The Benefits of Chlorine Chemistry in Titanium and Titanium Dioxide

PREPARED FOR:

Chlorine Chemistry Division of the
American Chemistry Council

By

Whitfield & Associates

December 2007

American Chemistry Council

The Benefits of Chlorine Chemistry in Titanium and Titanium Dioxide

Consumers benefit from titanium-based products in a variety of ways. First, titanium is a light, strong, and corrosion-resistant metal used in products ranging from artificial hips to aircraft engines. Second, titanium dioxide (TiO_2) is a commodity chemical used in paint and coatings, plastics, and pharmaceutical products. Chlorine chemistry has an integral role in the manufacture of both of these products. All titanium metal production and nearly 99% of United States and Canadian capacity for TiO_2 is based on chlorine chemistry (the chlorine percentage is smaller at 56% on a worldwide basis). In the United States and Canada, these industries are quite large, amounting to nearly $4 billion in sales at the wholesale level and much more at the consumer level. This report estimates the benefits of chlorine chemistry in the production of titanium metal and titanium dioxide pigments by examining the differences in costs and the utility to consumers between chlorine-free technologies that exist today or, in the case of titanium metal, substitution of chlorine-free materials at the product level.

In the absence of an economically viable chlorine-free route to the production of titanium metal, consumers would be forced to substitute other materials in the end use applications now held by titanium and titanium alloys. Titanium competes with other metals now in most applications, even in cases where the initial cost of the alternative material is lower per pound than titanium. In many applications titanium’s physical and chemical properties make its life cycle costs lower than the available alternatives. Life cycle cost and performance considerations make substitution for titanium quite difficult in many applications, particularly in the aerospace sector.

An alternative technology to manufacture TiO_2 uses sulfuric acid, so consumers could satisfy their requirements for these products without relying on chlorine chemistry. However, the chlorine-based technology has steadily gained market share since its inception some 50 years ago and its advantages in capital, energy and labor efficiency make it a popular technology that is widely chosen in large, new greenfield plants worldwide. It also produces far less waste material than the alternative sulfate-based process as that technology has been practiced historically, although that is less of an issue in more modern sulfate-based plants.

We estimate that the net cost to consumers in the United States and Canada for the substitution of alternative materials for titanium metal in aerospace, combustion turbines, consumer, architectural, and medical applications would be over $1.2 billion per year in initial and life cycle costs. For titanium dioxide, we estimate that the net cost to consumers for substituting chlorine-free processes would amount to $1.4 billion per year under favorable assumptions. In addition, approximately $5.5 billion of capital for new plant and equipment is avoided through the continued use of the chloride process.

Introduction

Titanium, the ninth most abundant element in the earth's crust, is found in nature in the form of various oxides, the most common of which is titanium dioxide. This material is never found in a pure state, however, but is always mixed with other minerals or found as a component of complex minerals that typically contain oxides of iron, manganese, magnesium, and other elements as well. The titanium in these minerals is not useful directly to consumers, but must be concentrated and purified through a series of metallurgical and chemical processes that involve chlorine chemistry.

Titanium metal is light, strong, and more corrosion resistant than most other ferrous and nonferrous metals and alloys. It has the highest strength-to-weight ratio of any metal – tensile strengths are comparable to steel but at a density that is about 45% lower. Its high melting point, strength at high temperature, and oxidation resistance make it well suited to use in high temperature, corrosive environments, such as those to which aerospace components and combustion turbines are exposed. Titanium's resistance to corrosion by most common acidic and saline solutions makes it valuable for use in extremely harsh conditions in chemical, metallurgical, and power plants. Smaller amounts are used as an alloying agent in steels and other metals and alloys, and find use in a variety of consumer goods and medical devices like artificial hips.

