Experimental Station
E. I. du Pont de Nemours & Co., Inc.
Wilmington
April 24, 1933

LITERATURE AND PATENT REFERENCES RELATIVE TO THE CHLORIDE PROCESSES FOR PREPARING TITANIUM OXIDE.

By: J. H. Peterson

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MEMORANDUM FOR DR. KRATZ

FROM J. E. PETERSON

LITERATURE AND PATENT REFERENCES RELATIVE TO THE CHLORIDE PROCESSES FOR PREPARING TITANIUM OXIDE

This memorandum lists patent and literature references which were compiled in connection with the economic survey of chloride processes for production of titanium oxide.

Literature References

The literature reference list is not a complete bibliography of titanium tetrachloride as it does not go beyond the year 1900. There is considerable literature prior to that date particularly on the preparation and properties of titanium chloride but this early work is completely reviewed in the standard reference works on inorganic chemistry. Here emphasis was therefore placed on the more recent work in this field. References were obtained from Chemisches Zentralblatt 1900-1907 and Chemical Abstracts 1907-1933.

Some of the references do not wholly apply specifically to titanium chloride but were included because of their relation to this subject. The list has been arbitrarily divided into three sections: (I) Treatment and Processing of Titanium Ores, (II) Preparation of Titanium Chlorides, and (III) Miscellaneous. Because of the general nature of a number of the references, the grouping is not in all cases particularly rigid but the classification was made to comply with the grouping used in the patent listing.

Patent References

The patent list covers patents which were thought to be most pertinent in connection with the preparation of titanium chloride and its use in the preparation of titanium dioxide. No attempt was made to extend the list to include patents on related subjects such as the preparation and utilisation of other similar chlorides ($AlCl_3$, $ZrCl_4$, $SnCl_4$, $SiCl_4$, etc.). A survey of such patents and also of the literature on these compounds, no doubt, would be of value if further work on the preparation and use of $TiCl_4$ is undertaken. The patent list was obtained from the following sources: Chemisches Zentralblatt, Chemical Abstracts, recent issues of the Patent Bulletin, Titanium Dioxide - Literature and Patent Study by Dr. Gatewood, Patents Relating to the Chloride Process by Dr. McKinney and a list taken from Dr. de Rohden's files also submitted by Dr. McKinney.

The patents have been grouped under five headings: (I) Ore Processing and Ore Attack, (II) Preparation of Titanium Chloride, (III) Hydrolysis of Titanium Chloride and Preparation of Titanium Chloride Solutions, (IV) Composite Pigments, (V) Miscellaneous.

(A) Literature References

I. Treatment and Processing of Titanium Ores

Lukens, Hiram Stanhope, J. Am. Chem. Soc. 35, 1464-69. A Study of Sulfur Monochlorides on Various Minerals. Various minerals heated in a stream of S_2Cl_2 to temperatures between 450° and 750°. Rutile is practically completely decomposed.

Monk, P.N., and Traill, R.J., Canadian Chemistry and Metallurgy 10, 137-39. Electrolytic Iron from Ilmenite. Ore heated with carbon, the material then extracted with $FeCl_3$ solution to remove the iron. The TiO_2 is not changed.

Schichuaki, I., J. Chem. Ind. 7, 543-47, March 1930. Preparation of Titanium Concentrates by Melting Titanium ores with Baryte.
$BaSO_4$, $CaCl_2$, coal and ore are mixed. $BaSO_4 + 4C = BaS + 4CO$; $BaS + CaCl_2 = BaCl_2 + CaS$; $CaS + FeOTiO_2 = CaOTiO_2 + FeS$; or without $CaCl_2$; $FeO.TiO_2 + BaSO_4 + 4C = BaOTiO_2 + FeS + 4CO$. FeS is dissolved in HCl. The $BaOTiO_2$ is chlorinated at 400° and converted into $TiCl_4$.

Smith, E.F., J. Am. Chem. Soc. 29, 269. Action of S_2Cl_2 upon Minerals. Rutile (powdered) decomposed almost completely by S_2Cl_2 forming $TiCl_4$.

Stähler, A., and F. Eschron, Ber. 44, 2906-15 (1911). Titanium XV.
Preparation of Ti metal; red. of titanium compounds; formation of trivalent Ti.

Gulyaboumkii, M.S., Snopova, K.V., and Rathov, V.I., Mineral Suir'e 6, 522-7 (1931).
A method described for reduction of Fe_2O_3 in oxidized ilmenite or titano-magnetite with H at high temperatures with separation Fe from TiO_2, the latter to be used in prepn. of Ti white.

Traill, R.J., Can. Dept. Mines, Mines Branch No. 655, 95-6. Report of investigations; hydrometallurgical laboratory. Metallization of Ilmenite. High grade TiO_2 concentrate obtained.

Traill, R.J., and McClelland, W.F., Am. Electrochem. Soc. Pamphlet, May 1929. Metallization of the oxide of iron in Ilmenite.

Traill, R.J., and McClelland, W.F., Can. Dept. Mines, Mines Branch No. 655, 96-101 (1926). Process for the treatment of ilmenite for the recovery of electrolytic iron and TiO_2 concentrate and other purposes.
Results in preliminary way indicate practicability of operating plate cell at 35 amp. per sq.ft. without causing undue Cl evolution at anode, by arranging a rapid flow of electrolyte through catholytic compartment of the cell.

Traill, R.J., and McClelland, W.F., Canadian Chem. & Met. 13,265-266, 272 (1929). Metallization of the oxide of iron in ilmenite.

II. Preparation of Titanium chlorides

Beloglazov, K.F., Contributions to the Study of the Natural Resources of the U.S.S.R. No. 56, 20-3 (1926). Report of the titanium commission on the experimental results in obtaining $TiCl_4$.
Briquets prepared from Ti ore (ground to 0.5 mm.) mixed with C and binder such as starch paste. Heated in absence of O_2 and then chlorinated. By direct chlorination of briquets it was possible to obtain $TiCl_4$ from ilmenite on large scale.

Brallier, P.S., Trans. Am. Electrochem. Soc. 49, 1926. The Chlorination of Metals.
$TiCl_4$ prepared from titanium carbonitride, containing 70-75 per cent Ti, by passing Cl over the charge in a steel furnace lined with carbon.

Chauvenet, Ed., Compt. rend. 152, 87-89. A General Method of Preparing Anhydrous Chlorides.
Method extended to apply to a large number of chlorides other than given in C.A. 3, 1255. Chlorinating power of CCl_4 inferior to that of C and Cl_2. Temperatures of 450° to 650° used.

De Carli, F., Atti. congresso naz. chim. pura. applicata 1923, 399. The use of iron alloys for prep. of halides. Preparation of $TiCl_4$, VCl_4, WCl_6, HBr_5 and $SiBr_4$ from respective iron alloys. In all cases the alloy was treated with halogen at 400 to 500°.

Ellis, H.R., Chem. News 95, 122. Preparation of $TiCl_4$ from Rutile.
Rutile powdered and heated to 500°. Mixed hot with Al powder in Hessian crucible. Reaction started by covering with dry TiO_2, Al powder and igniting with Mg. Mixture of Fe, Al_2O_3, Si, Ti heated to redness in stream of chlorine. Purified by distillation.

