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Article

Materials and their Biographies: The Case of Titanium and its Dioxide

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Abstract:
In this article, we are interested in analyzing the biography of metallic titanium (Ti) and its dioxide (TiO_2) from a historical, philosophical, and sociological point of view of some of its modes of existence. This biography does not suggest any anthropomorphization of material objects, rather, it is about an attempt to reconcile the reality of science in the present with its history to understand the particularities of materials in contemporary societies. We intend to investigate some properties and characteristics of the "natural" modes of existence and the new properties and implications when these materials gain a new mode of existence, the nanostructured one. This mode of existence refers to a new way of organizing scientific knowledge, an inflection which has been called technoscience, more concerned with what an object will become in the future, then with what it essentially is. In this sense, the proper chemical identity of these substances is one among other modes of existence, into this mode of existence, one must add others which can approach its biological, geological, cultural, technological, economic or geopolitical behavior.

Keywords: Biography of Materials; Modes of Existence; Titanium, Titanium Dioxide, Technoscience

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Introduction

Proposing analyses and reflections about contemporary sciences is a challenge for historians, philosophers and sociologists. How do one approach the material and scientific objects that are made available by sciences, technology and industries for society and the natural environments at the present time? Although it was during the 20th century that most sciences

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developed and structured themselves, be it from an institutional or social perspective, the majority of articles and books about the history of sciences cover periods prior to that. Many barriers are raised when investigating the history of science *in action* and its philosophical, social and environmental implications. For example, one of these difficulties constitutes the matter of the proximity of the historian, philosopher or sociologist, who has an intimate spatial-temporal relationship with scientists, governments and industries, but also faces secrets and patents, besides the complexity when it comes to these researchers understanding concepts and languages that are pertinent to current sciences (Söderqvist 2012). The historiography produced concerning the emergence of technoscience and nanotechnologies during the second half of the 20th century has faced these obstacles and has proposed varied analyses of these scientific and social emergencies.

Recently, the "biographical" genre has been used to converge historiographical, philosophical and sociological narratives, aiming to analyze both scientific objects and the particularities of several materials present in contemporary societies. It is important to observe, however, that when using the term "biography" of scientific objects and materials, one intends simply to make an analogy with their "lifespan", in which said objects acquire several "modes of existence." This narrative genre does not suggest any kind of anthropomorphization of material objects, nor does it attribute any "conscience" to them, but, as said by Lorraine Daston, it is intended to be an attempt to reconcile the reality of the present science and its history (Daston 2000). For Bernadette Bensaude-Vincent, although materials have a long history, the *science of materials* as a specific domain of investigation is fairly recent. This new discipline emerged in the USA around 1960 and is a result of the aggregation of multiple disciplines that were already well-established, such as metallurgy, chemistry, mechanical and electrical engineering, as well as more recent fields of solid-state physics. The science of materials deals with the individualities particular to each material and not the general concept of *matter*. It focuses on the technological and economic characteristics of materials, starting from the investigation of its structure, properties, performance, and processes. Thus, to write the biography of a material means, above all, making elements of the history of chemistry, physics and engineering converge with social, cultural, historical, geopolitical and environmental aspects, among others. Materials demand, therefore, the writing of "composed histories" (Bensaude-Vincent and Loeve 2018; Bensaude-Vincent 2022).

These biographies are composed of several modes of existence of a material. When and how does a specific chemical object start *existing*? We could settle for answers that bring us to the name of the person who discovered it and the description of the techniques employed by said scientist, but maybe we are settling for too little. The existence of a material object means more than its discovery or its invention, it means the object in question becomes part of a set of entities, with material properties that are particular to it, and which should be named and classified among the ones already known. The expression "modes of existence" has already been employed as a conceptual operator by philosophers such as Etienne Souriau (Souriau 2009), Gilbert Simondon (Simondon 1989), and more recently Bruno Latour (Latour 2019). The expression also seems appropriate to refer to material objects produced by the chemical science, with the goal of trying to understand the genre of ontology which engages the practices of chemists as a consequence of their own social demands (Bensaude-Vincent 2005, 215s). To understand the modes of existence of materials, the debate should not happen around the question of "what can I know?" but around the question of "what can I make?". Thus, we should not ask ourselves "what is" a chemical object, but "in which ways is it", which constitutes its modes of existence in the natural and social world.

