Vault

Titanium and Its Compounds

By

H. W. Ball

Dec. 4, 1930

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December 4, 1930

MEMORANDUM FOR DR. G. D. PATTERSON

FROM R. W. BALL

SURVEY OF INORGANIC CHEMICAL PROBLEMS VII - LITERATURE REVIEW

TITANIUM AND ITS COMPOUNDS

As a result of the literature survey and resulting conferences, it has been decided that the problem, "Development of Titanium Chemicals", is one which deserves consideration. This memorandum outlines in a brief way the occurrence, some typical compounds, and the more widely known uses of titanium, as described by Thornton in his monograph, "Titanium", and Hopkins in his book, "Chemistry of the Rarer Elements".

General Distribution

Although formerly regarded as one of the rarer elements, titanium is very widely distributed in the earth's crust. According to F. W. Clark's most recent calculations, titanium makes up 0.58% of known terrestial matter, standing ninth in order of abundance and next below magnesium. Titanium is nearly one third as plentiful in nature as magnesium, and the ratio of titanium to phosphorus and sulfur is more than 5:1 and 9:1, respectively.

In spite of the fact that titanium occurs in a large number of minerals, either as an essential or as an accidental ingredient, there are at present only two distinct species which are of economic importance, viz., rutile and ilmenite. Though most mineralogists are of the opinion that titaniferous iron ores are composed primarily of magnetite with intergrowths of ilmenite, at least one authority holds that titanium may be present as an integral part of the magnetite molecule itself. In view of this uncertainty, it seems well to tentatively include magnetite as a notable titanium bearing substance.

Another possible source of titanium is the peculiar type of rock which T. L. Watson has designated "nelsonite", occurring in the Amhurst - Nelson Counties Region of Virginia and in Roanoke County also to some extent. Watson and Tabler distinguished six varieties of "nelsonite"; but only two need be considered in this connection, viz., ilmenite - nelsonite and rutile - nelsonite, the former being essentially an ilmenite apatite mixture and the latter a rutile apatite mixture. These mineral aggregates have tempted the prospector; since not only would the titanium compounds be of value, but the calcium phosphate could be used for fertilizer as well. However, nelsonite has not yet been commercially utilized for several reasons. It should be noted, however, that a small amount of apatite remaining in the concentrated titanium minerals would not vitiate them for the manufacture of pigment to anything like the same extent as for use in iron and steel metallurgy; hence the future utilization of the nelsonite ores is more promising now than formerly.

Titanium Chemicals

The following, although by no means a complete list of titanium compounds, sets down the more important representative compounds of titanium.

TABLE

Representative Compounds of Titanium

No.	Name	Formula
1	Acetate	$NaTi_2(OH)_2(C_2H_3O_2)_5 \cdot 4H_2O$
2	Arsenite	$Ti_5O_8(AsO_2)_4$
3	Boride	Unestablished
4	Bromides and Related Compounds	$TiBr_3 \cdot 6H_2O$
		$TiBr_4$
		$Ti(OH)Br_3$ (?)
		$TiBr_4 \cdot 4NH_3$ (approx.)
		H_2TiBr_6 (in solution)
		$(NH_4)_2TiBr_6 \cdot 2H_2O$