Although it is often considered a commodity chemical, highly purified titanium dioxide (TiO_2) is manufactured and sold in a large variety of grades based on carefully controlled particle sizes and crystalline forms. Its utility is derived from its unique physical properties, particularly its brightness and a very high refractive index that is comparable to diamond. It is mixed with small amounts of other materials in its commercially available forms and finds widespread use as an opacifier and white pigment in paints and coatings, plastics, paper products, food products and cosmetics.[1] Its ability to reflect harmful ultra-violet (UV) light makes it a valuable additive in sunscreens, particularly for people with sensitive skin. Tables 1 and 2 list some common applications for titanium metal and titanium dioxide.

---

[1] Manufacturers of commercial grades of titanium dioxide have proprietary processes and formulations that are used to improve the properties of the chemically pure TiO_2 that forms the basic product, tailoring them for the specific applications intended. Consumption statistics are usually based on the formulated products, and that basis will be used here.

Table 1

Typical Applications of Titanium Metal[1] in the United States and Canada

Area	Application or Use
Aerospace and turbines	Engine rotors, compressor blades, nacelles, exhaust ducts, landing gear, firewalls, hydraulic systems, critical structural components, armor, spacecraft components
Industrial	Heat exchangers, vessels, piping components in chemical, power, pulp and paper, desalination and oil and gas plants. Alloying agent
Consumer and architectural	Architectural panels, automotive components, sporting goods, jewelry, electronics
Medical	Dental implants, artificial joints, pacemakers, surgical components

(1) Titanium metal includes pure and in all alloy forms.

Table 2

Typical Applications of Titanium Dioxide in the United States and Canada

Area	Application or Use
Coatings	Opacifier, brightener, pigment in indoor and outdoor paints, printing inks, paper products
Plastics, fibers, textiles and rubber	Opacifier, pigment and UV reflector
Food, cosmetics and pharmaceuticals	Brightener, white base pigment, UV reflector
Miscellaneous	Self cleaning glass, pollution abatement catalyst, ceramic glaze

On a volume basis, at least 95% of the titanium consumed in the United States and Canada has been in the form of titanium dioxide and less than 5% in the form of titanium metal. Demand for titanium metal historically has been highly volatile, tracking the irregular demand for product in the aerospace sector that accounts for between 60% and 75% of total consumption. Consumption in industrial applications, mainly for corrosion-resistant equipment, accounts for more than 80% of the balance, with the rest being used in consumer, architectural, and medical applications. Consumption of titanium in steelmaking includes scrap and ferrotitanium as well as titanium metal, and is used mainly in the production of carbon and stainless steels. The unpredictable nature of aerospace-driven demand can result in large and rapid changes in the prices of titanium metal sponge[2] and the alloys and mill products derived from it.

The demand for titanium dioxide is significantly more stable – it usually follows general economic activity quite closely and price swings for titanium dioxide are less pronounced than for the metal. In recent years consumption in coatings has amounted to about 50% to 60% of total demand, while consumption in plastics and rubber has amounted to about 25% to 30% of the total. Its use in paper consumes about 10% to 15% of the total, with all other uses amounting to less than 5% of demand. On a value basis, the market size for titanium metal sponge and titanium dioxide pigments in the United States and Canada in 2005 is summarized in Table 3.

Table 3
Estimated Market Size of Titanium Sponge and Titanium Dioxide Pigments in the United States and Canada, 2005
(Millions of US Dollars)

Product	United States[1]	Canada	Total
Titanium sponge[2]	520	40	560
TiO_2 pigment	2,660	520[3]	3,180
Total	3,180	560	3,740

(1) Source: U.S. Geological Survey Minerals Yearbook, *Titanium-2005*.
(2) The value of titanium mill products is size and shape specific, and is much higher than sponge which is the first commercial product.
(3) Apparent consumption estimated at 106,000 metric tons; SRI's Chemical Economic Handbook, "Marketing Research Report, Titanium Dioxide," August 2005.

In the following sections, we describe the chlorine-based technologies that are currently in commercial use for the production of titanium metal and titanium dioxide pigments, and the alternative technologies that are available for their production. We also discuss the substitutes that might be used for these processes and products and the costs that would be involved in providing them to consumers. The benefits of chlorine chemistry to consumers of chlorine-based titanium-containing products can be determined from the differences in the costs and utility to consumers of the chlorine-free substitutes and the chlorine-based ones they now use.