This article focus on analyzing some of the modes of existence of titanium dioxide (TiO_2), for it is a very informative case study about a material of great capillarization in the current production system (pigments, food, hygiene products, medicine, environment, metallurgy), moreover, it provides clues about the particularities of nanostructured materials. Thus, the goal is to describe and analyze some properties and characteristics of the modes of existence of "natural" titanium dioxide and the new properties and implications present when this material receives a new mode of existence, the nanostructured one. This mode of existence refers to a new way of organizing scientific knowledge, an inflection which has been called "technoscience". In this field of investigation, with the convergence of expertise promoted by "technoscience", a term employed by Gilbert Hottois to refer to the implications of new technologies in human societies and natural environments, we find the multiplication in the use of certain materials, besides the research and development of new ones, with even more surprising properties.

It is known that materials have numerous exclusive properties on the nanometric scale, including new behaviors in phase transitions, new thermal and mechanical characteristics, new reactivities (catalyzes), or even optical, electrical or magnetic behaviors that are unusual. Besides, the nanoscale of a chemical structure raises issues of great interest for the philosophy of chemistry. In this case, regarding the singularity of emergences of macro chemical and nanochemical levels from molecular or crystalline structures. This means that these emergences are not successive, but happen in a parallel way and generate original properties and behaviors (Zambon and Córdoba 2021).

For the philosophy of chemistry, a central point in this discussion is the ability of storing more information in an increasingly smaller volume of matter. The question regarding the limits of materiality is posed. As Cyrus Mody reminds us, even before Dalton's atomic theory, chemists were fully conscious that their discipline dealt, above all, with small objects, and contemporary chemistry is where canonically nanotechnological "artifacts" are born, such as nanotubes and buckyballs. In the past, due to the reductionist tendencies of certain perspectives of logical empiricism, and also because of physics' social prestige, chemistry was many times neglected by sociologists and philosophers. In fact, there has always been little exploration of how epistemology and the social practice of chemistry were distinct from physics. As it is the case with engineering sciences, however, there is now a genuine interest, which can be seen in the current literature, that points to the singular relationship chemists have with the instrumentation by approaching, for example, questions of purity and contamination in a very specific manner, with particular epistemic meanings, and thus, have a different kind of involvement with their experiments and representations compared to scientists in other fields. The recent literature brings to light the precise way in which chemistry is the science that makes 'epistemic things' — materials which pave the way for experimental work and that result in small and minuscule parts of the world to be scrutinized by it. The competence of chemistry is the creation of molecules, integrated into equipment, concepts and processes which allow chemists to *simultaneously* generate meaning and artifacts in the nanoscale (Mody 2004).

The occupation of the world by industrial products multiplied along the 20th century and the beginning of the 21st century, with increasing demand both in civil society as well as in the military apparatus. After the Industrial Revolution, we observed a growing movement of industrialization with an ever-growing *locus* for the chemical and pharmaceutical industry, as well as the creation of large private industrial laboratories. If coal, oil, cast iron or steel continued to be the most available materials made available for social use, new materials came onto the scene. It is the case of titanium, an extraordinary material which is highly resistant, low in density, and has an excellent corrosion resistance, making it attractive to various applications, such as in aircraft, engines and biomedical devices. If in its metallic mode of existence, titanium possesses great importance, the modes of existence of its "natural" dioxide manifest in much broader domains of our everyday practices. But there is no metallic titanium in the natural environment, it is extracted with great difficulty from its main natural composition, the titanium dioxide present in some minerals.