No.	Name	Formula
5	Carbide	TiC
6	Chlorides and Related Compounds	$TiCl_2$
		$TiCl_3$, $TiCl_3.6H_2O$
		$TiCl_4$
		$Ti(OH)Cl_3$
		$TiCl_4.8NH_3$
		$TiCl_4.PCl_5$
	Pyridine Addition Compound	$TiCl_4.6C_5H_5N$
		H_2TiCl_6, or H_4TiCl_8 (in solution)
		$(NH_4)_2TiCl_6.2H_2O$
	Aniline salt	$4C_6H_5NH_2.\ H_4TiCl_8$
7	Chromate	$Ti_2O_3CrO_4.2H_2O$
8	Citrate	$H_2K_2TiO(C_6H_5O_7)_2.H_2O$
9	Fluorides and Related Compounds	TiF_3
		TiF_4
		$TiF_4.2NH_3$
		K_2TiF_5
		H_2TiF_6 (in solution)
		$K_2TiF_6.H_2O$
		$2NaTiF_6.H_2O$
		$KCuTiF_7.4H_2O$
	Quinine Salt	$C_{20}H_{24}N_2O_2.H_2TiF_6.H_2O$
10	Formate	$K_2Ti_4(OH)_3(CHO_2)_{11}$
11	Hydride	Ti_4H_5
12	Hydroxides	$Ti(OH)_2$
		$Ti(OH)_3$
		$Ti(OH)_4$, or $TiO(OH)_2$
		$Ti(OH)_6$, or $TiO_3.3H_2O$
13	Iodides and Related Compounds	TiI_2
		$TiI_3.6H_2O$
		TiI_4
		H_2TiI_6 (in solution)
14	Nitrate	$Ti_5O_9(NO_3)_2.6H_2O$

No.	Name	Formula
15	Nitrides and Related Compounds	TiN
		Ti_3N_4
	Cyanonitride	Ti_5CN_4 (?)
16	Oxalates	$Ti_2(C_2O_4)_3 \cdot 10H_2O$
		$Ti_2O_3C_2O_4 \cdot 12H_2O$
		$K_2TiO(C_2O_4)_2 \cdot 2H_2O$
17	Oxides	TiO
		Ti_2O_3
		TiO_2
		TiO_3 (?)
18	Per-Compounds	$Na_2O_2 \cdot TiO_3 \cdot 3H_2O$
		$(NH_4)_3TiO_2F_5$
		$K_2TiO_2(SO_4)_2 \cdot 7H_2O$
19	Phosphates	$Ti_2O(PO_4)_2 \cdot nH_2O$
		$K_2Ti_2O_2(PO_4)_2$
		TiP_2O_7
20	Phosphide	TiP (?)
21	Silicides	Ti_2Si
		$TiSi_2$
22	Sulfates	$Ti_2(SO_4)_3$
		$TiOSO_4$
		$Ti_2O(SO_4)_3 \cdot 3H_2O$
		$CsTi(SO_4)_2 \cdot 12H_2O$
		$Na_2Ti_2(SO_4)_4 \cdot 5H_2O$
23	Sulfides	TiS
		Ti_2S_3
		TiS_2
24	Tartrate	$Na_2TiO(C_4H_4O_6)_2 \cdot 8H_2O$
25	Thiocyanates	$K_3Ti(CNS)_6 \cdot 6H_2O$
		$TiO(CNS)_2 \cdot 2H_2O$
26	Titanates	Mg_2TiO_4
		$(C_2H_5)_4TiO_4$
		$MgTiO_3$
		$Na_2Ti_2O_5$
		$Zn_2Ti_2O_7$
27	Titanosilicate	$CaTiSiO_5$

No.	Name	Formula
28	Other Organic Cpds.	
	Lactates	$HTiO_2H_3(C_3H_5O_3)_4$ (?)
	Thymate	$Ti(OC_{10}H_{13})_4$
	Salicylate	$H_2Ti(C_7H_4O_3)_3$
	Dihydroxymaleate	$2(TiO_2H)_2C_4H_2O_6 \cdot 5H_2O$
	Derivative of Nitrosophenyl-hydroxylamine	$Ti(C_6H_5N_2O_2)_4$

The Industrial Applications of Titanium and Its Compounds

1. Pigments
2. Alloys in Metallurgy
3. Dyes, Mordants, Bleaching Agents, Strippers, etc.
4. Refractory Materials (Glazes, Enamels, Glasses, and Bricks)
5. Smoke Screens and Pyrotechnics
6. Incandescent media for lighting purposes (Arc Lamp Electrode, etc.)
7. Cement
8. Gem stones (Natural and Synthetic)
9. Abrasives
10. Catalysts
11. Ink
12. Medicinal Preparations
13. Nitrogen Fixation
14. Phosphorus Pentoxide
15. Applications in Pure Science

1. Pigments

Colored Pigments

Titanium ferrocyanide is said to have been employed as a green pigment in lieu of the poisonous Schweinfurth green and other arsenical pigments. It does not seem, however, that this pigment is on the market at the present time--certainly not to any great extent.