Chlorine Chemistry in the Production of Titanium-Containing Products

Chlorine is a facilitator in the production of titanium sponge, the first commercial form of the metal, and of the titanium dioxide incorporated into pigments. That is, chlorine is used in the manufacturing processes to transform and purify the materials, but it is largely recycled within the production process and does not appear as a constituent in the final product. The net amount of chlorine consumed depends upon the purity of the starting material, but may be as low as 0.1 metric ton of chlorine per metric ton of product, appearing mainly as iron chlorides. Alternative, chlorine-free processes are also

---

[2] Titanium sponge is the first commercial metallic product of titanium ore processing. Further processing leads to titanium ingots and mill products.

practiced commercially. These processes generate much larger amounts of waste materials and will be described in detail in the next section. All current production in the United States and most production in Canada are based on chlorine chemistry.

A variety of minerals may be used as the starting materials to produce titanium-containing products and are available worldwide. Australia, South Africa, and Canada currently provide about 70% of the world's requirements. The most important starting materials consumed in North America are natural and synthetic rutiles, and titaniferous slags. Rutiles are natural minerals that are composed mainly of TiO_2 that is contaminated with other materials. High-grade rutiles may be upgraded to the required purity by physical beneficiation techniques, but lower grade rutiles may require thermal and chemical treatment, typically using chlorine-based processes, to produce so-called "synthetic rutile." Titaniferous slags are produced by reducing ilmenite-type ores, which are composed mainly of titanium-iron oxides, at high temperatures in electric furnaces. The natural and synthetic rutiles typically contain from about 90% to 95% TiO_2, while the slags may contain 85% to 90%. The impurities consist mainly of oxides of iron, silicon, and smaller amounts of other elements. One producer has the capability for direct feeding of secondary ilmenite ores.

The starting material of choice is mixed with coke and fed to a fluidized bed where reaction with chlorine gas takes place at about 1,000^{o}C. The major products of reaction are carbon monoxide, carbon dioxide, titanium tetrachloride ($TiCl_4$) and other volatile metal chloride vapors, and nonvolatile residues of silicon, zirconium, and other materials. The nonvolatile materials are separated from the gases, and the $TiCl_4$ and other condensable gases are separated from the noncondensable gases, which are treated to remove small amounts of chlorides, sulfur (from the coke), and carbon monoxide before they are released. The crude $TiCl_4$ is purified to remove the iron chlorides, small amounts of radioactive materials, and other impurities that would be chromophores or otherwise detract from product performance. Chromophores are compounds that are responsible for imparting color. The purified, liquefied $TiCl_4$ is the starting material for the production of both titanium metal sponge and titanium dioxide pigments.

Titanium metal sponge. Titanium metal is produced commercially from purified $TiCl_4$ by the Kroll process, which is a batch process that uses elemental magnesium to reduce the titanium. The $TiCl_4$ and magnesium are fed to reactors in which the temperature and composition of the reacting mixture are controlled carefully. Volatile magnesium chloride and solid titanium are the major products of the reaction, which is carried out under conditions that ensure very little excess magnesium and magnesium chloride remain with the sponge when the $TiCl_4$ has been consumed. The magnesium chloride is treated in electrochemical cells to recover magnesium and the chlorine gas is recycled to produce more $TiCl_4$ from the starting material. The residual magnesium and magnesium chloride retained on the porous sponge are removed and the sponge is sent to mills for further processing.

Titanium ingot is prepared by mixing the sponge with any required alloying agents, mainly aluminum and vanadium, and titanium scrap and melting the mixture under inert conditions in electron beam, plasma, or vacuum arc furnaces. The ingots or slabs are then converted into mill products such as castings, billets, rod, bar and wire, plate, sheet and strip, and pipe and tube for conversion to final product forms. Much smaller amounts of higher purity titanium required for electronic and semiconductor applications are produced by reduction with sodium instead of magnesium.