Kangro, W., and Jahn, H. Zeit fur anorg. und allg. Chem. 210, 385 (1933). Reaction of Chlorine on Metal Oxides. The reaction of chlorine at various temperatures on metal oxides including BeO, ZnO, CdO, Al_2O_3, TiO_2, V_2O_5, Nb_2O_5, MoO_3, WO_3, UrO_3. TiO_2 reaction studied at 850°, 1000° and 1200°. $TiCl_4$ formed in fairly large quantities at 1000° and 1200°. For apparatus see Kangro and Plugge, Z. Elektrochem. 36 (1929) 189.

Krieger, V.F., Contributions to the Study of the Natural Resources of the U.S.S.R. No. 56. Titanium and its Compounds No. 1. 23-33, 1926.
Reports of the titanium commission on the experimental results in chlorinating ilmenite.

Krieger, V.F., Contributions to the Study of the Natural Resources of the U.S.S.R. No. 56. Titanium and its compounds No. I, 76-108 (1926).
Ilmenite and coal in the form of briquettes subjected to action of Cl_2 at a temp. not higher than 750°. Products purified by dist. Drawings and description of apparatus given. Purification of product described in detail. All steps described.

Maksimenko, M.S., Contribution to the Study of the Natural Resources of U.S.S.R. No. 56. Titanium and its compounds No. I, 33-43 (1926).
Shortcomings of direct chlorination of ilmenite because of Fe content given. Process described for preparing TiC and chlorinating it. Ilmenite fused with C under high elec. potential. Metal fuses with slag. It is ground and separated magnetically. Fe content reduced from 34 to 12 per cent. Second step slag and coal, sawdust and NaCl placed in elec. furnace and heated as for carborundum process. TiC purified with HCl which removes CaC_2, $MgCl_2$ and Fe.

Maksimenko, M.S. and Eliseev, A., Contributions to the Study of the Natural Resources of the U.S.S.R. No. 56. Ti and its Compds. No. I, 43-7 (1926). A technical report on the experiments on the chlorination of TiC.
Apparatus described for chlorination of TiC. Allows easy temp. control, requires little electrical power, does not clog and gives only small quantities of $FeCl_3$. Drawings of apparatus are given.

Montemartini, C. and Losana, L., Giorn. di Chim. ind. ed appl. 6, 323-25. Reaction between HCl and nitrides.
Work carried out with AlN, Mg_3N_2, Ca_3N_2, Ti_2N_3, and BN at high temperatures by passing HCl over the nitrides, ammonia and the metal chlorides given off.

Oreshkin, S.I., Contributions to the Study of the Natural Resources of the U.S.S.R. No. 54, 14-20 (1926). Obtaining $TiCl_4$ from titanium carbide.
Conclusions from 4 series of expts: (1) TiC is decomp. by Cl_2 very easily; at 200° $TiCl_4$ is obtained. With 20-30% carbide in furnace, $FeCl_3$ does not hinder process as it is swept out by $TiCl_4$. $TiCl_4$ formed from TiO_2, C and Cl_2 at a higher temp. and more slowly than from TiC and Cl. This is because TiO_2 after treatment in elec. furnace is cryst. or fused.

Renz, C., Ber. 39, 849-50 (1906). Preparation of $TiCl_4$ and $ZnCl_2$.

Smirenskii, V.S., Contributions to the Study of the Natural Resources of U.S.S.R. No. 56. Titanium and its compounds, No. I, 47-9 (1926). A review of the methods for production of titanium tetrachloride.
No abstract given.

Vigouroux, E., and Arrivaut, G., Bull. Soc. Chim. (4) 1, 19. Preparation of $TiCl_4$.
Ferro titanium used as source material, treated with Cl_2

at low red heat. $FeCl_3$ and $TiCl_4$ separated due to differences in boiling point. Also remove Fe first by treatment of ore with dil. HCl. Residue heated and subjected to action of Cl_2.

Vigouroux, E., and Arrivant, G., Compt. rend., 144, 485. New Methods of Formation and Preparation of Titanium Tetrachlorides.
Reviews briefly historical aspects of prep. Used three methods for preparation from ferro titanium.
1. Ferro tit. heated to redness in stream of dry HCl.
2. Dil. HCl on ore, iron thus extracted. Residue treated as above.
3. Residues from above washed, dried and treated with Cl_2.

III. Miscellaneous

Agte, C. and Moers., Ztschr. Anorgan. Allg. Chem. 198, 233-75. Methods for preparing high melting carbides, nitrides and borides and description of their properties.
Methods described for preparation of nitrides, carbides, and borides of Ti, Zr and Ta and properties given.

Atanasiu, J.A., Bull. Chim. Soc. Romana Stunte 27,81-144 (1921). Hydrolysis of the systems TiX_4-H_2O.
A study of the mechanism of the hydrolyses of $TiCl_4$ and $TiBr_4$. Solutions prepared by dropping $TiCl_4$ into water agitated and cooled or by emulsifying $TiCl_4$ in purified paraffin and extracting with cold H_2O. Rates of hydrolysis at diff. temp. and dilutions studied. Pt reported as exercising a catalytic effect.

Auger, V., Compt. rend. 177, 1302-1304 (1923). Solubility of titanic acid in alkalis and alkali-carbonates. Crystalline titanium oxychloride.
Crystalline titanium oxychloride prepared from $TiCl_4$ and con. HCl by drying over H_2SO_4. A compound of the formula $TiO_2.HCl.3H_2O$ formed.

Baxter, G.P., and Butler, A.Q., J.Am.Chem. Soc. 46, 3117-21 (1926). A revision of the atomic weight of titanium, the analysis of titanium tetrachloride.
$TiCl_4$ carefully purified by fractionating and volumetrically analyzed by improved methods. At. weight = 47.90.

Baxter, G.P., and Fertig., C.J., J. Am. Chem. Soc. 45, 1228-33. Revision of the Atomic Weight of Titanium.
Atomic weights determined by analysis of $TiBr_4$ and $TiCl_4$ from purified materials.

Bonnath, A., Z. Phys. 14, 217-22 (1915). Photochemical reactions of compounds of rare elements.
TiO_2, Ti sulfate and $TiCl_4$ in alcohol or (COOH)$_2$ slowly turn black or brown as simple or complex salts are formed.

Bhatia, A.B., and Ghosh, S., J. Ind. Chem. Soc. 1; 667-97. Absorption on Titanium Oxide Gels.
Stability of TiO_2 gels toward dialysis studied. The coagulation of the gels by electrolytes also studied.

Billy, Maurice, Ann. de Chimie (9) 16, 5-54. A Study of Titanium. Method described for preparation and purification of $TiCl_4$. Methods given for preparation Ti and of the lower oxides of Ti. Per cents and preparation are also described.

Biltz, Wm. and Meineke, Erich, Z. anorg. Allgem. Chem. 111, 1-21 (1923). The Behavior of Certain Halides toward Halogens. Freezing point curves of a number of halides with Cl run. No compd. formed with $COCl_2$, $SiCl_4$, $TiCl_4$, $SnCl_4$ and $AsCl_3$.

