in treating more ore. Residual titaniferous material was chlorinated in another operation, or it was used directly or was purified by conventional methods.

The amount of iron and titanium recovered as volatile chlorides from ilmenite was effectively controlled by regulating the amount of reducing agent in the charge during chlorination, and with a carbon content within an optimum range, the major portion of the iron was removed without appreciably attacking the titanium.²⁷ If a proportion of carbon in excess of the optimum was employed, some titanium was volatilized as the tetrachloride, and with ore mixtures containing large excesses of the reducing agent the major portions of both iron and titanium were converted to chlorides and removed from the reaction chamber by volatilization. Within the temperature range of 700° to 1150° C., changes in the temperature did not require significant changes in the carbon concentration, but below this range a slight increase in the proportion was necessary to produce

best results. The optimum carbon concentration may be greatly changed, however, by mixing oxidizing gases, e.g., air and oxygen, with the chlorine. Most efficient results were obtained by chlorination above 500° C., but, in general, excessively high temperatures caused sintering of the ore and prevented proper distribution of the gases. Although reaction took place below 500° C., the rate was very slow and the heat developed was not sufficient to maintain the operating temperature. A working range of 700° to 1150° C. gave most efficient chlorination, as well as maximum iron removal with minimum losses of titanium. In a series of tests, samples were prepared by mixing various proportions of finely ground ore and carbon with 12 per cent molasses (based on the ore), and the compositions were formed into briquettes $\frac{1}{8}$ inch in diameter and baked at 400° C. to remove volatile hydrocarbons. These were then chlorinated at a uniform rate of 140 liters of gas per minute per kilogram of sample for 5 minutes at 980° C., employing chlorine-air mixtures of different compositions. With no added carbon other than that derived from the molasses, and employing chlorine with no admixed air, 79 per cent of the iron initially present in the ore was removed. A similar briquetted mixture containing 4 per cent added carbon, under the same chlorination conditions, resulted in removal of 97.5 per cent of the iron with a loss of only 3.4 per cent of titanium, while treatment in the presence of 6 per cent carbon resulted in the removal of 99 per cent of the iron and 22 per cent of the titanium.

The absolute and relative amounts of iron and titanium removed were changed considerably if a mixture of equal volumes of chlorine and air was used as the chlorinating agent. Thus, with 4 per cent carbon in the charge, 85 per cent of the iron was removed without significant loss of titanium, while at a carbon concentration of 8 per cent, approximately 95 per cent of the iron and only 5 per cent of the titanium were converted to chlorides. Employing a gas mixture of 20 per cent chlorine and 80 per cent air, and briquettes containing 8 per cent added carbon, 84 per cent of the iron and practically no titanium were reacted, while 13 per cent carbon resulted in removal of 95 per cent of the iron and only 5 per cent of the titanium. Ordinarily the temperature was maintained by regulating the rate of introduction of ore, carbon, chlorine, and air, but the reaction could be cooled, if desired, by introducing a diluent gas such as carbon dioxide or nitrogen.

According to a typical operation of the process, 100 parts ilmenite ore containing 26 per cent iron and 35 per cent titanium was mixed with 7 parts of carbon and 12 parts of molasses, and the composition

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greatly oxygen, by chlorides at temperatures of 980° C. The rate of reaction was maintained at the initial temperature. The residue contained 93.2 per cent titanium dioxide and 0.74 per cent ferric oxide. This corresponded to a removal of 99 per cent of the original iron with a loss of only 4 per cent of the titanium.

In general, the most desirable and most economical bonding agents for forming briquettes of this type were petroleum asphalt, natural asphaltum, tar, pitch, sulfite liquor from paper making, and bituminous emulsions.

By a very similar process²⁸ employing chlorine without admixed air, a uniform mixture of 100 parts ilmenite ore containing 26 per cent iron and 35 per cent titanium, mixed with 6 parts of coal and 12 parts of molasses, was made up into briquets having an average size of 1/2 inch and baked at 400° C. to remove volatile hydrocarbons. The final product contained 7.2 per cent carbon. Ten parts by weight of the briquetted mixture was heated to 815° C., and 20 parts chlorine was passed through the charge in a continuous stream. Temperature of the system was maintained at 815° C. The unreacted residue, containing 90 per cent titanium dioxide and 0.71 per cent ferric oxide, was chlorinated to yield a relatively pure titanium tetrachloride. Removal of iron from the original ore was 98 per cent complete, while the loss of titanium was only 4 per cent. After initiating the reaction, the briquetted ore and chlorine were introduced into the reaction chamber, together with a gaseous reducing agent, at such a rate that the temperature was maintained above 600° C. without adding air or a solid reducing agent other than that employed as a binder for the titanium-bearing material.²⁹ To prevent the upper part of the bed from cooling to cause condensation of vaporized ferric chloride, Cleveland³⁰ preheated the titanium material and regulated the rate of charging.

From another approach, ilmenite, chlorine, and a gaseous reducing agent, natural gas, were introduced into a reaction chamber at such a rate that the heat evolved by the chlorination maintained the temperature above 600° C.³¹ At this temperature the iron and titanium chlorides were volatilized as formed.

In chlorinating ores at elevated temperatures, heat may be conveyed from the chlorination residue to fresh starting materials by a stream of gas which does not enter into the reaction.³²

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SPHENE. A sphene concentrate containing 25.42 per cent titanium dioxide, 26.82 per cent silica, 28.45 per cent calcium oxide, 2.98 per cent ferric oxide, 1.32 per cent ferrous oxide, 1.29 per cent magnesium oxide, 0.13 per cent manganous oxide, 7.18 per cent phosphorus pentoxide, and 0.14 per cent water was chlorinated at temperatures between 290° and 900° C., although best results were obtained at 800° to 900° C.³⁵ In general, the chlorination of sphene was found to be much more difficult than of titanomagnetite. The chlorine distribution among the components of the concentrate was not favorable. Calcium chloride was formed rapidly, although the final recovery of titanium was almost complete.

CARBIDES. According to Oreshkin,³⁴ chlorine combined with titanium carbide faster and at a lower temperature than with a mechanical mixture of titanium dioxide and carbon. The former reaction took place at 200° C. Carbide prepared by fusing an ore, such as rutile or ilmenite, with coke in an electric furnace gave good yields on chlorination at an incipient red heat.³⁵ The crude titanium tetrachloride produced was freed from vanadium by shaking with sodium amalgam and from chlorine by distillation. The slag (soluble with difficulty) formed in the hearth of aluminum furnaces employing titaniferous bauxite contained, in addition to coal and lime, 45 to 47 per cent titanium as carbide and was readily attacked by chlorine at 400° to 500° C.³⁶ The titanium tetrachloride formed was separated from chlorides of iron and aluminum by distillation and converted to the sulfate by heating with sulfuric acid at 160° to 200° C. Hydrolysis of aqueous solutions of the sulfate salt by boiling for 7 hours gave a recovery of 96 per cent. Brallier³⁷ prepared the tetrachloride by passing chlorine over the carbonitride, containing 70 to 75 per cent titanium, in a furnace consisting of a steel shell lined with carbon slabs and cooled by a water spray.

In a commercial method of manufacture the ore or concentrate, usually rutile, was first heated with coke in an electric furnace to form the carbide or cyanonitride, and this product was treated with gaseous chlorine at elevated temperatures.