Titanium dioxide pigments. Titanium dioxide pigments are produced from the purified $TiCl_4$ by reoxidizing it with purified oxygen. The gas phase reaction is carried out in stages with temperatures controlled from 900^oC up $2,000^oC$. Mixing conditions, temperatures, and the addition of light metal chloride nucleating agents are controlled to give the particle size distribution desired in the final product. The solids produced under these conditions are in the rutile crystal form. They are separated from the reaction byproduct gases, mainly chlorine that is recycled to produce more $TiCl_4$, cooled and slurried in water for preparation of the finished products.

Commercial products are produced from the highly pure TiO_2 in the finishing section of the plant. Final control of the particle size, which may range from 0.2 to 0.5 microns, is achieved by wet and dry milling. The solids are also coated by applying a small amount of soluble materials such as silica, alumina, zirconia, and organics such as polyols and silicones to the solids. These additives are formulated to improve dispersibility, lessen yellowing, or provide other product-specific improvements and serve to differentiate various manufacturers' products. The coated solids then are washed and reduced in size to only a few microns in diameter and dried and packaged. Finishing is a capital, energy, and labor-intensive part of the process of manufacturing titanium dioxide pigment products.

Alternative Technologies for the Production of Titanium-Containing Products

Production of titanium dioxide. As mentioned above, commercially viable chlorine-free routes to the production of titanium dioxide exist, based on sulfate chemistry, so consumers could satisfy their requirements for these products without relying on chlorine chemistry. However, the chlorine-based technology has steadily gained market share since its inception some 50 years ago and its advantages in capital, energy, and labor efficiency make it the widely chosen in large, new greenfield plants worldwide. It also produces far less waste material than the alternative sulfate-based process as that technology has been practiced historically, although that is less of an issue in more modern sulfate-based plants. The current distribution of chlorine and sulfate-based titanium dioxide plant capacities is shown in Table 4.

Table 4
Titanium Dioxide Pigment Capacity by Region and Process, 2005
(Thousands of metric tons)

Region	Chlorine-Based	Sulfate-Based	Total Capacity	Percent Chlorine
U.S. and Canada	1,649	20	1,669	98.8
Balance of Americas	128	96	224	57.1
Western Europe	547	862	1,409	38.8
Central and Eastern Europe	0	234	234	0
Africa and Middle East	100	25	125	80.0
Japan	68	240	308	22.1
China	15	658	673	2.2
Oceana and Other Asia	404	141	545	74.1
Total	2,911	2,276	5,187	56.1

Source: SRI's Chemical Economics Handbook, Titanium Dioxide, August 2005.

The sulfate technology was commercialized some 80 years ago to provide pigments with more advanced properties than the lead and zinc-based materials that had been in use for centuries. The initial plants were small and operated inefficiently, generating large amounts of waste materials. By the mid 1960s, the sulfate process still made up more than 70% of North American capacity and an even higher percentage of titanium dioxide capacity in the rest of the world; it is still in the process of being displaced. Recent sulfate capacity additions in China have been in the form of small plants that would not meet the developed world's environmental safety and health standards. An announced major addition of chlorine-based capacity there will bring the share of chlorine technology to about 25% of the total.[3]

As is the case with the chlorine-based process, the sulfate-based process can accept a range of starting materials. Economic operation of the dissolution process, however, requires that the raw materials contain a minimum amount of iron to promote high rates and extents of recovery of the contained titanium. Therefore, the titaniferous slags used in this process contain only about 75 to 80% TiO_2, and their oxidation states are controlled to promote leachability. The sulfate process does not normally consume natural or synthetic rutiles,

---

[3] U.S. Geologic Survey Minerals Yearbook, Titanium -2005, February 2007,

but uses ilmenite ores that may have been upgraded to contain from about 45 to 60% TiO_2. In some cases blends of slag and ilmenite are used as feedstocks**.**