Bond, P.A., and Stephens, W.R., J.Am.Chem.Soc. 51, 2210-22, Oct. 1929. Systems formed by Certain Tetrahalides.
The solubility of $TiCl_4$, $SiCl_4$ and $SnCl_4$ in liquid SO$_2$ determined and the systems studied.

Bosch, F., and Meyer, L. Monats. Chem. 33, 1407-1429 (1912). Action of the silent electric discharge on a mixture of hydrogen and $TiCl_4$ vapor.

Brantley, L.R., and Eastman, A.G., J.Am.Chem.Soc. 52, 3736-62, 1930. The equilibrium between TiO_2, Carbon, TiC and CO at high temperatures.
See Hincke and Brantley, J.Am.Chem.Soc.52, 45-52. Thermodynamic data are given for the reaction: $TiO_2 + 3C = TiC + 2CO$. $\log_{10} p$ atm. $= 3.839 - 5024/T$
$\Delta F = 45,930 - 35.81\ T.$
$\Delta H = 45,930$

Chabrié, M., Bull. Soc. Chem. 29, 207 (1921), 35, 19, (1924). Oxychlorids of Titanium.

Delepine, M., and Lafore, J., Bull. Soc. Chim. 37, 263-6. Analytical Investigation of Carbonyl Chloride.
Estimation of carbonyl chloride in $TiCl_4$. $TiCl_4$ decomp. with HCl (dil) and CO$_2$ evolved is measured by aspirating into a mixture of KOH and Ba(OH)$_2$.

Freundlich, H., and Tuorbyna. Kolloid Ztschr. 51, 236-44. Coagulation of hydrophobic sols by electrolyte mixtures. Study of electrolyte coagulation of sols.

Friedrich, K., and Sittig, L. Zeit. f. anorg. u. allg. chem. 144, 169-84. Zeit. f. anorg. u. allg. chem. 141, 293-320. Preparation and Properties of Carbides.
Methods of preparation and properties of a number of carbides are given including Ti. Second reference deals with preparation of nitrides.

Guthier, A., Boris Ottenstein, Edith Leutheusser, K. Lorsen and F. Allen. Z. anorg. allgem. Chem. 162, 87-100 (1927). Colloidal syntheses with the aid of $TiCl_4$. I. Hydrolysis and oxidation products of $TiCl_4$.
Ag. soln. of $TiCl_4$ yields TiO_2 by dilu. heating and action of air: $TiCl_4 \rightarrow TiCl_3 \rightarrow TiClO_2H \rightarrow TiO_2H_2$. No definite hydrate formed. X-ray analysis showed TiO_2 lattice to be analogous to that of anatase or rutile, depending on sample of titanic acid.

Kowalevsky, M. v., Z. anorg. ch. 55, 189-95. The behavior of halogen derivatives of the carbon group.
Discussion of behavior of $TiCl_4$ and other halides of the carbon group compared with $SnCl_4$. Solutions of $TiCl_4$ described.

Lacroix, F.M., Proc. Nat Polytech. Inst. 2, 46 (1913). Heat transformation of polymorphic minerals.
Heating curves and tables of data for marlet, quartz, chalcedony, witherite, marble, iceland spar, aragonite, CaO, opal, magnetite, cassiterite, rutile, brucite and anatase.

Latimer, W.M., J.Am.Chem. Soc. 44, 90-7 (1922). The distribution of thermal energy in the tetrachlorides of C, Si, Ti, and Sn.
Sp. heat values for CCl_4, $SiCl_4$, $TiCl_4$ and $SnCl_4$ determined to give whole sp. heat curve. Entropy of these compds. at 298°K. calculated and entropy change in formation from elements determined.

Meyer, F., Ber. 56, 1908-14 (1923). Preparation of well-crystallized, anhydrous $TiCl_4$ and the mechanism of the reduction of $TiCl_4$ by hydrogen.

Morley, A.M., and Reed, J.F., J.Chem.Soc. 125, 16-26-34. See also J.Chem.Soc. 121, 441, 1122. The behavior of titanic acid toward HCl.
Two forms of titanic acid prepared and their behavior

described. Their behavior against various conc. of HCl described involving peptization, flocculation and solution.

Nichols, E.L., Physical Review (2) 22, 420-24 (1923). The luminescence of TiO_2.
Luminescence of TiO_2 described under various conditions such as temp., pressure, exciting radiation, etc.

Ramder, K.G., Kong. Norske Vidensk. Selskabs Skrifter 1929, No. 3, 119 pages. Molecular state and reactions of halogen compounds of elements of 4th and 5th groups of the periodic system.
Solubility, heats of solution and reactions are given for chlorides of the elements of the 4th and 5th groups of the periodic system.

Ralston, A.W., and Wilkinson, J.A., J.Am.Chem.Soc. 50, 258-64. Reactions in liquid H_2S.
$TiCl_4$ with H_2S forms only addition compounds $TiCl_4.2H_2S$ and $TiCl_4.H_2S$.

Roth, W.A., Naturwissenschaften 19, 860 (1931). Ordinal number and heat of formation.
Heats of formation of solid oxide (di) as determined by bomb combustion were: TiO_2 215.1 (± 0.3) Kg Cal, SiO_2 205.1 (± 0.5), CO_2 100, Zr 257.4 (± 0.6), Hf 271 (± 5), Th 292.0 (± 1.4).

Roth, W.A., and Becker, G., Zeitschr. physikal. Chem. Bodenstein-Festband 75-80, July 1931. The heat of formation of TiO_2. The heat of formation of TiO_2 was determined and found to be 215.1 ± 0.3 K cal. at 20°C.

Roth, W.A., and Becker, G., Z. Physik. Chem. A159, 1-26 (1932). Atomic Number and Heat of Formation.
A number of heats of formation determined including TiO_2 (rutile) 216.7 ± 3 Kg Cal. Heat of formation of chlorides calculated, $TiCl_4$ being 185 Kg Cal.

Rothkramschweig, W.A., Naturwissenschaften 32, 860 (1931). Atomic number and Heat of Formation.
Heat of formation of the oxides of Si, C, Ti, Zr, Hf and Th are plotted against the atomic numbers.

Rudge, E.A., and Francis Arnall, J.Soc.Chem.Ind. 47, 376-80 (1928). Titanium cyan-nitride and Titanium-oxychloride.
3 $TiCl_4.TiO_2$ prepared by treating TiN with Cl_2.

Schroder, A., Z. Krist. 66, 493-4 (1928). X-ray investigation of the structure of brookite and the physical properties of the three titanium dioxides. Beta-anatase (tetragonal holohedral) at 642°C. changes to alpha-anatase (probably tetragonal). This change reversed on cooling. At 915° ± 15° alpha-anatase changes to rutile, forming stable pseudomorphs.

Schwarz, R. and Richter, E., Ber. 62, 31-36. Study of Silicic Acids. Zur Kenntnis der Kieselsauren. Preparation and properties of silica gels described. $TiCl_4$ hydrolyzed at 0°C., the product washed with acetone. A product obtained having a formula $TiO_2.2H_2O$.

Stahler, Ber. 37, 4405 (1904); 38, 2619 (1905). Titanium I. Hydrates of $TiCl_3$.