ALLOYS. Favre³⁸ chlorinated alloys of titanium, iron, and copper, containing from 0.1 to 20 per cent of the latter element, and reported that the reaction began at 250° C. Such products were obtained by subjecting a mixture of a copper-magnesium-aluminum alloy and ilmenite to cupro-aluminothermic treatment, or by subjecting a mixture of copper and ilmenite to electrosilicothemy. A mixture of titanic and ferric chlorides was obtained by passing dry chlo-

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per cent titanium dioxide, 1.29 per cent calcium oxide, 7.18 per cent iron oxide, and 7.18 per cent silicon dioxide. The best results were obtained by chlorination of the concentrate in a vacuum furnace.

Combined with iron, titanium dioxide was reduced with a mixture of aluminum and carbon. The former was used using an iron ore. This process gave good results in the crude titanium dioxide. Shaking with the slag (soluble in furnaces) and lime, the product was attacked by hydrochloric acid. Ferric chloride formed by distillation was reduced at 160° to titanium trichloride salt by boiling. The product prepared by this method, containing a steel shell

concentrate, was reduced in a vacuum furnace to titanium metal, treated with

iron, and coprocessed with aluminum and carbon. The products were reduced by subjecting to a mixture of dry chloro-

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rine over powdered ferrotitanium at a dull red heat.³⁹ Industrial alloys containing up to 55 per cent titanium were employed. Titanium tetrachloride, being the more volatile, distilled past the ferric chloride in the reaction tube and condensed in a water-cooled worm. The product was colored red by ferric chloride, but because of its low solubility the greater part of this impurity was removed by filtration. Further purification by fractional distillation gave a colorless liquid which did not fume on exposure to air. According to a related method, most of the iron was dissolved from the alloy by treatment with dilute hydrochloric acid, and the residue, containing 80 to 90 per cent titanium, was chlorinated as in the previous operation. De Carli⁴⁰ treated an iron-titanium alloy with chlorine at 400° to 500° C. and purified the product by fractionation after allowing it to stand over mercury or copper.

The brittle mass obtained by plunging ilmenite, heated to 1000° C., into cold water, was pulverized, mixed with half its weight of aluminum powder, heated to 500° C., and the reaction was set off by a layer of dry titanium dioxide and aluminum, which was ignited by a magnesium flame. This reduced reaction product⁴¹ was placed in a combustion tube and heated to redness in a current of chlorine. Ferric chloride deposited in the cooler portion of the tube, while the titanous chloride was carried on to the condensing chamber and was purified by distillation. The first fraction contained some silicon tetrachloride and chlorine.

Helbig⁴² mixed titanium dioxide in gel form with powdered carbon and a small amount of the oxide of a metal of the sixth or seventh group of the Periodic System, dried the product, and treated it with chlorine at a red heat. Once initiated, the reaction proceeded exothermically.

In the absence of carbon, the approximate decreasing order of reactivity of chlorine at 1000° C. was reported to be iron oxide, magnesium oxide, calcium oxide, titanium dioxide, zirconium oxide, alumina, and silica.⁴³ More complex compounds containing these oxides, silicates, and spinel were less reactive. Furthermore, the rate of reaction depended upon the thermal history and was less for strongly calcined materials.

CONTINUOUS CHLORINATION. Ilmenite or similar raw materials were chlorinated in a continuous process⁴⁴ by introducing the ore, carbon, and chlorine into a reaction chamber at such a rate that sufficient heat was evolved by the reaction to maintain the temperature above 600° C. Maximum efficiency was obtained, however, at 850°

to 1250° C. For most purposes better results were obtained by holding the carbon content at 15 to 35 per cent of the ore. Proportions below this range were insufficient to insure complete chlorination of both iron and titanium components, while on the other hand excessive amounts made temperature control difficult. A quantity of briquets 0.25 to 0.75 inch in diameter was prepared from a mixture of 100 parts ore, 23 parts coke, and 14 parts molasses, and baked at 600° C. to drive off the volatile materials. These carbonized pellets were introduced at a rate of 120 pounds an hour into a furnace having a 15-inch internal diameter and preheated to 1000° C. Chlorine was introduced at the rate of 2 to 2.5 pounds per minute, and the temperature was maintained at 850° to 1000° C. throughout the run without externally heating the furnace. Vapors were withdrawn from the furnace as formed, and cooled to 40° C., with the result that 85 per cent of the ferric chloride and 25 per cent of the titanium tetrachloride condensed in this operation. The condensed chlorides were transferred to another part of the receiver, and the titanium tetrachloride was revolatilized by passing exhaust gases of the furnace over the mixture. Agnew and Cole⁴⁵ fed the briquetted material into the reaction chamber upon a movable framework base, and introduced chlorine above the frame and air below. Movement of the framework removed unchanged material and gangue from the reaction zone, which was maintained at approximately 600° C. To effect continuous chlorination of titanium dioxide in the presence of coke, Brallier⁴⁶ kept the temperature up to the required 700° C. by causing titanium carbide or cyanonitride to react simultaneously. According to another modification, the necessary heat for the reaction was supplied by introducing silicon into the reaction zone.⁴⁷ The silicon tetrachloride formed was separated by fractional distillation.

In a cyclic process,⁴⁸ selective chlorination of ilmenite or titaniferous iron ore was carried out in two steps at different temperatures to effect a separation of iron and titanium chlorides. Finely ground ore was mixed with powdered coal or charcoal and formed into briquets with the aid of a fatty or tarry bonding material, such as oil, tar, or pitch, and subjected to a reduction roast in a furnace or rotary kiln which also served for the chlorination vessel. The briquetted material was heated, in the absence of air, at 800° C. for 1 to 2 hours in a retort which was sealed, except for a small opening to allow escape of the gases driven off, and then cooled in the reducing atmosphere to 350° C. At this stage dry chlorine gas was passed through the reduced mass, and at this temperature iron only

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was attacked and the ferric chloride formed passed over in the vapor form and was condensed in a cooling chamber. The direction of flow of chlorine was then reversed, and the temperature was raised to 550° to 600° C. Within this range the titanium component was attacked and the resulting tetrachloride, containing traces of chlorides of iron, silicon, and vanadium, passed into a cooling tower where it was condensed. The crude material was purified by re-distillation.

However, by mixing a reducing gas with the chlorine, the two operations were carried out simultaneously and the ore was chlorinated directly without incorporation of coal or the formation of briquettes. Chlorides of iron, silicon, and titanium were formed successively as the temperature was increased, and these were separated by fractional distillation. After purification the titanium tetrachloride was dissolved in cold water, and the solution was neutralized with an alkali or alkaline earth metal base. The precipitate of orthotitanic acid was filtered, washed, and redissolved in strong sulfuric acid, and this sulfate solution was hydrolyzed by boiling to obtain a good yield of titanium dioxide of high purity. Slight hydrogenation, brought about by introducing the purified gas or by addition of metallic zinc to the liquor, facilitated the precipitation. The product was filtered, washed, and calcined for pigment use, and the filtrate, consisting primarily of dilute sulfuric acid, was concentrated for use in dissolving more gelatinous oxide.