Therefore, investigating how a material like titanium dioxide and its derivatives (which include its metallic form) come into existence takes us to a description of material, cognitive, institutional, social and environmental conditions which brought it to this *existence*. But, coming into *existence*, these chemical objects become materials that can behave in different ways. As we will see below, the proper chemical identity is one among other modes of existence of an atom, a molecule or a *composite*. To this mode of existence, others must be added, which can approach, for example, its biological, geological, cultural, technological, economic or geopolitical behavior. The variety of narratives which describe these different manifestations constitutes what the authors we cited above call the "biography" of scientific objects of materials, which attempt to describe the history of their presence in the natural and social world.

As Gaston Bachelard reminds us:

> When the lesson of things happens as *things* [such as] sulfuric acid and sugar, it is already a lesson of social things. In the same manner, hydrogen and oxygen are, in many aspects, if we dare to express in such a way, *social gasses*, high civilization gasses. (Bachelard 1963, 31)

We should not forget, however, about the socially situated character of sciences and the need, for their philosophies to consider their connections with societies and the natural environment, as well as reaffirming the intersubjective nature of scientific knowledge.

"Natural" Modes of Existence
Between Discovery and Existence: Metallic Titanium

From the 1790s, when it was first identified, until the mid-20th century, titanium, one of the most abundant metals of the Earth's crust, had a confidential presence restricted to the laboratories of chemists and dreams of metallurgists. The first announcement of its existence was published in 1791 in the *Crell's Annalen*, the main German-language science journal[3], by English chemist and clergyman William Gregor (1761-1817). Gregor managed to isolate, through chemical analysis, an unknown and still impure metal from a rock which contained the mineral known today as *ilmenite* which, according to him, had 26% of *calx* (oxides) of iron and manganese, 29% of siliceous earth and around 45% of a reddish lime, which was named *Manaccanite*, after Gregor's parish, located in Cornwall, in the southwest of England. The article was read by one of Germany's main chemists at the time, Martin Heinrich Klaproth (1743-1817), who was also an apothecary and an assiduous collaborator of *Crell's Annalen* (Klein 2007). While Gregor started from ilmenite to try to isolate the unknown metal, Klaproth isolated a metal with very similar characteristics from the mineral we today know as *rutile*, found in a rock extracted in Hungary. But as opposed to Gregor, Klaproth was not in agreement regarding the name of the new metal, *manaccanite*, because such a name was not following the new nomenclature rules Crell demanded for his journal, which was now following a new chemical language proposed by his French colleagues, Guyton de Morveau and Lavoisier, published in 1787 in Paris (Guyton de Morveau, Lavoisier et al., 1994/1787). Thus, Klaproth suggested naming the new metal titanium, from the Latin *titans*, in reference to the children of Gaia and Uranus. Because according to him:

[3] The science journal *Chemische Annalen* was first published in 1778 and was known as *Crell's Annalen* after its editor Lorenz von Crell (1744-1816), a chemist and professor at the University of Helmstedt. The journal had an important role in the formation of a community of German-speaking chemists (Hufbauer 1982).

> Whenever no name can be found for a new fossil which indicates its peculiar and characteristic properties (in which situation I find myself at present), I think it best to choose such a denomination as it means nothing of itself, and thus can give no rise to any erroneous ideas. In consequence of this, as I did in the case of uranium, I shall borrow the name for this metallic substance from mythology, and in particular from the Titans, the first sons of the earth. I therefore call this new metallic genus Titanium. (apud. Housley 2007, 5)