Stahler, A., and F. Bachman, Ber. 44, 2906-15. Titanium. Deals with preparation of $TiCl_3$ from $TiCl_4$ by reduction with H. Also decomp. of $TiCl_3$ by heating with H to form $TiCl_2$ and $TiCl_4$. $TiCl_2$ further reduced with H by heating to 1100°C., Ti of 94 per cent purity formed.

Treadwell, F.P., and Terebesi, L., Helv. Chim. Acta. 15, 1053-66 (1932). The Chlorination of Al_2O_3 with Cl_2 and Charcoal. Review of literature. Data calculated from coll. C, Cl_2 Al_2Cl_6, NaCl, HCl Al. For formation of $2AlCl_3$ gas at 600° from Al_2O_3, amorphous C and Cl_2 it is calc. that heat of reaction in Kg. cals and log K_p are resp. -5.7 and -14.8 (CO formed) or 45.3 and -15.7 (CO_2 formed).

Van Arkle, A.E., and de Boer, J.H., Zeit. f. anorg. allg. Chem. 184, 345-50. Preparation of pure Ti, Zr, Hf and Th metals. Method described for preparation of metals by reduction of chlorides with H_2 at high temperatures. From the metals the carbides, selenides, sulfides, and nitrides were prepared.

Wagner, R., Ber. 21, 960-2 (1888). J.Chem.Soc. 54, 557 (1888). $TiCl_4$ and Titanic Acid.

Walker, H.W., Ind.Eng.Chem. 11, 1061-5 (1925). Screening Smokes.
Titanium tetrachloride, p. 1063.

Young, R.C., and Schumb, W.C., J.Am.Chem.Soc. 52, 4233-39. Water-free lower bromides of titanium. Preparation of $TiBr_3$ and $TiBr_2$ from $TiBr_4$. $TiBr_3$ in benzol solution is reduced by Mg to $TiBr_2$ practically quantitative.

(B) Patent References

1. Ore Processing and Ore Attack

UNITED STATES PATENTS

668,266 of 2/19/01 to A. J. Rossi (Half to J. MacNaughton). Process of Producing Concentrates Containing High Percentages of Titanic Oxide.
Ore mixed with sufficient C to reduce iron and silicon but not Ti and also sufficient earthy bases to form a basic titanate with Ti. The mixture heated so that silicon and iron impurities remain and the Ti combined with the earthy bases.

921,686 of 5/18/09 to F. Fitz Gerald and F. W. Dennis (General Electric Co.) Production of Titanium Oxides.
Ilmenite subjected to reduction with powdered C forming a sintered mass. The mass crushed and the reduced iron removed from solid mass. Purification of mass by magnetic separation and acid treatment.

1,106,406 of 8/11/14 to Barton and Rossi (Titanium Alloy Mfg. Co.). Titanic Acid Concentrate and Method for Producing the Same.
Ore smelted with caustic soda and carbon. The mass dissolved in H_2SO_4 and hydrolyzed.

1,166,547 of 1/4/16 to Rossi and Barton (Titanium Alloy Mfg. Co.). Method of Obtaining Titanic Oxide and the Resulting Product.
Method for obtaining titanic oxide (TiO_2) from a substance containing it and iron oxide by melting said substance with an oxide of an alkali metal. The resulting melt digested with HCl in such an amount to combine only with the alkali metal and iron present.

1,239,912 of 9/11/17 to Andre Helbronner. Manufacture of Cement. A process for manufacturing white portland cement by mixing the ordinary ferruginous raw materials of cement with $CaCl_2$ heating the mixture progressively up to 1400°-1500° and submitting the mixture during heating to the action of superheated steam thereby volatilizing the metallic chlorides and collecting the white cement produced.

1,256,368 of 2/12/18 to M. P. Raffix (Societe P. Raffin and Fils). Concentration of Titanium Ores.
Ilmenite separated from silica, etc. by magnetic separation. The purified ilmenite mixed with pulverized carbon with an agglutinant, heated, treated with dilute acid to remove the iron and the titanium residues are washed and dried.

1,325,561 of 12/23/19 to Peder Farup (Titan Co. A/S). Process of Producing Refined Titanium-oxygen Compounds.
Process for producing titanium oxygen compounds from materials containing Ti and Fe by treating the material with HCl in such quantity and concentration and temperatures so as to bring about solution of the iron compounds but leaving the titanium compounds undissolved. The remaining titanium compounds are treated with another decomposing agent to dissolve them.

1,618,795 of 2/22/27 to F. E. Bachman. Titanic acid, Iron and Magnesia from Titanium Ores.
The ore is heated with C and alkali to reduce Fe to metal. The reaction product treated with acid to remove iron and the residue filtered off.

1,640,952 of 8/30/27 to S. J. Lubowsky (Metal & Thermit Corp.). Change of TiO_2 or Rutile into a Form Soluble in Mineral Acid.
TiO_2 or rutile heated with Mg to a temp. equal to Seger cone 18. The product then treated with H_2SO_4 and the resulting compound is dissolved in H_2O.

1,728,296 of 9/17/29 to A. E. Marshall (Maryland Pigments Corp.). Process of Making a White Pigment Base.
The process of making a white pigment base which comprises the steps of treating ilmenite sand containing silica with phosgene gas to remove iron therefrom, fusing the remaining silica and titanium oxide with an alkali and then precipitating these oxides to obtain a pure white pigment base.

1,734,034 of 11/5/29 to H. A. Gregory. Process for the Treatment of Ores for the Recovery of Titanium.
Ore mixed with powdered coal and soda ash, heated to redness, leached with H_2SO_4 to remove iron leaving a titanium oxide residue.

1,745,732 of 2/4/30 to G. J. Bancroft. Method of treating titanium ores by subjecting the ore to a reducing roast in the presence of fluorspar.

1,806,988 of 5/26/31 to W. H. Test. Process for Purifying Pigment Materials.
Reduction of iron oxide in pigment (where present as an impurity) by heating with C to 1000°, after which a stream of CO passed over mass forming iron carbonyl.

1,831,852 of 10/17/31 to Peder Farup (Titanium Pigment Co.). Treating Ti compounds containing Iron.
Process of treating Ti materials containing Fe which consists in subjecting said materials and a reducing agent to

a temp. sufficiently high to reduce Fe to metallic state but not the Ti compounds and treating the reduction product with H_2SO_4 sufficiently con. to dissolve the Ti comp. and without dissolving the metallic iron.

1,845,342 of 2/16/32 to B. D. Saklatwalla (Vanadium Corp. of America). Treatment of Titanium and Iron Containing Minerals.
Process of treating titanium-iron containing materials which comprises subjecting the materials without previous reduction to action of chlorinating gas in absence of reducing agent at a temp. sufficient to chlorinate the iron and remove it by sublimation while leaving the titanium residue substantially chemically unaffected.

BRITISH PATENTS

207,247 of 12/20/23 to C. Gardner and L. Tavener. Processing of Ti-containing Ores.
Ilmenite or similar titanium ore is melted with silicides of Na, Ca, etc. whereby slags of practically iron-free Ti and of Ti-free iron are obtained.