By another approach the purified titanium tetrachloride was dissolved directly in dilute sulfuric acid, and the hydrogen chloride liberated was passed into a solution of sodium hydroxide. The titanium sulfate solution obtained was subjected to thermal hydrolysis, as before. In either case the alkali metal (sodium) chloride liquor was electrolyzed to recover chlorine and the corresponding hydroxide, both of which were again used in the process. The ferric chloride was dissolved in water and reduced in solution to the ferrous salt by boiling with ferrous sulfide, according to the reaction, $2 \text{FeCl}_3 + \text{FeS} \rightarrow 3 \text{FeCl}_2 + \text{S}$. Sulfur was separated by filtration, and the solution was electrolyzed to recover chlorine for reuse and metallic iron as a by-product. Agnew⁴⁸ treated the effluent from the electrolytic cells with lime to precipitate the remaining iron as hydroxide, and used the separated hydroxide to neutralize more liquor prior to electrolysis so that the cyclic process resulted in no loss of iron.

As a vaporized mixture of chlorides of iron and titanium obtained from ilmenite was cooled, the ferric chloride condensed first, but

some of the solid remained suspended in the tetrachloride vapor and was carried over into other parts of the condenser system where it tended to clog the apparatus. This troublesome suspended material was removed from the vapors by spraying with cooled liquid titanium tetrachloride.⁵⁰ After removal of the iron component, the titanium tetrachloride was condensed to the liquid state. The initial condensation could be controlled to produce the required amount of liquid titanium tetrachloride to wash the suspended ferric chloride from the uncondensed vapors.⁵¹ Following this procedure the purified tetrachloride vapor was condensed to the liquid state without clogging the apparatus. By a similar process, the vaporized mixture was washed first with cold liquid titanium tetrachloride to remove the suspended ferric chloride and then with water to condense the tetrachloride and at the same time form an aqueous solution for hydrolysis.⁵²

AGENTS OTHER THAN CHLORINE. Chloroform⁵³ reacted with hot powdered titanium dioxide to form the tetrachloride, carbon monoxide, and hydrochloric acid. According to Chauvenet,⁵⁴ the chlorinating power of phosgene was inferior to that of a mixture of chlorine and carbon, because of the endothermic nature of the decomposition of carbonyl chloride.

Jeness⁵⁵ heated a gaseous mixture of chlorine and di- or higher chlorides of sulfur to near the boiling point of the sulfur compound, and passed the mixed vapors over heated ores to form titanium chloride and sulfur. Similarly, on heating rutile with sulfur monochloride, the iron and vanadium components were first attacked and distilled off as chlorides, leaving almost pure titanium dioxide.⁵⁶ The latter could be converted slowly to the tetrachloride, but the mixture was difficult to purify, since the titanium compound had about the same boiling point as sulfur monochloride.

Before chlorination, the titanium-bearing silt obtained as a waste product in purifying bauxite was treated with hydrogen sulfide to convert the iron component to the nonreactive sulfide.⁵⁷ Sulfur chloride, chlorine, or carbon tetrachloride was used successfully as the chlorinating agent.

By passing the mixed vapors, obtained by chlorinating clays or similar materials in the presence of coal, into a fused mass of equimolecular amounts of aluminum chloride and alkali metal chloride containing suspended solid alkali metal chloride, the iron and aluminum fractions were removed, leaving the silicon and titanium tetrachlorides.⁵⁸

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Purification of Titanium Tetrachloride

As already noted, the crude tetrachloride prepared by the chlorination of titaniferous materials usually contains free chlorine, together with small proportions of dissolved compounds of iron, silicon, vanadium, and other elements derived from the charge, and is of a yellowish or reddish color. This discoloration has been ascribed to vanadium oxychloride, ferric chloride, and uncombined chlorine. Since ferric chloride is only slightly soluble in the product, the greater part of it may be recovered, along with other suspended particles, by filtration after cooling to room temperature. The other constituents, with the exception of vanadium, may be readily separated by fractional distillation, and this impurity may be removed by a similar operation after treating the liquid with sodium amalgam⁶⁹ with gold, silver, mercury, copper, or bronze,⁶⁰ or with iron or carbon.

The vanadium in crude titanium tetrachloride is probably present as the oxychloride or tetrachloride, both of which are volatile liquids at ordinary temperature and cannot be recovered by ordinary distillation. Jenness and Annis⁶¹ found that the addition of small amounts (0.25 to 0.50 per cent) of certain organic materials to the crude tetrachloride caused the formation of vanadium compounds which were insoluble and nonvolatile at temperatures considerably above the boiling point of the titanium tetrachloride. These complex compounds were separated by distillation or by such mechanical methods as filtering or centrifuging. Effective organic compounds polymerized in the crude tetrachloride product and reacted with the vanadium during polymerization to form nonvolatile, readily separable compounds.

Examples of this type of compounds are rubber, crude or vulcanized, balata, art gum, polymerized sulfonated oil, soy-bean oil, cottonseed stearin, Russian mineral oil, and acetylene gas. Ordinary rubber was partly polymerized, but further polymerization took place, producing a black, brittle, granular solid. The resulting compound with vanadium was separated from the liquid by distillation, filtration, or centrifuging. Russian mineral oil contained a large proportion of naphthenate compounds which were the active agents. It also appeared that titanium tetrachloride was a good polymerizing agent. The action during polymerization appeared to consist first of forming an addition compound with the crude liquor, followed by a reaction between this and the vanadium, with the liberation of titanium tetrachloride and the formation of a finely polymerized prod-

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The extent of removal was dependent upon time, temperature of the reaction, and the per cent of agent employed. For instance, 0.10 per cent balata did not remove the vanadium after refluxing for 1 hour, but under the same conditions 0.25 per cent effected complete removal. Also, 0.5 per cent balata produced vanadium-free tetrachloride after only 15 minutes refluxing at 136° C., but contact with this proportion of agent at 20° C. for 16 hours did not effect complete removal. Vanadium was recovered quantitatively from the polymerization product.

According to Pechukas,⁶² crude titanium tetrachloride was purified and decolorized by treatment with carbon having absorptive or adsorptive properties, followed by distillation. Best results were obtained by using carbon black, such as lampblack, bone black, and gas black, although charcoal and petroleum coke were also found to be effective. The carbon containing the absorbed or adsorbed impurities or their reaction products was recovered and regenerated for further use. Dependent upon the initial color of the liquid and the proportion of carbon used, the time and temperature of the operation were capable of considerable variation. If the discoloration was secured by liquid contact, refluxing at atmospheric pressure (136° C.) for a period of time in excess of 10 minutes, followed by distillation, was found to give a yield of purified titanium tetrachloride above 99 per cent. In treating the vapors, any convenient temperature above the boiling point of the liquid proved satisfactory.

In an example, 100 parts of crude yellow titanium tetrachloride was agitated with 4.1 parts lampblack and heated under a reflux condenser at 136° C. for 15 minutes, after which the treated liquor was distilled rapidly to yield a colorless liquid.