Even though it was not isolated in its purest form, titanium started to be recognized as a *simple body*, earning the status of a chemical element in Mendeleev's periodic table. Titanium then started to be represented with a symbol (Ti) and a mass number (50 – in the 1869 table) which characterized it, and when the number of protons in the nucleus started to characterize the singularity of chemical elements, it started to be identified by its atomic number (22) and located in the fourth group of the current periodic table (IUPAC). The arrival of electricity as a new instrument in the chemical laboratory along the 19th century was important for the isolation of several metals, such as sodium and potassium, and was also the case for titanium, although still in impure samples. In its pure form, the metal was only isolated by Matthew A. Hunter in 1910 with the collaboration of General Electric at the Rensselaer Polytechnic Institute, in Troy (New York). He heated titanium chloride ($TiCl_4$) with metallic sodium in a steel container, under pressure (the Hunter process). Finally, William Justin Kroll, in 1946, managed to isolate titanium for commercial purposes, by reducing $TiCl_4$ with metallic magnesium (the Kroll process). Using magnesium instead of sodium made the process cheaper, which helped with the emergence of titanium's social, industrial, and environmental existence (Quian and Froes 2015).

If the metallurgic method developed by Kroll proved to be fundamental for research in isolation of titanium, it was undoubtedly pushed by the quest for new materials brought on by the Cold War between the USA and the USSR. In the USA, the production of titanium on an industrial scale began in 1948 with Dupont Inc., although, starting in the 1950s, other chemical products industries started to produce titanium, which was destined, above all, to the aviation industry. In the USSR, the industrial production of this metal started in 1957 and was made by VSMPO (Verkhnaya Salda Metallurgical Production Association) and was mainly destined for the manufacturing of deepwater high-performance submarines (Housley 2007). But if in its origin, metallic titanium, which has high production costs, was first proposed for the construction of aircraft and submarines, it also started to be employed in the manufacturing of several objects. Thus, the metallic mode of existence of titanium broadened its uses and applications, as it was employed, for instance, in the manufacturing of jewelry and watches or even yet in architecture, such as in the titanium cladding of the panels in the Guggenheim Museum Bilbao, in 1997 (Moiseyev 2006; Browne 2014, 132).

The high production cost of metallic titanium is not associated with a shortage of the raw material, but with the large amount of energy and technology necessary to isolate this highly reactive metal from other elements, specifically oxygen. Titanium can be found in materials that are relatively abundant on the Earth's crust, such as ilmenite ($FeTiO_3$), titanite ($CaTiSiO_5$) and rutile (95% TiO_2). The material presents allotropy. It has a crystalline close-packed hexagonal structure (alpha phase) when in room temperature and remains stable until 882°C. Above this temperature, its structure is altered and becomes body-centered cubic (beta phase). Above all, it draws attention to — hence, the growing increase in its production all over the world — its chemical and physical properties and, as a direct consequence, its wide range of important applications. An excellent refractory metal, for its melting point (1668°C) and boiling point (3287°C) are high, and its thermal and electrical conductivities are low. It is as resistant as iron, yet 45% lighter. It is 60% heavier than aluminum, although around twice as resistant, which reflects its low density (4,54g/cm^3) and its elastic modulus above 12,7 x 10^4 Mpa. It is, then, a substitution and complementary metal for the industry, just as its alloys with metals such as aluminum, magnesium, iron, or vanadium (Sha and Malino 2009). The titanium industry is organized in such a way that it forms oligopolies, companies that control the whole production line, and that are currently concentrated mainly in the USA, Russia and China (Seong, Younossi and Goldsmith 2009).

Finally, although titanium is an element abundant in minerals, it is not found in large quantities in the human body. However, the surface of titanium is among the most biocompatible known surfaces, consequently, this metal started to be widely used in the manufacture of biomaterials such as dental and orthopedic implants (Brunette et. al. 2001). Besides absorbing part of the industrial production of titanium, which contributed to the growth of its market, research and development in the conception of biomaterials made of titanium also constitutes one of the best examples of the necessary interdisciplinarity between basic and technological sciences. That is because the creation and production of these biomaterials is dependent on research developed by disciplines such as physics, chemistry, metallurgy, mechanics, surface science, interface and colloid science, as well as biological sciences and engineering (Oshida 2007).