The feedstocks are digested in agitated, concentrated sulfuric acid (80-95%) at temperatures above 140°C, with the exothermic heat of reaction increasing the temperature to 180-200°C. Reaction residues are separated by filtration and washed to recover the soluble titanium and iron compounds, mainly titanyl sulfate, ferrous and ferric sulfates, and the sulfates of other impurities in the feedstocks, such as aluminum, manganese, and magnesium. Any ferric iron present is reduced to the ferrous state by addition of scrap iron and the resulting solution is clarified, generating additional solid residues that must be neutralized and disposed. The clarified solution then is cooled to remove most of the ferrous sulfate that is sold as “copperas” for use in water treatment and other applications. These operations require very careful control of temperatures and solution compositions to maximize recovery of TiO_2, and reduce consumptions of raw materials and energy, and the formation of wastes.

The titanyl sulfate-containing solution is then subject to hydrolysis by prolonged contact with steam, and crystals of hydrated titanium dioxide are produced upon cooling the mixture. The type of seed crystals added to the hydrolyzing mixture determines the final crystal form, anatase or rutile, and the particle size distribution is managed by careful control of process conditions. The hydrate crystals are separated and washed to remove soluble salts, are reslurried in acid and “re-leached” to remove final traces of iron and other metals, and may be “re-seeded” for final control of crystal size distribution and form. The purified TiO_2 is washed and the solids are calcined in direct-fired kilns. The calcined material is treated in a finishing section of the plant in essentially the same manner as practiced in chlorine-based plants.

In older plants, or in situations with lax environmental standards, the spent acid from hydrolysis, at 20% to 25% H_2SO_4, and dilute acid streams from washing steps are neutralized, usually with lime, and the resulting voluminous gypsum sludge is disposed. Modern plants reconcentrate the acid and remove soluble salts so that the acid can be recycled. The salts are decomposed to recover the sulfate values for recycle. These operations require significant additional capital investment and operating costs, but reduce waste volumes greatly.

The batch or semi-batch nature of this technology lends itself to the production of multiple grades of material from the plants. If the seed crystals added to the hydrolysis step are derived directly from within the later stages of the process as described above, the product will be in the anatase crystal form. Certain specialty products require this crystal form, and the rutile form is preferred for most high volume coating applications. Some producers, therefore, use small amounts of the chlorine-based rutile crystal form of TiO_2 as seeds to promote the production of bulk rutile form product. It would not, of course, be possible to produce such material in the absence of chlorine chemistry.

Production of titanium metal. Commercial production of titanium metal began almost a century ago based on the Hunter process. This process used elemental sodium to reduce $TiCl_4$ and was ultimately displaced by the Kroll process that is based on the use of the less costly, recyclable magnesium as a reductant. The Hunter process is chlorine-based and so cannot be considered as an alternative in this evaluation. Carbothermic reductions, such as those practiced in the manufacture of iron and silicon, cannot be considered as potential process routes for the production of elemental titanium because titanium carbide compounds will be formed upon reduction of the oxides in preference to formation of the metal.

In spite of the improvements that have been made over the years, the high cost and complexity of the Kroll process have provided ample incentives for researchers to attempt to develop alternate process routes. Many process variations and alternative chemistries have been investigated in the laboratory. A few have been tested at somewhat larger scale, but none have been commercialized. The FFC Cambridge[4] process, for example, has demonstrated technical success at the bench but numerous engineering and economic problems remain to be addressed before it can be commercialized.[5]

The FFC process is based on the electrolytic reduction of TiO_2 in a bath of molten calcium chloride that contains dissolved calcium. Poor current efficiency, the need to deal with removal of impurities from the $CaCl_2$/Ca melt, problems with materials of construction, and scale-up issues make it unlikely that such a process can be commercialized in the near term. In any case, like the Hunter process, chlorine chemistry is integral to its operation so that it cannot be considered as an alternative here.

In the absence of a technically and economically viable chlorine-free route for the production of titanium metal, consumers would be forced to substitute other materials for titanium if they could not enjoy the benefits of chlorine chemistry.

The Benefits of Chlorine Chemistry in the Production of Titanium-Containing Products

The benefits that consumers derive from access to chlorine chemistry for the production of titanium dioxide-containing pigments and titanium metal can be determined by estimating the additional costs that they would have to bear if the current, chlorine-based technologies were not available.