According to Gage,⁶³ crude titanium tetrachloride was purified by distillation after treatment with lower chlorides of titanium. These compounds could be formed in place by reducing a portion of the original compound, as for instance with hydrogen. In an actual operation, 100 parts of crude yellow titanium tetrachloride was treated with 5 parts of the trichloride, heated under a reflux condenser at 135° C. for 2 hours, and then distilled rapidly in an atmosphere of dry carbon dioxide. The condensate was a clear, colorless liquid. Metallic impurities, such as compounds of iron, vanadium, and manganese, were precipitated from the crude material by treatment with an active sulfide, such as hydrogen sulfide or arsenic sulfide,⁶⁴ or by passing hydrogen sulfide into the liquid in

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the presence of 0.05 to 0.5 per cent ferric stearate or other heavy metal soap.⁶⁶ A process developed by Meyers,⁶⁶ effective in removal of vanadium compounds, consisted of mixing an alkali metal soap with the tetrachloride, followed by evaporation. No heating was required. From 0.1 to 1.0 per cent of a sodium or potassium soap of stearic, myristic, palmitic, oleic, or lauric acid gave best results, and the vanadium content was reduced below 0.001 per cent. Meister⁶⁷ added 5 to 10 g. crystalline ferrous sulfate per liter to crude titanium tetrachloride, refluxed for 1 to 6 hours, and distilled to get a product of high purity. Purification was similarly effected by a simple distillation after refluxing with small quantities of alkali metal hydroxide, powdered iron, tin, antimony, or copper and water.⁶⁸ In an example, 4 g. to 10 g. sodium hydroxide, 1 g. to 5 g. water, and 3 g. to 20 g. zinc powder were added to 1 liter of crude tetrachloride, the mixture was refluxed for 2 to 4 hours at atmospheric pressure, and distilled to get a colorless product containing less than 0.001 per cent vanadium. At the same time iron was reduced to less than 0.001 per cent, calculated as ferric oxide. From another approach, the vaporized material was heated at 800° to 1000° C. in the presence of hydrogen to reduce the impurities to solid compounds which were readily separated.⁶⁹

Stoddard and Pietz⁷⁰ purified titanium tetrachloride in a pilot plant by distillation with copper. One and one half per cent copper was the minimum amount that produced a colorless product. The powder used was prepared by reducing finely ground cuprous oxide with hydrogen. In a specific test, a colorless product was obtained by distillation after heating the crude tetrachloride with 1.5 per cent copper powder at 98.5° C. for 15 minutes. Oleic acid also gives good results, but it offers several disadvantages.

Hydration or Dissolution of the Tetrachloride

In dissolving anhydrous titanium tetrachloride in water, an initial turbidity usually occurs as a result of the separation of oxychlorides or hydrous oxides. These compounds can be redissolved, however, if additional amounts of the anhydrous tetrachloride are added. Investigations revealed that the original precipitates were caused by the great rise in temperature that accompanies hydration. If no cooling was provided, the temperature of the solvent rose to above 100° C., until a concentration corresponding to 130 g. titanium dioxide and 250 g. hydrochloric acid was reached. At this point hydrochloric acid gas was evolved, and precipitation began to be

apparent. If more tetrachloride was added, the temperature decreased and the suspended material gradually dissolved to give a clear concentrated solution. The decrease in temperature in the second stage of the process occurred because the heat of evaporation of the hydrogen chloride was greater than the heat of solution of the titanium tetrachloride.

Because of losses of hydrogen chloride, the clear solutions obtained by this method contained tetravalent titanium and chlorine in an atomic ratio less than the theoretical 1 to 4, and usually about 1 to 2.7. Concentrations corresponding to 550 g. titanium dioxide and 600 g. hydrochloric acid per liter were readily attained.

Better results were obtained by employing dilute hydrochloric acid instead of water as the initial solvent.⁷¹ Hydrogen chloride started boiling off at a lower temperature; the rise in temperature was less; and the degree of precipitation was decreased. Clear solutions of any practical concentration were obtained by mixing the anhydrous material in a similar manner with dilute aqueous titanium tetrachloride containing more than 150 g. free and combined hydrochloric acid per liter.⁷² Dissolution in this manner was accompanied by a small increase in temperature and copious evolution of hydrogen chloride so that the final product contained a lower proportion of chlorine than that corresponding to the chemical formula $TiCl_4$. The working solvent was prepared by dissolving titanium oxychloride in an excess of concentrated hydrochloric acid and adjusting the product to a concentration corresponding to 60 g. titanium dioxide and 160 g. hydrochloric acid per liter. Once in operation, a portion of the clear concentrated solution was diluted with water and used as the initial solvent.

The process was carried out in a continuous manner by running the anhydrous tetrachloride and aqueous solvent simultaneously into a dilute titanous chloride solution containing more than 150 g. hydrochloric acid per liter. A typical product contained the equivalent of 550 g. titanium dioxide and 600 g. hydrochloric acid per liter, which corresponded to an atomic ratio of titanium to chlorine of 1 to 2.6.

Following these methods of preparing solutions of titanium tetrachloride, local overheating occurred, caused by the high heat of solution, with the result that some of the compound was lost by volatilization. This loss was reduced by vigorous agitation of the system and by cooling, but it could not be entirely avoided by these precautions. However, if the anhydrous material was introduced below the surface of the aqueous solvent, with constant agitation, losses resulting from evaporation were almost entirely avoided.⁷³

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One or more submerged pipes were employed for the anhydrous material; by passing a current of dry air or inert gas along with the tetrachloride, backing up in the pipes was prevented and danger of clogging by the basic precipitates was minimized. Water, hydrochloric acid, or dilute solution of the tetrachloride served as suitable solvents in the process.

Dissolution was also carried out in a continuous manner by simultaneously introducing the anhydrous material and the aqueous solvent through submerged feed pipes into a small initial quantity of the solution from a previous run. Concentration of the titanium chloride was adjusted by regulating the rate of addition of the two components. The product was removed continuously through an overflow outlet in the vessel.

Precipitation of Titanium Dioxide

Three general methods of obtaining titanium dioxide from titanate chloride have been employed: (1) hydrolysis of aqueous solutions by heating, by dilution, or by addition of alkali; (2) by introducing anhydrous titanium tetrachloride in the vapor phase, along with steam, into a reaction chamber; (3) by heating the anhydrous material in the vapor phase, admixed with air or oxygen at a high temperature, either indirectly or in a direct flame.

HYDROLYSIS OF SOLUTIONS BY BOILING. Titanium dioxide may be obtained commercially from the tetrachloride by hydrolytic precipitation effected by heating its aqueous solution or by bringing the anhydrous material in the vapor phase into contact with steam in a reaction chamber. By regulating the conditions and employing a suitable seeding agent, titanium dioxide of pigment grade can be produced. In large-scale operation, the splitting operation has the advantage that chlorine is recovered directly rather than hydrochloric acid. Before use, however, the tetrachloride must be carefully purified, a step not so important in the methods involving hydrolysis of aqueous solutions, since most of the objectionable impurities remain dissolved in the acid hydrolysis liquor.

Thermal hydrolysis of chloride solutions in the presence of nuclear titanate acid, precipitated from a separate portion of the solution by moderate heating after reduction of the acidity to a pH of between 2 and 3 either by dilution or by neutralization with an alkali, yielded a product which on calcination gave a pigment of the rutile type having a correspondingly high tinting strength.⁷⁴ Such seeding compounds obtained at low acidity, for instance a pH of 5 to 7, had

little nucleating power. On the other hand similar products obtained from very acid solutions, for example those having a hydrogen ion concentration greater than pH 2, were very active, but stabilization required particular care. Very active nuclei were found to be less stable at high temperatures and were cooled quickly to preserve their effectiveness. To obtain the maximum degree of stability, the seed was subjected to a controlled cooling at a rate dependent upon the original acidity, and the temperature was maintained during the precipitation.

