

THE PRODUCTION AND USES OF TITANIUM

Commercially titanium has so far had a short but most interesting history. It was over a hundred years ago however, when this element was first discovered. Williams Gregor, an English clergyman, found evidence of the metal in black sand, in a stream-bed at Tregonwell Mill, Cornwall in 1791. The name titanium was given by a German chemist, Martin Klaproth, four years later. The mineral rutile in which he found this element is noted for its strength and hardness. He selected "titanium" derived from the mythological Titans - "the first sons of the earth".

Titanium does not occur in a pure form but is usually found as an oxide in the mineral rutile or in combination with iron in the ore ilmenite. The element itself is a dark gray non-crystalline powder with a specific gravity of 1.25 which is rather light for a metal.

I have here sample(s) of sands and mineral(s) from which titanium is produced - rutile (and ilmenite).

Titanium differs from almost all the other elements by its peculiar capacity of uniting with nitrogen at high temperatures. This promises a cheap means of preparing ammonia direct from the atmosphere. In turn, this leads to the manufacture of fertilizers and explosives. Used as an alloy with other metals, titanium gives a hardness and toughness to steel and imparts a fine lustre to silver.

Titanium has always been erroneously classed as a rare metal. It may surprise you to know that this so called "rare metal" far exceeds in abundance in the earth's crust the "common metals", copper, zinc, lead or tin. Titanium is found in all continents on the globe. In this country alone there are twenty-three states in which titanium occurs.

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The mineral rutile which is at least 94% titanium oxide is found most extensively in the United States in Nelson County, Virginia. The second largest deposit is in Norway, then comes Canada, Australia, and Madagascar. It also happens that the principle deposits of ilmenite are in Nelson County, Virginia. Other United States sources are the sands at Jacksonville Beach, Florida and Redondo Beach, California. Foreign deposits are at Ivry Quebec; in India in the magnetic sands of the Travancore and in Africa in the Senegal coast sands. In Brazil, Australia and Norway ilmenite is also found.

The above locations readily show that for a rare metal, titanium has a very wide distribution and also that in the United States occur some of the greatest deposits.

Most of the titanium oxide used in this country, however, is obtained from the Travancore sand of India. The reason for this is that the cost of production is so very much lower in India than in the United States. Furthermore the Indian sands are situated very near deep water so large ocean freighters can load the ore directly after extraction. Ocean freight service like this, half way around the world, can compete with the much higher priced and shorter railroad transportation in the United States. Therefore, the ore is delivered to this country at about the same or for less cost than it can be produced here. If a high protective tariff was made for domestic titanium probably all titanium oxides made in this country would be derived from American ores, but we would have sufficient resources to more than adequately take care of the demand for many years to come.

The metal titanium is never used commercially in the pure state. Instead, there is usually obtained from the ore an oxide of the metal. In the production of titanium oxide rutile has the advantage of being an almost pure oxide 94% or over. Ilmenite contains

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only about 50% titanium oxide but the type generally used has the advantage of being mostly in the form of sand so that extraction is easy and little crushing is necessary.

Very briefly, the manufacture of titanium oxide is as follows: The ilmenite sand is first crushed extremely fine and then heated with sulfuric acid, both iron and titanium dissolving in solution part of the iron crystallizes out. Then the solution is diluted with water on cooling and reheated which draws the titanium out and the remaining iron stays in solution.

One of the reasons titanium dioxide is such a brilliant opaque paint pigment is due to its high refractive index, (that is, the extent to which light falling on it is reflected by the particles of pigment). If, instead of precipitating the titanium hydroxide pure, it is thrown down on a base of barium sulphate, the resulting calcination (heating to a powder form) is more readily controlled to give a uniform product, and the pigment produced has a refractive index considerably higher than either of the two compounds of which it is composed. The usual proportion of such pigment is titanium dioxide - 25% and barium sulphate - 75%. This is known as Titanium White B.

A short description of the manufacture of Titanium White is that the crude ore is first freed from impurities by mechanical treatment at the mines. The concentrate in the form of a coarse grit is shipped to the factory where it is dried, ground into a fine powder and then decomposed with sulfuric acid. The resulting solution of titanium and iron sulphates being stored in tanks ready for the next process. Meanwhile, barium sulphate is prepared by precipitation, and after washing, the wet precipitate is pumped into vats. Here the

titanium solution is added to it, the mixture being warmed and agitated, with the result that the titanium sulphate is hydrolyzed and titanium hydroxide precipitated on the particles of barium sulphate. The composite precipitate is washed free from the iron sulphate, passed into a rotary furnace where it is dried and calcined. This last process has to be watched carefully as the refractive index of the pigment depends greatly in properly regulating the calcination. The produce is then cooled, ground and packed for shipment.

The above is a very brief description of a rather difficult chemical process. Practically the whole cycle of operations has to be carried on under highly acid conditions, which means that most of the plant has to be constructed of wood and lead due to the corrosion of other metals.