Titanium Dioxide: Its Existence and Plurality of Presences

Titanium dioxide came into existence in the beginning of the 20th century. Its industrial production started in 1917 in Norway when chemists Peder Farup (1875-1934) and Gustav Jebsen (1884-1952) developed an industrial method to extract a white material from ilmenite, which could be used as a pigment in various kinds of paints (Korneliussen et al., 2000). This new white pigment started being widely used by modernist artists, such as in architecture with Le Corbusier and in painting with Kazimir Malevich (*White on White*, 1918) (van Driel 2018). When they came into existence, the whiteness and chemical stability of this material soon expanded its applications. But what made it become present in a plurality of places?

Titanium dioxide (TiO_2), also known as titanium (IV) oxide is a naturally occurring oxide with applications in paints, medical devices, hygiene products, ceramic composites, additives, textiles, water treatment systems, the food industry, paper production and pharmaceutical additives. It is known as "titanium white" or "white powder" due to its brightness and to being a potent opacifier, that is, its coating abilities. Titanium dioxide is a nontoxic, nonhygroscopic, nonvolatile material. It is important to highlight its high chemical stability. It does not dissolve in water, organic solvents, acids (except hydrofluoric and sulfuric acid), nor in alkalis.

The properties of TiO_2 are determined by the morphology of its particles, the size of its crystals and its crystal structure, which depend on choosing the best method for its synthesis and final thermal treatment. Some of its methods include sulfate, chloride and precipitation. Among its important properties, one can highlight the thermal stability and the capacity of absorbing and dispersing UV light, as it has a high refractive index (n=2,7). Its coating capability is not even comparable with that provided by the possible alternatives. The formulations of paints containing other white pigments would require higher quantities and many more layers of paint to obtain the same coating effect. All crystalline forms of TiO_2 offer photoactive properties. The differences in these properties can be characterized by the differences in band gaps in the electronic structure of TiO_2. When UV light is irradiated with an energy superior to its band gap, electrons of the valence band of titanium dioxide are promoted to the conduction band, generating an e– electron which is responsible for the photocatalytic activity of the material and electron holes (h+). Electrons combine with oxygen in the atmosphere to produce active O_2, while the holes combine with water or water vapor in the atmosphere to form radicals OH•. These hydroxyl radicals are strong oxidizing agents and can, therefore, easily oxidize and thus decompose several organic pollutants, such as oils and fats. Anatase is the form that presents the highest photoactive capacity (Siwinska-Stefanska 2017; Musial 2020).

Titanium dioxide is a common additive in many food items, personal hygiene products and other consumer products used massively by us. After use, it can easily get into the sewer system, and later, penetrate in the environment as treated wastewater, released in superficial waters or biosolids applied onto agricultural land, incinerated residue or solids derived from landfills (Weir et al., 2012). Dyes are used extensively in the beverage and food industry because they confer aesthetic appeal to the products, which would, without them, be colorless or have an unpleasant appearance. Therefore, titanium dioxide (E171) is among the most used food colorings, exactly because it makes candy, ice cream, sweets and bubblegum more visually attractive. Its cost is low and its handling easy, and it does not interfere with the flavor of the food. Regarding personal hygiene products, such as toothpaste and sunscreen are the ones presenting a larger amount of TiO_2, after all, it has both its whitening property, an important value for contemporary western society, and can also filter UV rays.

We have observed, over the last decades, an important increase in the search for new solutions in terms of lithium-ion battery technology, as these are, after all, the main technologies for storing energy: "Currently, the greatest challenge in the design of these batteries is to find an optimum combination of cathode and anode materials, as these largely determine the cell's parameters, including capacity, voltage, reversibility of the charge/discharge reaction, and chemical stability" (Janus 2017). Among a wide range of available materials, titanium dioxide and its derivatives were chosen as good anodes for these batteries, as they allow for the design of devices with low levels of safety concerns. In addition, this class of materials offers thermal stability, low cost, biocompatibility, relatively high surface area and porosity, a wide electrochemical range and enhanced cyclical performance due to its superior electrical conductivity. These characteristics make titanium based derivatives a good candidate to replace the commonly used carbon (graphene) as an anode material in LIBs.