As a rule, a proportion of nucleating compound from 5 to 8 per cent of the titanium dioxide to be precipitated was required, and it was not essential that the seed dissolved in the main hydrolysis solution. Nuclei less active than normal were employed in larger proportions, and for the same results concentrated solutions required more seeding agent than dilute solutions. Freshly prepared titanous chloride solutions were more reactive than older ones and thus required less nucleation.

Titanium prepared in accordance with this process was of the rutile crystal form, and the resulting pigments had higher tinting strengths than the anatase products obtained from sulfate solutions.

In a typical operation, a chloride solution containing the equivalent of 150 g. titanium dioxide per liter and having an atomic ratio of titanium to chlorine of about 1 to 3 was employed for hydrolysis and for preparation of nuclei. A portion of the solution was treated with aqueous sodium hydroxide to bring the pH to 2.5, heated at 80° C. for 30 minutes to develop the nucleating property, and cooled quickly to below 50° C. The solid product precipitated in this manner was the active seeding agent and was usually separated and washed before use, although the original suspension in the mother liquor was effective. A quantity of the seeding material containing 7 g. titanium dioxide was added to each liter of the original chloride solution and the mixture was heated at 100° C. Hydrolysis proceeded rapidly and was complete in 10 minutes. The precipitate of hydrous titanous oxide was washed, treated with 2 per cent potassium bisulfate, heated slowly to 900° to 950° C. in a rotary calciner, and held at this temperature for 15 minutes.

According to another approach, anhydrous titanium tetrachloride, free from iron, copper, and vanadium, was allowed to run into 18 per cent hydrochloric acid, and the resulting oxychloride was dissolved in water to produce a solution containing the equivalent of 320 g. titanium dioxide and 353 g. hydrochloric acid per liter. Dilute aqueous sodium hydroxide at 40° C. was added to a portion

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of the solution, with agitation, and during the procedure the temperature rose to 60° C. The amount and concentration of the reagents were so chosen that after mixing the pH of the solution was 2 and the strength corresponded to 30 g. titanium dioxide per liter. This liquor was then heated to 80° C., held at this temperature for 30 minutes, and cooled to below 60° C. by adding cold water in such proportion as to bring the concentration to 20 g. titanium dioxide equivalent per liter.

The remainder of the original solution was then mixed with concentrated hydrochloric acid to yield a liquor in which the atomic ratio of titanium to chlorine was 1 to 4, and seed was added to supply titanium dioxide equal to 8 per cent of that to be precipitated. After dilution with water to 55 g. titanium dioxide and 100 g. hydrochloric acid per liter, expressed as hydrolysis products, the liquor was heated to 90° C. in 12 minutes and held at this temperature for 30 minutes to effect hydrolysis. The washed precipitate was reslurried in water to 250 g. per liter solids, treated with potassium bisulfate in an amount equal to 1.5 per cent of the titanium dioxide, dewatered, and calcined at 950° C. for 30 minutes. Both pigments were of the rutile crystal modification, and after milling and pulverizing by the conventional methods exhibited tinting strengths one fourth to one third higher than the best anatase products.

Similarly, titanium tetrachloride seeded with a sol prepared by heat-treating a diluted portion of the same solution gave a hydrolysis product which, after calcination at moderate temperature, exhibited the rutile crystal structure and the high tinting strength corresponding to this modification of titanium dioxide of pigment grade.⁷⁵ Heat treatment developed the nucleating property of the sol, and both temperature and time were important, since over-curing lessened the effectiveness of the product. Longer periods of heating at lower temperatures were required to develop the maximum nucleating efficiency. Best results were obtained by curing solutions, containing the equivalent of 10 to 20 g. titanium dioxide per liter, at 80° to 90° C. for 10 to 15 minutes. The resulting sol presented a slight opalescence, and the particles could not be separated by the conventional methods of filtration and washing. However, the degree of dispersion of the colloidal titanic oxide and its homogeneity did not seem to have a great influence on the nucleating property of the sol.

Tetrachloride solutions for hydrolysis contained the equivalent of 140 g. to 160 g. titanium dioxide per liter, and the proportion

of nuclei was from 5 to 9 per cent of the total titanium dioxide. Solutions of high purity gave products of higher opacity and better pigment properties, although the presence of iron and organic impurities was not found to be detrimental to efficient nucleating properties of the sol. Any ferric iron was reduced to the ferrous state to prevent its precipitation with the titanium.

To illustrate, 1 liter of an aqueous solution of titanous chloride, containing the equivalent of 15 g. of the dioxide, was transferred to a flask fitted with a mechanical stirrer and a reflux condenser, and heated to 80° to 85° C. After 10 minutes at this temperature, 1250 ml. of an untreated solution at room temperature was added, containing the equivalent of 150 g. titanium dioxide per liter, and the mixture was heated to boiling and refluxed for ½ hour. The precipitate was filtered, washed, calcined, and pulverized to yield a pigment of the rutile crystal form having a tinting strength 20 to 25 per cent higher than the conventional anatase product along with excellent color and brightness.

Barksdale and Plechner⁷⁶ prepared very effective nuclei by heat-treating dilute solutions of titanium tetrachloride to which an alkaline agent had been added to convert from 10 to 60 per cent of the potential or active hydrochloric acid to a salt that would not hydrolyze under the conditions subsequently employed. The efficiency of the nucleating composition, and the quality of the pigment obtained, were found to depend upon a number of co-related factors which may be more conveniently described separately.

The solutions employed were prepared by diluting commercial titanium tetrachloride with water; because of losses of hydrochloric acid gas by volatilization, the proportion of chloride was usually less than that corresponding to the chemical formula $TiCl_4$, and in some solutions was as much as 10 to 15 per cent. However, the method was also applicable to solutions produced indirectly, as by dissolving orthotitanic acid in hydrochloric acid or by adding alkaline earth metal chlorides to solutions of titanium sulfate. Iron and other polyvalent heavy metals, present as impurities, were reduced to the more stable toward hydrolysis, lower valent form, by electrolytic means or by adding zinc, scrap iron, or sulfurous acid. Concentrations expressed as hydrolysis products, according to commercial practice, between 250 g. and 400 g. per liter titanium dioxide and 450 g. to 640 g. per liter hydrochloric acid, gave best results, and at the same time permitted more economical operation of the process. Such solutions were used for hydrolysis and for preparation of the seeding agent.

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In preparing nuclei, an alkaline compound was added to a portion of the original solution in such proportions that from 10 to 60 per cent of the potential hydrochloric acid, normally from 30 to 45 per cent, was neutralized. The composition of the alkali used was of minor importance provided that it formed a compound nonhydrolyzable under the conditions of processing, and such bases as calcium hydroxide, potassium carbonate, sodium hydroxide, aqueous ammonia, sodium sulfide, and certain organic amines fulfilled this requirement to a high degree. It is evident that the chlorides of these agents were soluble in water and that they dissolved in the solution. Calcium oxide, in addition to its low cost, gave optimum results but since it was relatively insoluble in water, it was added in the form of a slurry or in the solid state.

Concentration of nuclear solutions from 5 g. to 30 g. per liter titanium dioxide proved effective, but best results were obtained within the range of 10 g. to 20 g. per liter. Obviously the potential hydrochloric acid was less than that corresponding to the normal salt.