384,281 of 2/2/33 to L. Pellereau, E. Jacmart and C. LeBris. Titanium Oxide Pigments.
Ilmenite, Na_2CO_3 and C are heated together at 800°C. in rotary furnace and discharged with cold water. Product leached with weak basic lye at 80°C. to remove alkali, soluble silicate and aluminate. Solution treated with CO_2 recovered from heating process thus regenerating Na_2CO_3. Iron removed from mass by treatment with dilute H_2SO_4. Residual TiO_2 dissolved in con. H_2SO_4 at 150° to 180°C. with increase to 200° to 225°C. at which temp. the solution is hydrolyzed. A composite pigment formed if $BaCO_3$ first added.

GERMAN PATENTS

500,564 of 6/23/30 to J. Brod , G. Kab, F. Klein (I.G.). Reduction of titanium iron ores by means of a reducing agent and chlorine.
The ore is treated with Cl_2 and CO at such temperatures and at such concentrations that only the TiO_2 remains. The TiO_2 thus produced is iron-free.

507,151 of 9/13/30 to I.G. Attack of titanium ores by means of concentrated HCl, heat and the addition of catalysts.

525,908 of 12/15/27 to Hans Ginsberg (Vereinigte Aluminum-werke A.-G.). Titanium dioxide.
Fe reduction in low Ti content minerals.

560,051 of 12/6/32 to Carl Adolphe Klein. Making a Ti Pigment.
Melting rutile or ilmenite with $NaCO_3$ in presence of a reducing agent, with or without flux, grinding the slag, removing the Fe magnetically, heating with H_2SO_4, stirring up with H_2O and boiling in presence of organic substances, washing the precipitate, drying and calcining.

594,099 of 9/4/30 to Siemens & Halske, A.G. Preparation of Titanium Carbide.

FRENCH PATENTS

632,888 of 1/17/28 to Granular Iron Co. Steel Production.
Iron-titanium ore reduced with carbon forming metallic iron. The product ground and the iron magnetically separated. The iron is then smelted.

677,370 of 3/7/30 to Soc. Miniere "La Barytine" and M. H. Waffin. Decomposition of iron titanium ores.
Mixtures of ore with coal and soda are much more easily reduced when an alkali chloride is added such as NaCl. Lower temperature can thus be used for the operation.

MISCELLANEOUS PATENTS

Can. 258,871 (U.S. 1,542,250) of 3/9/26 to J. Irwin and [illegible]. Monk (U.S. Whittemore). Titanium Oxide.
Ground Ti-Fe ore mixed with C (25 to 30%) heated to 900-1050°. The iron is dissolved and removed after which the TiO_2 is dissolved in H_2SO_4 and the solution hydrolyzed and the TiO_2 calcined. The iron in ore is reduced by heating substantially above 800°C.

II. Preparation of Titanium Chloride

UNITED STATES PATENTS

1,179,794 of 4/18/16 to L. E. Barton (Titanium Alloy Mfg. Co.). Method and Means for Producing Titanium Tetra-chlorides.
Method of producing $TiCl_4$ by mixing together a titaniferous material and a carbonaceous material containing volatile matter, heating the mixture until devolatilized and subjecting the resulting cinder to the action of chlorine. Chlorination temperature not to exceed 750°C.

1,434,485 of 11/7/22 to A. L. Duval d'Adrian (E. F. Drakenfeld & Co.). Process of Recovering Metals.
Process of obtaining Cr, Zr, V, Mn, Co, Ag, Ni in form of oxides or chlorides or other chlorine compounds from their respective ores, or from residues containing above metals by subjecting an ore or residue to a heat treatment in the presence of chlorine gas for combining the iron of the ore or residue with chlorine gas and then removing the iron chloride from the ore or residue.

1,434,486 of 10/7/22 to A. L. Duval d'Adrian (E. F. Drakenfeld & Co.). Process of Recovering Metals.
Same as U.S. 1,434,485 except the ore or residue is subjected to a heat treatment at successively higher temperatures in the presence of chlorine gas to form chlorides and then selectively condensing the chlorides at different temperatures to separately deposit the chlorides of the metal or metals of the ore or residue being treated.

1,526,319 (also F-184,948) of 3/3/25 to Carteret and Devaux. Process for the Preparation of Oxygenated Compounds of Titanium and Pigments Containing such Compounds.
A cyclic process for treating titanium ores containing iron, comprising heating in a reducing atmosphere passing successive currents of halogen gas through the ore, in opposite directions, and at different temperatures, whereby iron and titanium halogen compounds are volatilized, separately collecting the halogen compounds, and treating the latter to regenerate halogen gas for use in the halogenation step.

1,707,257 of 4/2/29 to Charles de Cohden (Commercial Pigments Co.). Titanium tetrachloride.
Fe-Ti material and carbon mixed with a colloidal suspension of TiO_2, the mixture dried and finally chlorinated.

1,815,011 of 9/2/19 to F. P. Berlin, (Basex Laboratories). Process of Making Titanium Oxide.
Process of making titanium oxide which consists of exposing finely powdered titaniferous ore to a high heat in presence of chlorine gas and passing the volatilized titanium chloride into a solution of glucose, forming titanium oxide and then filtering, washing, and drying to form a fine dry powder.

1,845,342 of 2/16/32 to Pyranji . Saklatwalla (Vanadium Corp. of America). Treatment of Ti and iron containing materials.
Subjecting materials without previous reduction to action of chlorinating gas in the absence of a reducing agent at a sufficiently high temp. to chlorinate iron and remove it by sublimation while leaving the titanium residue chemically unaffected.

1,888,996 of 10/29/32 to M. J. McInerny, F. F. Williams, M. L. Glaze (Minerals Increment Co.). Apparatus for Manufacturing Volatile Chlorides.
Apparatus described for chlorination of ore mixed with carbon at a temperature of about 600°C. Apparatus is applied particularly for chlorination of titanium containing materials and the recovery of $TiCl_4$ and separation of $FeCl_3$.

BRITISH PATENTS

141,908 of 6/23/20 to General Electric Co. Halogen Compounds.
Apparatus described for preparation of liquid halogen compounds of Si, B and Ti by reaction of the metals or carbides with the halogen. Heat abstracted from the reaction zone by a special cooling jacket. Conditions arranged so no subhalides are formed.

176,811 of 4/13/22 to Consortium fur Elektrochemische Industrie-Ges. Metallic and Non-Metallic Chlorides.
Inorganic chlorides prepared by passing Cl_2 containing sulfur chloride over a heated mixture of an oxide and carbon. $SiCl_4$ and $AlCl_3$ preparation particularly described. The mixture of Cl_2 and S_2Cl_2 may be formed in situ by adding sulfur compounds such as pyrites or a sulfate to the mixture of carbon and oxide.

207,555 of 1/23/24 to P. Pipereaut and A. Helbronner. TiO_2 and Ti salts.
Preparation of $TiCl_4$ from ilmenite by first removing iron followed by chlorination of TiO_2 with C and Cl_2 and heat. The $TiCl_4$ is treated with dry H_2S forming TiS_2 which is used in preparation of titanium pigments.

275,945 of 10/5/27 to I.G. Chlorides.
Pertains to Al, Be, Ca, Cr, Fe and Ti chlorides. Ore of material mixed with carbonaceous material and binder and coked. The dried pieces then chlorinated in a shaft furnace. Chlorides are separated by fractional condensation.