In the case of titanium dioxide-containing pigments, consumers would have the option of switching to the same or very similar products manufactured by the sulfate route. In the case of titanium metal, consumers would be forced to select alternate materials if an economically viable chlorine-free route to titanium sponge could not be developed. In the following sections we describe the considerations leading to our estimates of the consumer benefits derived from chlorine chemistry for these products.

The benefits of chlorine chemistry in titanium dioxide-containing pigments. While titanium dioxide-containing pigments are manufactured and formulated carefully in hundreds of grades that are tailored to the specific requirements of the applications in which they are consumed, they appear to be priced more like undifferentiated commodity materials. When cyclical effects are smoothed out, average prices (adjusted for inflation) for these materials have decreased steadily over the years. In spite of impressive increases

---

[4] This process is named after three University of Cambridge scientists, Derek J. Fray, Tom W. Farthing, and George Z. Chen.

[5] G.Z.Chen et al, Nature, 407: 361-364, 2000.

in operating efficiencies and reductions in costs, producers generally have not been able to make reinvestment level returns on their products. Overcapacity has existed at times and low-cost debottlenecking and incremental expansion projects at existing plants generally have been sufficient to meet increases in demand.

The brief process descriptions given above show that the sulfate-based process is considerably more complex than the chlorine-based one. It is carried out in batch or semibatch processes that are more difficult to scale up to large sizes, so that economies of scale are difficult to achieve. The typical sulfate-based plant has only about one third of the capacity of typical chlorine-based plant, but it has more production lines and unit operations and may require approximately twice as much real estate. It also consumes more labor, energy, and raw materials, although the raw materials may be less costly per unit of TiO_2 contained than those used in most chlorine-based plants. The net result is that the capital requirements per unit of production, as well as costs of production, for sulfate-based plants that meet current environmental standards are higher than those for chlorine-based plants.

Demand for chlorine-free titanium dioxide-containing pigment would have to be met by the construction of new sulfate-based capacity. The necessary investments would not be made unless product prices were increased sufficiently to permit the producers to obtain adequate returns on the new capital investments. If the producers attempted to increase prices too much, consumers might substitute other, less expensive, and less effective pigments and this substitution could involve some loss in utility in the products. Plastics and coatings exposed to sunlight might experience reduced lives due to UV-induced damage, for example.

Depending on its size, location, infrastructure availability, and environmental requirements, capital requirements for new sulfate-based capacity could be quite high. Producers could reduce costs significantly below greenfield plant levels by undertaking brownfield expansions[6] at or adjacent to existing chlorine-based plants and retaining use of the existing finishing operations, utilities, and service facilities. Assuming that such measures would be generally possible, we estimate that new investments of the order of \$5.5 billion would be required for the new capacity necessary to meet the demand for these pigments in the United States and Canada. The higher operating costs of the sulfate-based plants and imposition of the required returns on the investments would cost consumers in the United States and Canada of the order of \$1.4 billion per year. If the producers were not able to site the new plants in proximity to existing ones to utilize existing infrastructure and finishing facilities as has been assumed here, capital requirements could be as high as \$9 billion and the cost to consumers as high as \$2.1 billion per year.

The benefits of chlorine chemistry in titanium metal. In the absence of an economically viable chlorine-free route to the production of titanium metal, consumers would be forced to substitute other materials in the end use applications now held by titanium and titanium alloys. Titanium competes with other metals, alloys, and materials now in most applications, even in cases where the initial cost of the alternate material is lower per pound than titanium. In many applications, titanium holds significant share because its unique

---

[6] A greenfield site is land not previously developed, while a brownfield site is land previously used for industrial purposes that may have access to previously developed utilities and services.

physical and chemical properties make its life cycle costs lower than the available alternatives. Life cycle cost and performance considerations make substitution for titanium quite difficult in many applications, particularly in the aerospace sector. Some possible substitutes for titanium in its various applications are presented in Table 5.