Processes have been patented for the manufacture of colored pigments which depend upon roasting highly titaniferous iron ores in a state of fine subdivision at not too high a temperature either alone or in admixture with sulfuric acid.

The resulting product is in the former case of a reddish color while in the latter it is inclined to yellow. It is claimed by the inventor that the yellow pigment is especially useful in the preparation of rust-preventing paints, and that the color produced is lighter than was hitherto obtainable with paints of this character. However, other writers have stated that these pigments did not prove to be economically successful.

White Pigments

The use of titanium dioxide in white pigment such as Titanox (25% TiO_2 + 75% barium sulfate) is being thoroughly investigated within the Company and requires no discussion in this memorandum. In the preparation of enamels, Titanox has been introduced in very noteworthy amounts. Such enamels have great covering power and may be baked at a higher temperature than was formerly permissible. Furthermore, Titanox has been used with good results in the manufacture of lacquer, printing ink, wallpaper, rubber, oil-cloth, linoleum, roller shades, etc.

2. Alloys

The use of ferro-titanium in the steel industry is rapidly gaining favor, especially in the United States. The effect of titanium is two-fold: (1) its striking affinity for both oxygen and nitrogen makes it efficient for the removal of the last traces of these elements; (2) it apparently has the unique property of causing the separation of occluded substances like oxides and sulfides of iron and magnesium, silica, slag, etc. As ordinarily used, very little, if any, of the titanium remains in the steel; hence its purpose is purely that of a cleansing agent. The fluidity of the slag is increased because of the exothermic reactions which accompany the removal of the impurities; hence the separation of the slag is more nearly complete. The importance of removing oxygen, nitrogen, and iron oxides is becoming more and more evident, as experiments tend to show that these impurities are more troublesome than small amounts of sulfur.

3. Dyes, Mordants, Bleaching Agents, Strippers, etc.

As early as 1885 J. Barnes called aggention to the fact that salts of titanium could be used advantageously in mordanting yarn. For this purpose he employed a solution of titanic chloride to which some sodium acetate had been added, and obtained pleasing colors on the cloth with alizarin and other dyestuffs. Since then various compounds of titanium have found favor in the textile industry for the fixation of color on the fabric. Among these may be mentioned the tartrate, tannate, double sulfate, $Na_2TiO(SO_4)_2 \cdot 2H_2O$, double oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, etc.

Besides serving as a good mordant for basic dyestuffs, titanium tannate in oxalic acid solution produces yellow and golden shades on the cloth, particularly on mercerized cotton, thus acting as a dye itself.

Titanium, in the form of tartrate of tannin-titanium, has been applied in calico printing.

Titanous salts have been suggested for use as stripping agents. To this end the chloride, $TiCl_3$, and double sulfate, $Na_2Ti_2(SO_4)_4 \cdot 5H_2O$ are generally employed. The two best strippers of reducing character are said to be titanous chloride, which acts in an acid bath and a combination of formaldehyde and sodium hydrosulfite, which is used in an alkaline solution. Titanous salts are also said to be good bleaching agents.

Titanium compounds are used on a rather extensive scale in the leather industry. The most important salt is the oxalate of titanium and potassium. When vegetable tanned leathers are to be dyed with basic coloring matter, the potassium titanium oxalate, like tartar emetic, serves a double purpose of acting as a mordant and of precipitating any free tannin that might otherwise diffuse into the bath and throw down the dyestuff. Titanium salt is used as a striker with logwood to produce black, and is said not to embrittle the leather, as do salts of iron. It may also be used alone to produce on the fiber a yellowish-brown color due to titanium tannate, which is permanent and especially suited to shoe leathers.