From an industrial point of view the price at which a material can be supplied is an important consideration, and titanium white offers exceptional possibilities in this respect. The price of most other white pigments, white lead, zinc oxide, etc. depends largely on the market for the metal concerned, and so is often subject to fluctuations. But there is no other industrial call for titanium of any importance. In any case the available supplies of ore vastly exceed possible demands; therefore, the price depends solely upon the cost of production. At first, when production was on a small scale, development was handicapped because the price compared unfavorably with that of other white pigments. Lately increased demand and increased efficiency of production have caused the price of titanium white to decline until now it can compete on equal terms apart from its special advantages.

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The latest prices of several pigments on the New York market are as follows: Titanium Dioxide - 18¢ a lb; Titanium White B - 6 $\frac{1}{2}$ ¢; Titanium White C - 7¢; Lithopone - 4 $\frac{1}{2}$ ¢; White Lead 7 $\frac{1}{4}$ ¢ and Zinc Oxide 6 $\frac{1}{4}$ ¢. However, titanium white is much lighter than other pigments and lead is much heavier. Also, a gallon of titanium paint would cover much more surface than the same amount of any other pigment paint. Based on this measure the white lead is most expensive, lead and zinc next, then Lithopone, while titanium pigment is the cheapest of all.

Titanium compounds have only been manufactured to any extent since the war, but in this short period our government has issued more than a hundred patents on various manufacturing processes dealing with titanium. By far the greatest use of titanium is in paint pigments, but this is not the only one by any means. Other uses are in inks, oil cloth, sealing wax, smoke screens, fireworks, arc lamp electrodes, cement, rubber toys, linoleum, artificial leather, gem stones, medicinal preparations, fertilizers and cosmetics.

As for the properties of titanium paint pigments, their remarkable opacity or obliterating power is perhaps the most important. Along with this is their brilliant whiteness which is due to a great extent, as mentioned before, to the high refractive index of the pigment particles. Titanium pigments produce the most brilliant white paint known.

Here is a sample of titanium pigment we use in the manufacture of some of our white paints.

Another characteristic is their chemical stability. Most paints are discolored by chemical fumes present in the atmosphere of large cities. Titanium paints are unaffected by such fumes, especially sulfur fumes, which easily discolor some paints. Also the titanium

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pigments being so stable will not react at all with any vehicle with which they are mixed as other pigments do to a slight extent.

Finally, the insolubility of titanium pigments gives them another important characteristic; this is that they are non-poisonous. They have been fed to rabbits, guinea pigs and even humans without any ill effects whatever. I have an article here by Noel Heaton and Englishman, who conducted an unusual experiment on himself. Mr. Heaton says in part:

"I adopted the procedure used in the case of an X-Ray meal, about a pound of (titanium) pigment being made up into a sort of porridge with water and a little glucose and swallowed after starving for about 24 hours in order to eliminate previous meals and insure that the alimentary canal should be completely exposed to the mixture. The progress of the pigment through the body was watched by means of an X-ray tube and fluorescent screen and radiographs taken at intervals. The whole system was thus continually exposed to any possible action of the pigment for 24 hours, and I can honestly say that I have never felt the slightest ill-effect; if anything, my health has improved since the experiment rather than the reverse."

If Mr. Heaton had made a meal of white lead instead, he would probably have died within 24 hours. Zinc Oxide or lithopone would have at least made him very ill.

From the start, when titanium pigments were first used in making paint, our company was very much interested in this new pigment. Surveys were made of various ore deposits and several manufacturing processes were studied. However, after careful consideration, it was

decided that our company would not engage itself in production of titanium pigment. We are able to buy the necessary pigments from several manufacturing companies which are well equipped to take care of our needs at very reasonable rates.

Our purchases of titanium pigment have increased tremendously in the past three years. Last year we bought 1500 tons of Titanium White B while the year before the purchases amounted to 1100 tons and three years ago to 560 tons - almost a threefold increase in three years. Titanium White C (which is about the same as Titanium White B except that a calcium base is used in its manufacture rather than a barium base) shows even a greater increase. 1118 tons were purchased last year which is ten times more than was purchased three years ago. Last year, we also bought 160 tons of pure titanium dioxide which is about twice as much as was purchased the year before. I do not want to lead you to think from these figures that our use of titanium is exceptionally large. Compared with lithopone, for instance, it is rather small. Last year we manufactured 20,000 tons of lithopone and only used 2778 tons of titanium pigments or about one-seventh as much.

Titanium is only used in a few of our paints: 5 Semi-lustres; 4 Flat-tones; 2 Enameloids and most important of all- S.W.P. Gloss White for outside use. Here is the outside Gloss White label which states that 36 $\frac{1}{2}$ % of the pigment is titanium pigment.

In closing, I wish to explain that titanium pigments will by no means replace the regular lead, zinc and lithopone pigments that we have been manufacturing for some time. Titanium has a limited field but is, as yet, unsurpassed in that field. That is, where a very brilliant white of great obliterating power or a chemically inert, or non-poisonous pigment is needed, titanium pigment is the only kind to use.

The first commercial white pigment used in modern manufactured paints was, of course, white lead. Later this was improved by adding zinc oxide. Still later lithopone was invented and has been in general use for the past 25 years. These represent steps forward in research for a brighter, stronger, more stable white pigment. Titanium is just the latest step in this endless search for improvements. But titanium is not the goal,- our Company is ceaselessly searching for new materials and experimenting with different compounds striving to better present pigments wherever possible and inventing new ones.