Table 5
Substitutes for Titanium and its Alloys in Various Applications

Application or Use	Possible Substitute Materials
Aerospace-high temperature, turbines	High nickel alloys, cobalt-containing alloys
Aerospace-structural	High strength alloy steels, aluminum alloys (2x,5x,6x), carbon fiber composites, various intermetallics
Industrial (a wide range of requirements for corrosion resistance)	Various austenitic stainless steels, duplex stainless steels, super-austenitic steels, chrome-moly steels, Monel, Inconel®, Hastelloy®, tantalum, various plastics, composites and rubber for lower temperature applications
Consumer, architectural	Stainless steels, alloy steels, coated steels, aluminum alloys, various plastics, precious metals
Medical	Tantalum, certain plastics

While there are many choices of alternate materials in the industrial use of titanium for corrosion resistance, the choices usually are much more limited in specific applications because the service requirements may preclude the choice of certain materials. Titanium may be specified in preference to stainless steels in process equipment such as vessels and heat exchangers even though it may cost twice as much (or more), because its use would extend the service life of the equipment and reduce downtime for maintenance, for example. Under these circumstances eliminating titanium would increase life cycle costs for the component. In other specific applications, the temperature or corrosive nature of the environment might preclude the use of less expensive materials such as stainless steels, plastics, rubbers or composites, and titanium normally would be specified in preference to more expensive materials such as Inconel®, Hastelloy® or tantalum.

Substitution generally would be somewhat easier technically in consumer and architectural applications where numerous choices exist for substitutes, many of them available at lower cost than titanium. In these cases consumers generally have selected titanium-based products for specific performance or aesthetic reasons, and would suffer some loss in utility if they were not available. Substitution in medical applications is also possible, but at higher initial cost. We estimate that the increase in initial and life cycle costs for replacing about 10 metric tons per year of titanium metal with other materials in industrial, consumer, and medical applications would be of the order of $200 million per year, mostly for the increased initial costs of more corrosion resistant materials and the increased maintenance costs for other substitutes.

The most difficult substitution issues, however, arise in aerospace and combustion turbine applications. The benefits of titanium in these areas arise from its high temperature strength, corrosion resistance, and its high strength-to-weight ratio, particularly for the types of alloys typically specified such as Ti-6Al-4V. This material's strength-to-weight ratio is two to four times that of typical high nickel alloys and alloy steels. It is also about 50% to 200% stronger per unit weight than the aluminum alloys used in aerospace structural applications. While titanium is more expensive than the aluminum alloys and high strength steel alloys, it is less expensive than the high nickel alloys or cobalt-containing alloys that can substitute for it in various applications in the engines and turbines. Substituting some of these materials for titanium in a specific application might reduce the material cost of the part, but its weight could be substantially higher. This is significant, since modern passenger aircraft may use from 10 to more than 50 metric tons of titanium in their engines and airframes, depending on the model.

Aircraft are designed to maximum allowable take-off weights, which include the empty weight of the aircraft plus the weights of the passengers, cargo and fuel. Therefore, extra weight in the airframe and engines must be offset by decreases in the allowable weights of passengers, cargo and fuel. Decreasing the latter would compromise performance by restricting the aircrafts' range, while fewer passengers or less cargo would result in revenue losses to the carrier. The new Boeing 787 series airframes were designed to contain about 15% titanium and 50% composite materials to reduce both weight and life cycle costs, whereas the previous generation Boeing 777 series airframes contained about 50% aluminum. The design weight of the new 787-8 aircraft had been estimated to be about 110 metric tons, some 15% lighter than comparable aircraft, but the first prototypes built weighed about 2.5 metric tons more than their design targets. Subsequent builds may meet the weight target by incorporating more titanium into their designs, but it is believed that the prototypes had to be sold at a discount because of their extra weight. The higher strength-to-weight ratios of titanium alloys compared with high nickel and cobalt-containing alloys results in weight saving in aircraft engines and combustion turbines, and this, with other design advances, leads to increases in efficiency as well. The newer engine designs are of the order of 10% more efficient than previous generations, reducing fuel consumption over the operating life. These savings, plus the weight savings achieved through the use of composites and titanium in the airframes, reduce fuel consumption by 20% compared to earlier designs. Substitution of other materials for titanium will increase material costs for airframes and engines and increase the life cycle cost of aircraft operation by increasing fuel use. Excluding the costs of performance losses in military applications, we estimate that the costs to consumers in the United States and Canada of substitution for titanium where it is used currently in aerospace and combustion turbine applications to be about $1.0 billion per year.