347,137 of 1/22/30 to I.G.
Chlorine compounds formed by simultaneous action of chlorine with gases of combustion of a reducing flame on an ore, oxide or salt. A rotating furnace may be used with CO as the fuel and the ore briquetted with coke, coal, etc. Treatment of ilmenite for production of $TiCl_4$ and $FeCl_3$ mentioned.

GERMAN PATENTS

334,249 of 10/3/21 to Otto Priese. Method of Preparing $TiCl_4$. A mixture of CO and Cl_2 passed over heated TiO_2 or titanic acid. If carbon in small amount is mixed with titanium compound a higher yield of $TiCl_4$ is obtained than without C.

371,600 of 5/8/23 to Carteret & Devaux. Method for preparing $TiCl_4$ from Ti ores rich in iron. A mixture of ground ore and reducing material heated in a reducing atmosphere at 600°. The charge is then successively chlorinated at different temperatures forming $FeCl_3$ and $TiCl_4$ which are separated.

453,367 of 12/5/27 to I.G. Apparatus for Preparing Chlorides of Titanium and Silicon. Apparatus described for preparing $TiCl_4$ and $SiCl_4$.

FRENCH PATENTS

544,837 of 9/30/22 to Carteret & Devaux. Process of preparing titanium compounds and pigments. Titanium ore is ground and mixed with carbonaceous material and heated in a reducing atmosphere. It is later heated in a stream of chlorine at 350° and 550-600° forming $FeCl_3$, $SiCl_4$ and a very little $TiCl_4$.

543,234 of 8/29/22 to Carteret & Devaux. Process for Preparing TiO_2 and Pigments Containing TiO_2. Ground Ti ore chlorinated with CO and Cl, and $TiCl_4$ distilled. This changed by reaction with water to the oxychloride and calcined. $TiCl_4$ may be dissolved in dil. H_2SO_4 and boiled or dissolved in water and precipitated with alkali. $Ti(OH)_4$ may be dissolved in H_2SO_4 and treated with $CaCO_3$ or $BaCO_3$. The mass is then filtered and calcined.

548,691 of 1/20/23 to Consortium fur Elektrochemische Industrie. Preparation of water-free chlorides. Mixtures of titanium ores and coke are treated and Cl_2 and S_2Cl_2 passed over the charge. The reaction temp. is lowered by use of various chlorides, such as $FeCl_3$, $AlCl_3$, $ZnCl_2$, $MnCl_2$.

548,691 of 1/20/23 to Consortium fur Elektrochemische Ing. G.m.b.H. Preparation of water-free Chlorides. Method for preparing various chlorides by passing S_2Cl_2, Cl_2 over metal compounds heated with carbon. Also by addition of sulfur compounds to the oxides or ores and heating in a stream of Cl_2 or S_2Cl_2.

638,051 of 5/15/28 to I.G. Chlorides and Bromides of Silicon and Titanium.
Use of a special metal contained and covering system as apparatus for obtaining $TiCl_4$ and $SiCl_4$.

MISCELLANEOUS PATENTS

Austrian 114,181 of 9/10/29 to I.G. Preparation of water-free metal chlorides which are volatile at the formation temperature.
Metal oxides are mixed with a coking material forming a very porous material when heated in a coking oven. A stream of chlorine passed over the mass and the chlorides condensed. The unused chlorine is recovered.

Russ. 16,658 of 9/30/30 to I.I. Sirokomski. Method for preparing titanium tetrachloride.
Ilmenite treated with coal and H_2SO_4 at a high temperature. The residue is leached and the solution reduced with iron fillings to ferrous iron and after addition of H_3PO_4 is heated. The precipitate is treated with dil. acid and washed, treated with NaOH and the precipitate dissolved in HCl.

III. Hydrolysis of Titanium Chloride and Preparation of Titanium Chloride Solutions

UNITED STATES PATENTS

1,223,356 of 4/24/17 to L. E. Barton (Titanium Alloy Mfg. Co.). Titanic-oxide Product and Method of Obtaining the Same.
Method of obtaining a product consisting essentially of titanic oxide by dissolving $TiCl_4$ in a bath comprising H_2O and H_2SO_4, distilling hydrochloric acid and calcining the residue.

1,451,399 of 4/10/23 to F. S. Low (Weaver Co.). Process of Producing Halogen Acids.
The process of producing a halogen acid by vaporizing a halide which combines with H_2O and directly treating such vapor with water vapor.

1,504,673 of 12/8/24 to J. Blumenfeld. Titanium Pigment. Hydrolysis of titanium solutions by first removing excess H_2SO_4 with $BaCl_2$.

1,755,512 of 4/22/30 to Reginald H. Monk (One half to John Irwin). Production of Amphoteric Hydrated Oxides of Metals by Hydrolysis.
In the manufacture of amphoteric hydrated oxides of

metals by hydrolysis, the improvement which consists in adding to a solution of a salt of the metal to be hydrolyzed a small amount of an oxide of the metal previously prepared in a manner other than by hydrolysis for the purpose set forth.

1,758,526 of 5/13/30 to Werner Mecklenberg. Production of Titanium Dioxide.
Seed hydrolysis of titanium salt solutions. All claims apply to hydrolysis of sulfate solutions but disclosure mentions chlorides.

1,842,620 of 1/26/32 to R. J. McInerny and E. F. Williams and H. L. Glaze. (Minerals Improvement Co.). Method of Manufacturing Titanic Hydroxide.
Process described for manufacturing hydroxide by vaporizing the chloride and discharging it into a collector along with water vapor. Apparatus arranged so as to have a forced circulating system whereby the solids are precipitated from the vapor mixture. The remaining vapors are drawn off from an otherwise closed system.

1,850,286 of 3/22/32 to A. Mittasch, E. Lucas, R. Griesbach (I.G.). Process for Making Finely Divided Metal Oxides.
The process of producing finely divided titanic oxide which comprises burning $TiCl_4$ distributed in an atmosphere of oxidizing gas in a flame produced by a gassified combustible matter.

1,885,934 of 10/1/32 to Max Mayer (Krebs Pigment & Color Corp.). Art of Producing Oxides of the Fourth Group Metals.
In the manufacture of oxides of fourth group metals from fluid halogen compounds of such metals, the method which consists in incorporating said compounds in solid salt non-reactive on said oxides and decomposing said compounds by treating the mass with steam.

1,899,572 of 2/28/33 to P. Kubelka (Krebs Pigment & Color Corp.). Dissolving TiO_2.
In a process for the preparation of a $TiCl_4$ solution, the step which comprises introducing TiO_2 into an agitated aqueous solvent below the surface of said solvent.

1,899,573 of 2/28/33 to P. Kubelka (Krebs Pigment & Color Corp.). Process of preparing clear solutions of $TiCl_4$.
In a process for the preparation of a clear aqueous $TiCl_4$ solution, the step which comprises dissolving $TiCl_4$ in an aqueous $TiCl_4$ solution containing 150 grams of HCl free acid combined per liter.