Proper curing of the nuclei was a function of both temperature and time of heating, and could be followed roughly by the degree of turbidity developed, which reached a translucent stage. In general, 10 minutes at 80° to 90° C. developed the nucleating property to the maximum degree, although the same results were obtained by holding the system at a lower temperature for a longer period of time, for instance at 70° to 75° C. for 1 hour. The exact change in the solution was not established, but a large part of the titanium component was converted from the crystalloidal to the colloidal condition. Partial neutralization did not render the solution of titanic chloride more susceptible to precipitation during the subsequent heat treatment, as might be expected, but on the contrary made it more stable. Such a solution, after treatment with the alkali, could be heated for a longer period of time at a given temperature without precipitation of titanic oxide. However, with both solutions precipitation would finally occur, but curing was not carried to this stage. The greatest efficiency of the nuclear composition, as measured by the properties of the pigment obtained, was found to be the combined effect of the partial neutralization and the heat treatment.

In carrying out the hydrolysis step, the manner of mixing the components was not particularly important, but for convenience the nuclear composition was usually added to the solution of titanium chloride to be precipitated. The nuclei were employed at the temperature formed or cooled to room temperature, and the hydrolysis solution could be preheated to the evolution of hydrogen chloride

gas. Titanium, supplied to the hydrolysis mixture by the seeding composition of from 1 to 10 per cent of the total, exerted satisfactory nucleating properties, but from 4 to 6 per cent yielded titanium dioxide of the best pigment properties.

The efficiency of the nucleation and the quality of the resulting products were influenced by the final concentration of the hydrolysis mixture, and values from 125 g. to 150 g. per liter titanium dioxide proved most satisfactory. After mixing the nuclear suspension with the chloride solution water was added, if necessary, to adjust the concentration to the desired value. If the hydrochloric acid content exceeded 225 g. per liter, hydrogen chloride gas was evolved on boiling, and arrangement for its recovery or disposal was provided. The seeded mixture was heated to boiling and maintained to bring about the hydrolytic reaction. A yield of 97 per cent or better was usually obtained after $\frac{1}{2}$ hour, in some tests in 15 minutes, and rarely was it necessary to continue the boil for 1 hour.

In an actual operation, a solution prepared by diluting commercial titanium tetrachloride with water and containing 340 g. per liter of the dioxide and 545 g. per liter hydrochloric acid (expressed as hydrolysis products), was employed. To a portion of this solution containing the equivalent of 15 g. titanium dioxide was added 7 g. hydrated lime (the equivalent of approximately 1 mole of hydrochloric acid per mole of titanium tetrachloride), with stirring. This partially neutralized clear solution was diluted with water to 1 liter, heated to 85° C. in 20 minutes, held at this temperature for 10 minutes, with agitation, and cooled rapidly to room temperature. The product was an opalescent colloidal solution of titanium dioxide. This composition was added rapidly to 1000 ml. of the original solution, with constant agitation, and 500 ml. water was introduced to adjust the final concentration to 144 g. per liter titanium dioxide. The seeded mixture was heated from room temperature to boiling in 30 minutes, and refluxed for 1 hour to precipitate 97 per cent of the titanium as hydrous oxide. This product was filtered, washed with water acidified with sulfuric acid to prevent peptization, and calcined at 800° C. for 1 hour to produce a pigment of the rutile crystal form having excellent brightness and color and the very high tinting strength of 1750 by the Reynolds method.

A nucleating composition, prepared by heating a titanium tetrachloride solution containing the equivalent of 5 g. to 30 g. of the dioxide per liter and 0.5 to 2.0 mole proportions of a nonoxidizing univalent anion such as chloride, acetate, or formate, at 80° to 90° C. for 10 to 15 minutes to develop a decided opalescence, accelerated

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and directed the thermal hydrolysis of relatively concentrated aqueous solutions of the tetrachloride.⁷⁷ The cation had no appreciable influence upon the hydrolysis, but only colorless compounds, for example, calcium chloride, sodium metaborate, and potassium acetate, were of practical value. Approximately 5 per cent of the nuclear suspension, based on the titanium content, was required, and the hydrolysis product after calcination at a relatively low temperature was of the rutile crystal modification and had the correspondingly high hiding power and brightness. Von Bichowsky⁷⁸ prepared a solid nucleating agent corresponding to the formula $Ti(OH)_3Cl \cdot 5H_2O$ by evaporating a solution of titanium hydroxy chloride. The product was effective in the hydrolysis of chloride and nitrate solutions.

To produce titanium tetrachloride solutions more amenable to directed hydrolysis on addition of external nucleating agents, the initial solution was subjected to heat treatment at a temperature below that at which titanium dioxide would be precipitated, and the residual colloidal material was coagulated and separated.⁷⁹ This heat treatment removed residual components which would have a nucleating influence.

Hydrolysis is effected without introducing externally prepared nuclei by adding concentrated titanium tetrachloride solution to hot water and boiling the resulting mixture to complete precipitation of the titanium dioxide.⁸⁰ The solution is added to the water at a sufficiently slow rate to insure the initial formation of colloidal titanium dioxide particles which serve as seed for the product formed later in the process. In general, the concentration of the chloride solution and ratio of solution to water are such that, after hydrolysis, the resulting liquor has a composition corresponding to constant boiling hydrochloric acid. Yields of 96 per cent are obtained in $\frac{1}{2}$ hour, and the washed and calcined product gives a rutile pigment of excellent covering power and brightness. In an example, 1000 ml. of a titanium tetrachloride solution containing 300 g. of titanium dioxide and 480 g. of hydrochloric acid, expressed as hydrolysis products, was added in 5 minutes to 1000 ml. of boiling water, with constant agitation. The mixture was heated to boiling in 15 minutes and refluxed for 30 minutes to effect hydrolytic precipitation of the titanium. This precipitate was filtered, washed, and calcined, without further treatment, at 850° C. to produce a pigment of the rutile crystal form possessing excellent brightness and color and having a tinting strength one third higher than that of the commercial anatase products. A similar process employs more dilute solutions.⁸¹

Readily filterable hydrous titanous oxide of high purity was obtained by the thermal hydrolysis of aqueous solutions of the tetrachloride containing not more than 0.1 mole of polyvalent negative coagulating ion derived from oxalic, tartaric, phosphoric, or citric acids or their alkali metal salts per mole of titanium dioxide.⁸² Alternatively, the same results were obtained by adding the tetrachloride solution to hot water containing the coagulating ions. The mixture was boiled to complete the precipitation of the titanium. Since hydrous titanous oxide was readily peptized in dilute aqueous hydrochloric acid, better results were obtained by employing very dilute sulfuric acid as the washing liquor.

According to a specific operation of the process, anhydrous titanium tetrachloride was dissolved in water to obtain a solution containing the equivalent of 15 per cent titanium dioxide. All iron present was reduced to the ferrous condition. To prevent reoxidation during processing, about 2 g. per liter of titanous ions was formed. One thousand pounds of this solution was added in 1 hour to 7000 pounds of boiling water containing 2 pounds of citric acid, and by the end of the mixing operation 95 per cent of the titanium had precipitated as hydrous oxide in a coagulated form that was easily filtered and washed. The washed pulp was calcined at 700° to 1000° C. to produce a rutile pigment of good color and high tinting strength. By employing specially purified raw materials, titanium dioxide pure enough for a standard in volumetric analysis was obtained by this method.⁸³ A precipitate of high quality was obtained by hydrolytic decomposition of aqueous titanium tetrachloride in the presence of 25 to 30 per cent sodium sulfate.⁸⁴ At 69° to 72° C., 10 per cent solutions gave highest yields and 5 per cent solutions the poorest, although at 98° to 101° C. there was no difference in recovery from solutions containing from 5 to 20 per cent titanium tetrachloride.