Bask, Be Happy, Stay Healthy

Sure, a dose of sunshine can lift spirits and drive the blues away. Increasing evidence suggests that everyday sunshine is a determinant of health and has an important role in preventing or ameliorating many afflictions, including depression, cancer, and postoperative pain. But prolonged exposure on unprotected skin can hasten the skin's aging process and even increase one's risk for melanoma. With sunscreen usage, however, one can enjoy sunshine and reduce the damaging effects of ultraviolet rays.

According to Euromonitor, sun care products (includes sun protection, after sun, and self-tanning) generated over $1 billion in sales in United States during 2005. Over the period 2005-2010, the sun care market in the United States is expected to grow approximately 9%. Sun protection products (e.g. sunblocks, sunscreens) contributed over $800 million to the 2005 sales figure.

Sunscreens help protect our skin from sun damage by absorbing and scattering UV rays. For years, the sunscreen industry has focused predominantly on guarding against UVB. Sun protection factors (SPFs) listed on sunscreen containers are a measure of a product's protection against UVB. Generally, the higher the SPF, the greater the protection against UVB rays. UVB is the light that hits the skin surface and causes redness and burning. It also increases one's risk for skin cancer. However, UVA penetrates deeper into the skin than UVB and creates harmful free radicals when it interacts with certain chemicals in the skin.

There are two broad categories of active ingredients: chemical and physical.

Chemical sunscreens, such as PABA (para amino benzoic acid), oxybenzene, and avobenzone, work by absorbing UV rays and require some wait time after application and before sun exposure. Some chemical sunscreens absorb into the bloodstream and raise potential safety concerns. Some require reapplication every twenty minutes to be effective. Physical blockers, on the other hand, do not require the same wait time to be effective; they work by sitting on the surface of the skin and reflecting UV rays. Blockers offer little absorption and no adverse health effects have been reported. The two leading physical blockers are titanium dioxide and zinc oxide. Titanium dioxide has a very high refractive index – surpassed only by diamond – which makes it a valuable sunblock. In fact, scientists say that titanium dioxide and zinc oxide are among the only chemicals capable of shielding both UVA (skin-wrinkling) and UVB (cancer-causing) rays and, therefore, help in fending off potentially deadly skin cancer. According to the Centers for Disease Control and Prevention, skin cancer affects some one million Americans each year, a number that continues to grow.

Both titanium dioxide and zinc oxide leave a white film after application, which can be cosmetically undesirable. This effect can be minimized by using nano-sized particles – extremely small particles measured in nanometers (a billionth of a meter). Once the particle size of physical blockers are reduced to such scale, however, it raises questions about their effect on human health and the environment, as they are more chemically reactive and more easily absorbed by the body. The European Union cosmetic regulatory body reviewed the toxicity of zinc and titanium nano-ingredients in sunscreen and stated that "nanoscale titanium does not pose toxicity concerns including dermal penetration, cytotoxicity, phototoxicity, and genotoxicity." However, they determined that nanoscale zinc sunscreen formulations, posed potential penetration concerns as well as possible DNA damage.

Recently, the Environmental Working Group (EWG) tested over 800 sunscreen products and reported that sunscreens without titanium oxide and zinc oxide "could accelerate by an average of 20 percent the skin damage, premature aging wrinkling and UV-induced immune system damage linked to UVA exposure." The next time you bask in the sun, consider the safety and efficacy of your TiO_2-containing sun protection product.

Source: Scientific America; Environmental Working Group; Global Cosmetics Industry (GCI) Magazine