1,899,574 of 2/28/33 to P. Kubelka (Krebs Pigment & Color Corp.). Process of preparing concentrated clear solutions of $TiCl_4$.
In a process of preparing an aqueous solution of $TiCl_4$ comprising adding $TiCl_4$ to an aqueous solvent, wherein the solution becomes turbid and precipitates titanium oxygen compounds at low concentrations, the step of adding titanium tetrachloride to said turbid solution.

BRITISH PATENTS

185,374 of 10/25/22 to Carteret and Devaux. Titanium Oxide. Crystalline oxide free from iron prepared from iron-free $TiCl_4$. $TiCl_4$ solution neutralized to precipitate the hydrated oxide. This is dissolved in 25 per cent H_2SO_4. The solution boiled to precipitate the oxide. Precipitation is facilitated by slight hydrogenation which may be effected either by direct addition of gas or by addition of zinc to the solution. The amorphous oxide precipitated is calcined to yield the crystalline oxide.

258,313 of 10/10/26 to J. Y. Johnson (Badische Anilin & Soda Fabrik). Oxides.
A metal carbonyl, volatile metal halide or silicon halide mixed with combustible gas, vapour or liquid, the mixture ignited and the resulting metal oxides are separated from the products of combustion. $TiCl_4$ mixed with coal gas and ignited. TiO_2 formed is separated from exit gases by electrical precipitation.

274,072 of 9/7/27 to Carteret. Titanium Pigments.
A white pigment prepared by precipitating TiO_2 on a powdered base such as silica or aluminum silicate such as kaolin or fossil silica. Titanium oxide precipitated from $TiCl_4$ solution to which a little HCl has been added. Acid about theoretical for reaction $TiCl_4 + 4H_2O = 4HCl + Ti(OH)_4$. The TiO_2 precipitated by boiling, the mass dried and calcined.

307,661 of 5/5/29 to J. Blumenfeld (Verein f. Chem. & Met.Prod.). Metallic oxides; silica.
The formation of oxides of Ti, Zr, and similar metals from corresponding halides is conducted with the latter in dispersion in an inert medium extractable from the oxides by leaching. Decomp. effected by steam at say 300–400°C. The decomp. mass further heated to 800–1000° before leaching out alkali, salt, etc.

356,492 of 10/21/31 to J. Blumenfeld. Titanium Dioxide.
Titanium oxide formed by bringing vaporized $TiCl_4$ into contact with steam preheated to a temperature of 300–400° or other temp. below 500°C. in a heated reaction space. The TiO_2 is collected at 200–400° to prevent absorption of HCl.

GERMAN PATENTS

443,087 of 4/19/27 to Soc.Anon.Comp. Generales des Produits Chimiques de Louvres.
Preparation of white crystalline TiO_2 for pigment purposes by heating mixtures of metal sulfates with titanium halogen compounds. The salts are washed out after the precipitation of TiO_2.

551,446 of 8/18/32 to Verein fur Chem. & Met. Prod.
Making TiO_2 from $TiCl_4$ by passing separate streams of $TiCl_4$ and steam into a reaction chamber at 300-400°C.

531,207 of 11/12/31 to I.G.
Reaction of steam with metal chlorides in vapor form to obtain inorganic pigments.

533,836 of 12/17/31 to Verein f. Chem. & Met. Prod.
Preparation of TiO_2 by dispersing $TiCl_4$ in alkali chlorides of sulfates and passing steam over the mass during a gradual increase of temperature. The steam is cut off and the mass calcined at a temperature above 800° after which the soluble salts are washed out.

534,968 of 5/25/27 to P. Farup (Titan Co. A.S.). Solutions of titanium.
Solutions of Ti are prepared directly by decomp. of Ti containing materials with acid. A diluent-containing one or more acids or mixtures of acids and salts is added during decomposition.

V.78.30 of 2/11/32 to Verein fur Chem. & Met. Prod. (Application)
Process for preparing titanium dioxide from $TiCl_4$.

FRENCH PATENTS

572,890 of 6/14/24 to Carteret & Devaux. Titanium Oxide.
Preparation of TiO_2 by heating $TiCl_4$ with O_2 forming TiO_2 and Cl_2. $TiCl_4 + 2\ O = TiO_2 + 4Cl$.

580,458 of 11/7/24 to Compagnie Generale des Produits Chimiques de Louvres. Titanic acid and titanium compounds.
Titanium halogen compounds are treated in vapor phase with metal oxides or sulfates or metalloid compounds.

580,459 of 11/7/24 to Compagnie Generale des Produits Chimiques de Louvres. Titanic acid.
Titanium halogen compounds in vapor form are converted to TiS_2 which is hydrolyzed with steam forming titanic acid.

710,732 of 8/28/31 to Maxime A. Minet. Simultaneous Preparation of TiS_2 HCl and pure sulfur.
Coke oven gas washed with dil. alkali. To the washed gas is added equal amounts of H_2S and CO_2. The dry gases are then mixed with $TiCl_4$ vapor and the mixture passed through an oven heated to a dull red heat. TiS_2 and HCl are formed. This is calcined at 400°, the sulfur is given off. By roasting further a white TiO_2 is obtained.

MISCELLANEOUS PATENTS

Belgian 358,837 of 7/20/32 to J. Blumenfeld.
Making ZrO_2, TiO_2 and the like by dispersing halides of Zr, Ti, etc. in soluble alkali metal salts, treating with steam, calcining and leaching.

IV. Composite Pigments

UNITED STATES PATENTS

1,155,462 of 10/5/15 to L. E. Barton (Titanium Alloy Mfg.Co.).
Composite titanic-oxide pigment and method of producing same. Applies to addition of a compound, capable of forming an insoluble sulfate, to a titanic sulfate solution and digesting the mass to form a composite pigment. Method of treating titanic sulfate solution which comprises adding thereto a chloride of an alkaline earth metal forming an insoluble sulfate and digesting the mass to form a composite pigment. Patent applies particularly to use of $CaCl_2$.

14,289 (original 1,155,462) Reissued 4/24/17 to L. E. Barton (Titanium Alloy Mfg. Co.). Composite titanic oxide pigment and Method of Producing the Same.
Process variations added to those given in U.S. 1,155,462 for preparing a composite pigment from $CaCl_2$ and titanium sulfate solutions.

1,189,229 of 7/4/16 to L. E. Barton (Titanium Alloy Mfg. Co.).
Titaniferous Products and Method of Producing the Same.
Ore digested with H_2SO_4, dissolved in H_2O, a soluble salt, added to form an insoluble sulfate, the insoluble sulfate withdrawn and solution is hydrolyzed. Calcium chloride is claimed as the salt for precipitating the insoluble sulfate.

1,223,375 of 4/24/17 to L. E. Barton (Titanium Alloy Mfg. Co.).
Composite Titanic-Oxide Pigment and Method for Producing the Same.
Titanic sulfate solutions are mixed with an extender or with

a salt such as $CaCl_2$ capable of forming an insoluble sulfate and the charge is electrolyzed at a temperature of 90-95° precipitating basic titanium sulfate on the extender particles.

1,236,655 of 8/14/17 to L. E. Barton (Titanium Alloy Mfg.Co.). Composite Titanic Oxide Pigment and Method of Producing the Same.
Method for treating a titanic sulfate solution which comprises adding thereto barium chloride and digesting the mass so as to produce a composite precipitate comprising an insoluble sulfate and titanic acid.