Darling⁸⁵ obtained finely divided titanium dioxide by passing the tetrachloride, in vapor form, into a boiling solution of glucose. During the process, glucose was converted to glutaric acid. Jenness⁸⁶ added the tetrachloride to a solution of hydrochloric acid to form a mixture of basic chlorides in the form of a dry yellow granular powder, and separated and calcined the product to obtain fluffy white titanium dioxide of pigment grade.

Processes for the manufacture of titanium dioxide pigments from siliceous minerals of the sphene class were reported by Alessandrini.⁸⁷ If the finely ground ore was heated with hydrochloric acid of concentration above 15 per cent, the titanium values were dis-

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solved and held in solution during the extraction step, along with calcium compounds and minor constituents of the ore such as iron, magnesium, aluminum, and vanadium, leaving a residue composed essentially of silica. However, to hasten dissolution of the soluble constituents, and to obtain a maximum recovery of titanium, an excess of 10 to 20 per cent hydrochloric acid was employed. The mixture was heated under reflux at 40° to 50° C. for several hours to avoid loss of hydrogen chloride before the strength of the acid had been reduced by reaction, and to build up a concentration of titanous chloride sufficient to prevent hydrolysis at the higher temperatures employed in the later stages. During the next 24 hours the temperature was raised gradually to the boiling point, and heating was continued until no more titanium dissolved. Since compounds of polyvalent elements such as iron were more readily attacked by the acid and were more stable toward hydrolysis in the lower valent condition, the reaction was carried out in the presence of 1 to 2 per cent of a reducing agent such as titanous chloride or stannous chloride. Iron, for example, was reduced before the titanium, and the added agent was not sufficient to reduce an appreciable amount of the tetravalent titanium. The final solution, containing most of the titanium of the original ore as chloride along with nonhydrolyzable chlorides of calcium, magnesium, ferrous iron, aluminum, and other metals, and some free hydrochloric acid, was cooled and separated from the siliceous residue by decantation or filtration. It was then concentrated to the desired strength by vacuum evaporation and subjected to thermal hydrolysis to precipitate the titanium as hydrous oxide. By leaving the silica suspended in the original solution, composite pigments were produced.

In an example, 1000 pounds of finely ground sphene (100 to 200 mesh), analyzing 32 per cent titanium dioxide, 29.6 per cent silica, 18.7 per cent calcium oxide, 12.9 per cent alumina, 1.43 per cent ferrous oxide, 4.29 per cent ferric oxide, 1.12 per cent magnesia, and 0.10 per cent manganese oxide, was mixed with 8300 pounds of 29.5 per cent hydrochloric acid in a vessel fitted with a reflux condenser and held initially at 40° C. for 4 hours to avoid loss of hydrogen chloride. During the next 24 hours, as the acid concentration was reduced by reaction, the temperature was raised gradually to the boiling point, about 107° C. At this stage the reaction had practically ceased and the mixture was cooled and filtered. Ninety-four per cent of the titanium was recovered in the filtrate, which weighed 9100 pounds and contained 300 pounds titanous oxide equivalent, 1420 pounds free hydrochloric acid, and 369 pounds calcium chloride.

This solution was next subjected to the usual reducing treatment, concentrated in a vacuum evaporator at 50° C. to 11 per cent titanium dioxide, and poured into three volumes of boiling water containing an amount of oxalic acid equal to 0.05 per cent of the titanium dioxide to be precipitated. The liquor was heated to its boiling point in a tank provided with an outlet for the recovery of hydrochloric acid, and held at this temperature until 95 per cent of the titanium was precipitated as hydrous oxide. The hydrolysis product was filtered, washed, calcined, and pulverized to produce a practically pure titanium dioxide pigment of the rutile crystal form possessing excellent color and brightness and high tinting strength.

In a cyclical process, ilmenite ore was extracted with hydrochloric acid to leave a titanium dioxide concentrate which was chlorinated to form the tetrachloride.⁸⁸ The titanium tetrachloride was dissolved in water and hydrolyzed by boiling to precipitate the dioxide. Hydrochloric acid liquor formed during hydrolysis was used to extract more ilmenite ore. Leach liquor from the first step was electrolyzed to yield iron and chlorine, and the chlorine was used to form more titanium tetrachloride.

Dutt⁸⁹ prepared titanium dioxide from solutions obtained by dissolving the residue from bauxite, after the Bayer process, in hydrochloric acid. Such solutions contained up to 100 g. per liter titanous chloride; any considerable excess of hydrochloric acid was neutralized and the iron component was reduced to the ferrous state. Sodium acetate was added in an amount equal to one tenth of the titanium tetrachloride present, and the liquor was boiled to precipitate hydrous titanous oxide. After almost complete neutralization, the filtrate was treated with barium salts to precipitate barium vanadate.

Barton⁹⁰ treated a sulfuric acid solution of ilmenite with barium chloride, filtered off the insoluble barium sulfate formed, and heated the resulting chloride solution at 100° C. for 5 to 8 hours to effect hydrolysis. The precipitate of hydrous titanous oxide was washed, dried, and calcined to produce a product of 98.2 to 99.8 per cent purity. By an opposite approach,⁹¹ the clear solution obtained by dissolving 1 volume of titanium tetrachloride in 2 volumes of water was mixed with 0.35 volume of 95 per cent sulfuric acid and heated to distill off the hydrogen chloride. Heating was continued until fumes of sulfur trioxide were given off. During this period the temperature rose to 150° C., and most of the hydrochloric acid was recovered. The residue, consisting of a white friable mass that contained 77 to 80 per cent titanous oxide, 18 to 20 per cent sulfur trioxide, and 2 to 3 per cent chlorine, was transferred to a calcining

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furnace and heated to expel the remaining acids, leaving relatively pure, friable titanium dioxide of chalky appearance having a specific gravity of 3.65. Paint films pigmented with this material had a bluish cast, apparently because of its amorphous nature and very fine particle size.

A solution of titanium hydroxide in 2 molecular proportions of hydrochloric acid was boiled with sulfuric acid in the presence of kieselguhr and aluminum silicate to effect hydrolysis.⁹² Similarly, aqueous titanium tetrachloride was neutralized to precipitate a gelatinous oxide, and this product was washed and redissolved in 25 per cent sulfuric acid. The solution was boiled to bring about hydrolytic reaction. Precipitation was facilitated by slight hydrogenation, which was accomplished by direct introduction of the gas or by addition of zinc.⁹³ The amorphous oxide was calcined to produce a crystalline pigment.