4. Refractory Materials (Glazes, Enamels, Glasses, and Bricks)

The purer grades of rutile are used to impart a beautiful, soft yellow, under-glaze color to pottery. Titanium is one of the comparatively few substances that can be used for under-glaze painting in the decoration of porcelain, the effects so obtained being in many ways superior to those obtained by painting upon the glaze. As a yellow ceramic pigment, titanic oxide is much less expensive than oxide of uranium and admits of greater variation in shade than does oxide of iron. It may also be used in admixture with other substances, thus giving the manufacturer greater latitude of choice as to the possible tone of color that may be produced. Great care is necessary in the firing, for in contact with reducing gases titanium gives objectionable off-colors.

Rutile is likewise used in making artificial teeth, for which purpose the amount added to the paste varies from 0.5 to 5 per cent according to the color desired.

Titanium dioxide acts as a crystallizer for producing crystalline glazes on art pottery, there being but few bodies known that have this property.

When added in certain proportions titanic oxide develops opacity in enamels, the colors being chiefly grayish-white or yellowish-white. Titanium enamels have been experimentally studied by R. D. Landrum and L. J. Frost, who report that, although there are some technical difficulties yet to be overcome, it should be possible to develop them to a point of real practical value. Such enamels are chemically inert, resistant to abrasion and capable of withstanding high temperatures.

"Siloxide", a substitute for vitreous quartz, has been made by adding a small quantity of either zirconium or titanium oxide or both to silica. The glasses contain from 0.5 to 2 per cent of zirconium or titanium, though 1% gives the best result. These glasses are in some respects mechanically better than fused quartz, are more resistant toward substances of alkaline nature and have a greater viscosity at higher temperatures. They can be worked in the oxyhydrogen flame. The titanium glass is blue in color, but otherwise it resembles closely the zirconium glass, resisting devitrification even better than the latter. "Siloxide" was being manufactured in Germany in 1912.

Titanic oxide (melting point, 1560°C.) is used in the making of bricks, and ilmenite as a constituent of puddling furnaces.

5. Smoke Screens and Pyrotechnics

Titanium tetrachloride came into great prominence during the war as a material for producing toxic smoke. Its value in this connection depends upon the fact that the colorless liquid is quickly hydrolysed in moist air, forming the dense hydrate $TiCl_4.5H_2O$. If the amount of moisture is excessive the hydrolysis is complete, giving HCl and $Ti(OH)_4$, which has less obscuring power. In case the latter reaction takes place, the density of the cloud is greatly increased by adding ammonia which forms a cloud of ammonium chloride. If, however, ammonia reacts with titanium tetrachloride in the absence of moisture, $TiCl_4.6NH_3$ is formed, which has less obscuring power. Consequently, when titanium tetrachloride is used in shells it is generally planned to disperse it with a high explosive, and after a few moments ammonia from a separate compartment is also dispersed. In this manner the total obscuring power is 50% higher than is obtained from silicon tetrachloride. The latter is more volatile, therefore more easily handled from a nozzle, and requires a very wet atmosphere for giving its highest obscuring power. Consequently, it is better adapted for use in the navy, but in the army titanium tetrachloride is used in shells and grenades.

C. Baskerville states that titanium has been employed in pyrotechnics because of the beautiful light it produces during combustion; but he gives no further details.

6. Incandescent Media for Lighting Purposes

One of the most remarkable applications of titanium is the use of its compounds, dioxide, suboxide, or carbide, in arc lamp electrodes. It is stated that among all the metals titanium possesses the highest point of electrovaporization and furnishes the richest spectrum as far as the number of lines is concerned. Moreover, it has been found that of the many substances tried for prospective use in arc light electrodes, those containing titanium give the highest efficiency in candle power per watt consumed.

In accordance with patents granted to J. T. H. Dempster, the General Electric Company of Schenectady, N. Y. manufactures an electrode in which titanium oxide is the chief light-giving material.