1,285,473 of 12/24/18 to L. E. Barton (Titanium Alloy Mfg.Co.). Composite Titanic Oxide Product and Method of Producing the Same.
Similar to U.S. 1,155,462 and U.S. 1,205,144 except that a predetermined amount of extender or reagents forming an extender is added to the titanium sulfate solution before hydrolysis.

1,396,924 of 11/15/21 to M. H. Buckman. Process for Producing Composite Titanium Pigments.
The process of obtaining composite titanium pigments which comprises heating together with carbon and sulfur a titanium-bearing material and a solid inorganic compound of the metal which is to accompany Ti in the pigment, subjecting the sulfide melt to action of an acid solvent such as HCl, precipitating from resulting solution both Ti and accompanying metal and subsequently roasting the precipitate.

1,766,592 of 6/24/30 to J. Blumenfeld (Commercial Pigments Corp.). Production of Composite Pigments containing Titanium Dioxide.
An aqueous colloidal dispersion of TiO_2 made with HCl or by adding $BaCl_2$ to an acid filter cake. The peptized TiO_2 is mixed with $BaSO_4$, $CaSO_4$, etc. and calcined.

V. Miscellaneous

UNITED STATES PATENTS

723,217 of 3/17/03 to Howard Spence. Manufacture of Titanous Chloride.
A process for obtaining titanouschloride from titanic chloride by subjecting an aqueous solution to an electric current in an electrolytic cell divided by a porous partition.

1,099,674 of 6/9/14 to F. J. Tone (Carborundum Co.). Process for Treating Electro-Metallurgical Products.
Process of removing impurities from electrometallurgical products used for abrasive or refractory purposes which consists in treating said products with chlorine gas in sufficient quantities to combine with the impurities present.

1,501,587 of 7/15/24 to G. A. Doremus (Titanium Pigment Co.). Titanic oxide concentrate and method of producing the same.
In the treatment of titaniferous-ferruginous materials to extract therefrom titanic oxide, the steps which consist in digesting said materials in HF withdrawing the resulting solution from undecomposed portions and treating it to production of titanic oxide.

1,830,581 of 11/3/31 to Ludwig Weiss (Deutsche Gold & Silber Scheideanstalt vormals Roessler). Process for the Manufacture of Opacifying Oxides.
A process for the manufacture of opacifying oxides which consists in reacting the vapor of a water-soluble compound of the group of elements consisting of Zr and Sn with a hydrating substance and heating the product formed.

1,835,829 of 12/8/31 to F. von Bichowsky (Titanium Corp.). Methods for Producing Ti Compounds.
Method for production of TiO_2 by action of hypochlorous acid upon titanium nitride in the presence of H_2O and sodium phosphate.

1,843,427 of 2/2/32 to Simon Lubowsky (Metal & Thermit Corp.). Method of Making Magnesium Titanate.
Making the titanium of rutile available by briquetting ground ore with a mixture of alkaline earth oxide and sufficient charcoal to reduce any ferric iron to ferrous and baking the briquettes under brick making conditions at a temp. not exceeding Seger cone. 14.

BRITISH PATENTS

173,236 of 2/8/22 to J. W. Marden (Westinghouse Lamp Co.). Method for preparing rare heavy metals.
Method for reducing salts of Zr, Ti, B, Th, Va, W.

184,132 of 9/27/22 to Carteret and Beveux. Titanium Oxide.
Residual acid is eliminated from titanium dioxide by treatment with an alkaline earth chloride solution. The oxide is then washed with milk of lime or baryta to remove hydrochloric acid produced, and is finally dried. Reference to Br. 185,374.

389,041 of 7/2/29 to Monk & Irvin. Metal Oxides.
Hydrolysis of solutions of salts of amphoteric metals of group IV of the periodic table carried out by addition of the solution of an oxide of the metal concerned prepared by precipitation with an alkaline compound such as ammonia or Na_2CO_3. The preparation of hydrated ZrO_2 is described.

374,820 of 6/22/32 to L. E. Barton and C. E. Reynolds (Titanium Pigment Co.). Manufacture of Titanium Pigments. Use of an "ameliorating" agent during calcination. Sulfate, nitrate, carbonate or hydrate of Na or K added to raw pigment to extent of 0.5 to 10 per cent (usually about 0.5 to 0.75 per cent) and raw pigment calcined in presence of salt. Patent claims improved tinting strength (covering power) and examples given indicated that per cent of rutile was increased by use of salts without loss of color.

GERMAN PATENTS

453,120 of 11/29/27 to Georg Klaschewski (Silesia, Verein Chemischer Fabriken). Preparation of Hydrated Titanic Acid.
Hydrolysis of titanium salt solutions by superheated steam.

531,476 of 1/19/28 to Eugen Rishkevich (Deutsche Gold-und Silber-Scheideanstalt, vormals Roessler). Zirconium oxide.
Highly dispersed ZrO_2 is prepared by heating $Zr(OH)_4$, $ZrOCl_2$, etc. with aq. solutions or suspensions of volatile fluorides and removing the moisture by heating above 500°C. $ZrOH_2O$ is heated with a soln. of NH_4F. The product is heated to 750° to drive off H_2O and the fluorides.

FRENCH PATENTS

544,622 (Br. 173,236) of 9/26/22 to Westinghouse Lamp Co. Method for preparation of rare metals.

556,283 of 7/16/23 to Carteret & Deveaux. Pure Hydrochloric Acid.
Distillation in vacuum of concentrated solutions of chlorides.

558,240 of 8/23/23 to Carteret & Deveaux. Titanium Pigment. Titanium oxide which has been precipitated from acid solution is freed from the acid by grinding with H_2O and MgO and washed.

676,280 of 2/20/30 to Soc. Miniere & Barytine. Titanium whits. Refers to treatment of titanium hydrate prepared from sulfate solutions and has to do with the removal of sulfate with $CaCl_2$, NH_4Cl, etc. Does not apply directly to chloride.

682,986 of 6/4/30 to Vereinigte Stahlwerke Akt.-Ges. Removal of Iron from Inorganic Materials.
Clays, bauxites, etc. are freed from iron by treating with reducing gases to change the iron into $Fe(CO)_5$. Material is treated with CO at a temperature of 200°C. and high pressure. The reaction is increased by means of catalysts.

38,131 addition to 682,986 of 4/1/31 to Vereinigte Stahlwerke Akt.-Ges. Removal of Iron from Inorganic Materials.
Treatment of iron containing materials with reducing gases following by Cl_2 at a temp. of 300°C. to 500°C.

686,553 of 7/28/30 to Titan Co. Preparation of Titanium Pigments.
Precipitation of TiO_2 from $TiOSO_4$ solutions in which $BaSO_4$ is suspended. The addition of chlorides, fluorides, phosphates can be appropriately used.

MISCELLANEOUS PATENTS

Swiss 143,564 of 2/2/31 to I.G. Preparation of Water-Free Metal Chlorides.
The metal oxide is mixed with coal and the heated mass treated with CO and Cl. The patent is particularly applied to preparation of $AlCl_3$.

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