In the economic sphere, titanium dioxide is consumed more as paints, coating, plastics and papers. China, which continues expanding sectors such as plastics and coatings, should considerably increase the use of dioxide over the next few years. For example, China has consumed about 32% of the world's production of TiO_2 between 2014 and 2017, and this amount is expected to increase at an annual growth rate of around 3,5% over the next five years. The Chinese market will also boost general market growth, specially in the construction industry due to the high demand for anticorrosive coatings in architecture. In the USA, paints and coatings are key sectors, but the contribution of the plastics industry will increase over the next few years. If the predicted demand grows according to the forecast (4% to 5% a year), production capacity should increase up to 300 thousand cubic tons a year. Also in Europe, the most relevant sectors for application of TiO_2 are paints, coatings and plastics, which represent a 650 billion euro market. We are, therefore, analyzing a material with gigantic growth potential in the economic sector and thus, with a high degree of capillarization in society and the environment (Parrino 2021).

It is important to mention that titanium dioxide is a substance with merely an aesthetic function and thus, does not aggregate any nutritional value. In fact, the use of this additive started being questioned after analyses indicated that particles of the substance could accumulate in the human body. Since 2016, the European Food Safety Authority warns of the need for further studies, for genotoxicity — the ability of substances to damage genetic information in cells — of particles of titanium dioxide cannot be ruled out, and it is not possible to establish an acceptable daily intake (ADI). The EFSA manifestation subsidized the decision by the European Commission about the food additive, stipulating that the use of E171 will be banned in countries of the European Union after a transition period.[4] In Brazil, titanium dioxide has its application as a food additive regulated by the Brazilian Health Regulatory Agency (Anvisa). Technical note nº 30/2021/SEI/GEARE/GGALI/DIRE2/ANVISA contains precise information about the food coloring function of titanium dioxide[5]. From the note, one can infer that Anvisa understands there is sufficient evidence to indicate how more restrictive measures about its use in food are pertinent, measures which would demand an update of prevailing regulations. Currently, bill nº 2257/22 is being discussed in the Chamber of Deputies, which forbids the use of titanium dioxide in food manufacturing, as well as the import of goods containing this substance.

If natural titanium dioxide raises such important questions about its safety regarding human health, we will see that in its other mode of existence, in a nanometric scale, the uncertainty and unpredictability will appear in a fundamental manner, because although they present in the same structure, their properties are totally altered, and can engender serious ethical, medical, epistemological and social problems. It is important to note that between the beginning of regulation in Europe about the use of titanium dioxide in the food industry in the 1950s, until its ban in 2021, we have a significant inflection moment. It happens in the beginning of the 2000s, exactly when the industry starts providing titanium dioxide in nanostructured forms (Boutillier et al., 2022). If we are to be aware of its natural mode of existence, recent studies point to the danger of titanium dioxide particle absorption at a nanometric scale.

The Emergence of a New Mode of Existence: Nanotechnology and Nanochemistry

Just as the metallic titanium industry, a new way of organizing scientific and technological research was also born within the context of the Second World War and the Cold War. This is in reference to the projects aiming at the dissolution of frontiers between science and technology, which led to the idea that science and technology would be transformed into something new, a *technoscience*. Some philosophers and historians of contemporary science consider technoscience a result of the so-called "Big Science", whose model would be the Manhattan Project. Its ramifications would be the result of a state policy applied in the United States starting in 1945, guided from directives stemming from the famous Vannevar Bush report (*Science, the Endless Frontier*) which was drafted by request of President Roosevelt (Echeverria 2003). A similar movement can be seen in the governance of the Soviet State in the post Stalin era. The de-Stalinization of the Soviet Society did not only involve the abolition of the cult of personality of Josef Stalin, but also led to broader intellectual changes in relation to what was called "scientific forecasting and future studies" (Rindzeviciute 2016). Certainly, the creation of the *Akademgorodok* (Academic City), located in Western Siberia, characterizes this reorganization of Soviet scientific research, which brought it closer to those practiced in the USA and in European countries[6]. As we have seen, however, the term *technoscience* was first used by Belgian philosopher Gilbert Hottois, who, since the 1970s, employed it to denote the new emerging relationship between science and technology. His philosophical goal was to counter the theoretical and linguistic reductionism of analytic philosophy which, according to him, was disconnected from the scientific-technological