The present industrial status of the titanium arc is embodied in the following statement by E. R. Berry: "While it is no doubt true that the luminous arc lamp has certain operating difficulties which are not shared by the nitrogen filled tungsten lamp, it is not true that the latter lamp supplanted the arc lamp, as there are at the present time about 300,000 of these lamps in use. Owing to the superior quality of the light, the luminous arc lamps are still proving very desirable units for certain types of street lighting."

Titanium dioxide has been tried as a component of gas mantles; but it has been shown to be unsatisfactory.

7. Cement

F. C. Zokel, in a patented process, claims that a quick-hardening and chemically resistant cement may be obtained as a by-product in the smelting of titanic iron ores in either the blast or electric furnace using limestone as the flux. With proper adjustment of the ingredients of the furnace charge, the slag consists essentially of calcium titanate, $CaTiO_3$, with subordinate amounts of ferrites, aluminates and silicates of calcium. This slag, when finely ground, constitutes a cement that within 24 to 48 hours will attain a higher degree of strength than Portland cement under the same conditions. Reasonable amounts of magnesia may replace a part of the lime, but too much magnesia is objectionable.

8. Gem Stones

Natural Stones

The following titanium minerals when cut and polished have been used in jewelry: (1) clear crystals of rutile, (2) nigrine, (3) inclusions of fine rutile crystals in transparent quartz, known as "flèches d'amour", (4) octahedrite, (5) titanate, (6) benitoite, and (7) polycrase.

Synthetic Stones

A. V. L. Verneuil, who successfully synthesized the ruby, has also prepared sapphires by fusing together with an oxyhydrogen torch of special construction a mixture consisting of 98 per cent of aluminum oxide, 1.5 per cent of iron oxide, and 0.5 per cent of titanium oxide.

The synthetic ruby can be made by virtually the same process, the red color being obtained by introducing a small quantity of oxide of chromium.

In 1913 I. N. Levin stated that 10,000,000 carats of rubies and 6,000,000 carats of sapphires were being produced annually and that the demand was increasing.

9. Abrasives

There has been described a titaniferous emery that is claimed to have commercial value as an abrasive. The rock is made up of the minerals ilmenite, magnetite, corundum, and spinel.

The nitride of titanium Ti_2N, is said to be an extremely hard substance.

Patents have been granted to L. E. Saunders for the manufacture of an abrasive material in the electric furnace, which, though essentially aluminous, contains also noteworthy amounts of ferric oxide, titanic oxide, silica and lime.

10. Catalysts

The use of titanium has been suggested as a catalyst in the preparation of a good many types of organic compounds and also in the cracking of petroleum.

11. Ink

The compound formed between titanium and logwood has a deep black color and may therefore be used as an ink. It is described as being a permanent fluid that undergoes no change after being used.

12. Medicinal Preparations

The therapeutic applicability of titanium compounds is said to be very limited and unimportant. J. Pick has used certain salts of titanium, especially the sulfate and salicylate, as local remedies in the treatment of eczema, lupus, rhinitis and conjunctivitis, and claims to have obtained beneficial results. He asserts further that all organic and inorganic titanium compounds, provided they are soluble in water, check the putrefaction of protein and that the salts are not poisonous when taken internally.

13. Nitrogen Fixation

Owing to the readiness with which titanium combines with nitrogen, and with carbon and nitrogen to give the cyano-nitride, a good deal of experimenting has been done with the view to utilizing these reactions for the fixation of atmospheric nitrogen.

14. Phosphorus Pentoxide

Another interesting invention is that of S. Peacock involving the use of titanium dioxide as a means of liberating phosphorus pentoxide from potash or natural calcium phosphate. The residual calcium titanate could be used as a source of other titanium compounds. The reaction takes place at a high temperature, and the process is continuous, a special furnace having been designed for the purpose.

$$Ca_3(PO_4)_2 + 3TiO_2 = 3CaTiO_3 + P_2O_5$$

15. Applications in Pure Science

It is conceivable that a limited market for titanium and its compounds might be found in its use in a variety of ways in purely scientific research. One such application is the use of pure titanium for the production of spectra in astronomical investigations.

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Robert W. Ball

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