Gelatinous titanic oxide of exceptional purity was obtained by treating aqueous titanium tetrachloride with an alkali metal carbonate.⁹⁴ On boiling in a bath slightly acidified with sulfuric acid, the precipitate passed into a dense unctuous mass of pigment grade. Hydrous oxide, prepared by heating dilute tetrachloride solutions in air, acted as a strong protective colloid.⁹⁵

The reactions of chloride solutions of titanium were carried out in an iron vessel surrounded by a casing through which water flowed.⁹⁶

According to Atanasiu,⁹⁷ the rate of hydrolysis of titanic chloride solutions increased with temperature and dilution, and platinum exerted a catalytic action. The reaction was bimolecular, indicating a series of consecutive reactions between the colloidal and aqueous phases. Alcohol diminished the rate. Such solutions yielded hydrolysis products which gave rutile directly on calcination.⁹⁸ If precipitation was carried out in the presence of sulfate or phosphate ions, however, products were obtained which on moderate calcination showed the crystal structure of anatase but were transformed at higher temperatures into rutile.

VAPOR PHASE HYDROLYSIS WITH STEAM. Very finely divided, soft, and uniform titanium dioxide of pigment grade was obtained by the hydrolytic reaction between vaporized anhydrous titanium tetrachloride and steam or water vapor at temperatures of 300° to 400° C.⁹⁹ The vapor phases were heated separately to the required temperature before being introduced into the reaction chamber to prevent undesirable low-temperature reactions. For example, two

saturation vessels, constructed and operated after the fashion of an ordinary wash bottle, were employed to produce the vapors. One was charged with titanium tetrachloride and held at 120° C.; the other was charged with water and heated to 80° C. Air was passed through to produce two gaseous streams consisting of air and titanium tetrachloride, and air and steam in the volume ratio of approximately 1 to 1. The two gaseous mixtures were preheated separately to 400° C., and introduced simultaneously into an upright cylindrical reaction vessel heated externally to 400° C., in such proportions that for each liter of reaction space 1 liter per minute of the steam and air mixture (0.5 liter steam) and 0.1 liter of the tetrachloride-air mixture (0.05 liter titanium tetrachloride vapor) entered. The vapors were directed so as to transverse the reaction vessel in a downward direction, where they reacted to form titanium dioxide and hydrogen chloride, and the products passed into a dust chamber heated at 200° to 400° C. to prevent condensation or adsorption of the hydrochloric acid on the titania during the precipitation. Hydrochloric acid vapors emerging from the dust chamber were condensed and reused.

Even at decomposition temperatures as low as 300° C. titanium dioxide, practically free from chlorides, was obtained in almost quantitative yield, while the material separated at 380° to 400° C. possessed covering power equal to pigments produced from sulfate solutions calcined at 900° C. By this method a product suitable for direct use as pigment was obtained without the necessity of a calcination step.

According to a related process, vapors of titanium tetrachloride and water were injected into a closed collector maintained at an elevated temperature to effect hydrolysis, and the products of reaction were discharged tangentially to produce a forced circulating action within the chamber.¹⁰⁰ The titanic oxide was collected on a porous diaphragm while the hydrochloric acid gas and air passed through the openings.

A homogeneous finely divided titanium dioxide was obtained by the action of steam on titanium tetrachloride in admixture with a solid, inert, water-soluble salt, such as an alkali metal chloride or sulfate, at an elevated temperature.¹⁰¹ One hundred parts titanium tetrachloride was mixed with 200 parts finely ground potassium sulfate to form a plastic mass which was heated to 300° to 400° C., and a current of steam was passed over the mix for 1 hour. Steam was then shut off, the temperature was raised to 800° C. and maintained for 15 to 30 minutes. The mass was cooled to room tempera-

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ture, leached with water to remove the potassium sulfate, and the residue of titanium dioxide was further washed, dried, and pulverized for pigment use.

Thermal Splitting

In general, the reaction between titanium tetrachloride vapor and steam produces coarsely crystalline dioxide not well suited for pigment purposes. Furthermore, it is extremely difficult to provide apparatus that can resist the action of moist hydrochloric acid at the high temperatures employed. These difficulties were overcome, however, and a soft finely divided titanium dioxide of excellent pigment properties was produced from vaporized tetrachloride by a process in which the splitting reaction was brought about by oxygen or air at temperatures above 1000° C.¹⁰² In carrying out the process, a saturation vessel, constructed and operated on the lines of a wash bottle, was charged with titanium tetrachloride and heated at 120° C. Nitrogen was passed through to produce a gaseous product consisting of approximately equal parts of the two constituents, and this mixture was 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 were so regulated that for each liter of reaction space there was 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 reacted to form titanium dioxide and chlorine, and the products were discharged into a dust chamber where separation was brought about. Titanium dioxide produced in this manner possessed excellent pigmentary properties and did not require subsequent processing.

To minimize coarsening and undesirable crystallization of the particles during the splitting reaction, the gaseous mixture of tetrachloride and air was raised rapidly to the reaction temperature. The gases were preheated, but to minimize premature reaction they were not mixed before reaching the splitting chamber, which was already heated to the required temperature. The choice of splitting temperature above 1000° C., and the gas velocity, could be regulated within wide limits.

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

Finely divided titanium dioxide was obtained by bringing vapors

of the tetrachloride into the direct flame of a combustible gas or vapor.¹⁰³ For example, purified coal gas was loaded with titanous chloride vapors and ignited in air. Highly dispersed titanium dioxide resulted, and owing to its high specific volume it was carried along with the gas currents and separated in a chamber provided with several filtering materials or in precipitators of the Cottrell type.

By subjecting vaporized titanium tetrachloride to thermal decomposition in the presence of oxygen, titanium dioxide of pigment grade was produced without the formation of large crystals by keeping the vapors out of contact with hot surfaces within the chamber during the splitting reaction.¹⁰⁴ Apparently titanous oxide formed adjacent to the hot walls of the reaction vessel, deposited on the surface, and served as seed which grew to form large crystal agglomerates, and these reduced 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, were 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 were 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. was also maintained. The collected titanium dioxide, in powder form, was further calcined to remove the last traces of chlorine. Pechukas and Atkinson¹⁰⁵ employed a special calcination chamber to heat titanium tetrachloride vapor with oxygen at 400° to 800° C. to produce a pigment of improved properties. Schornstein¹⁰⁶ 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, titanous chloride and air were preheated separately to 1000° to 1100° C. and passed into a reaction chamber maintained at 750° C. by means of a cooling jacket.¹⁰⁷ The proportion of chloride to oxygen was 1 to 4. During the reaction a yellow-green flame burned at the outlet of the preheating tube and a pigment smoke issued from the other side of the reaction vessel. The pigment was very voluminous and possessed excellent whiteness.

To minimize crystal growth and produce titanium dioxide of pigment grade, the chloride vapor was not allowed to come into contact with hot surfaces of the reaction chamber. This was effected by

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maintaining an atmosphere of nitrogen around the tetrachloride inlet.¹⁰⁸ A temperature of 1000° C. was employed. The same result was attained by causing the titanium tetrachloride vapor to react with an oxygen countercurrent in a vertical cylindrical furnace, and withdrawing the evolved chlorine so that it surrounded the area of introduction (inlet) of the tetrachloride.¹⁰⁹ This procedure prevented reaction from taking place at the hot surfaces.

A modified pigment was prepared by passing a hot vaporized stream of titanium tetrachloride over a metallic oxide to form a chloride of the metal and disperse it in the vapors.¹¹⁰ The mixed chlorides were then decomposed in a suitable chamber by reaction with oxygen at high temperature. After filtering from the gas stream, the mixed oxides were further purified by calcination to remove the last trace of chlorine.