[4] https://www.efsa.europa.eu/en/news/titanium-dioxide-e171-no-longer-considered-safe-when-used-food-additive
[5] https://www.dropbox.com/s/6oua8erwny02jo1/SEI_ANVISA%20-%201526798%20-%20Nota%20T%C3%A9cnica.pdf?dl=0
[6] This city of science was established in 1958 and was idealized by mathematician Mikhail Alekseevich Lavrentev (Josephson 1997).

reality and its value judgment implications (metaphysical, epistemic, ethical, social, economic, environmental, military and more) (Hottois 2006).

The NBIC acronym condenses the four engines of technosciences, which focus on the investigation of the most intimate part of the matter: the fields of **N**anotechnology, **B**iotechnology, **I**nformation technology and **C**ognitive science. Technosciences, as experimental sciences, operate on the frontier between knowing and doing, where the question is about *what is it*? Becomes *how does it work?* It is about operationalizing nature by intervening in its processes, even if matter itself, especially living matter, keeps moving, in a constant process of coevolution. One can notice that, while the ontology of modern science turns itself to the investigation of the being-object, abstracting certain characteristics considered essential and that distinguish it from the other beings, and theories search for, by means of universalization, validation for each time and place, technosciences move towards the goal of recreation from the fundamental bricks of matter. In one, emphasis is on the essence of the objects, in the other, on their existence. With technoscience we find, thus, a collapse of the fundamental distance between subject and object, between natural and artificial, instituted since the beginning of modern science in the 17th century, an ontology of substances, and the emergence of a process ontology, more concerned with what one object will become in the future than with what it essentially is (Bensaude-Vincent 2013). Because this "essence" can transform into conflict with the environment, with the human body, with the social environment. From there maybe we can think more about ontological pluralism, other than an ontology that is unique and *a priori*.

It was in this context, then, of institutional, economical, epistemological and political reorganization of sciences and technologies that a new domain of investigation came about, which would be practiced on a scale that would open the doors for a new world, a *nanoworld*, whose dimension corresponded to one billionth of a meter. It concerns the appearance of nanotechnology. Richard Feynman and, later, Eric Drexler first introduced the conceptual possibility of atom manipulation, of "shaping the world atom by atom" and its consequences for the industrial field (Feynman 1960, 22-36; Drexler 1986/1992). Here we observe an interesting example of how difficult it is to work with the history of sciences in the present, for although Feynman's conference ("There's Plenty of Room at the Bottom", 1959, American Physical Society at its meeting at Caltech in Pasadena, California) is considered the origin of nanotechnology by several authors, including Drexler, historians have demonstrated that this influence in the experimental field was much smaller than the commonly admitted in the promotional rhetoric of nanotechnology. In fact, the myth of the precursor must also be put aside in the historiography of contemporary sciences. Finally, nanotechnology does not need to be considered as something with a precise beginning and following a clear line of historical causality (Toumey 2008, 133-168).

Feynman's conference was, without a doubt, inspiring, but it was the arrival of the scanning tunneling microscope, capable of obtaining images at an atomic level which, in fact, broadened the perspective for a growing increase of analysis capacity and manipulation at a nanometric scale. In 1981, Gerd Binnig and Heinrich Rohrer, both winners of the Nobel Prize in Physics (1983), developed this equipment, which supplied the first images of individual atoms onto the surfaces of materials, specifically silicon and gold. The scanning tunneling microscope is used in industrial research and is fundamental for obtaining images of metallic surfaces at an atomic scale. It provides a three-dimensional profile of the surface and thus offers information to characterize surface roughness, observe defects on it and determine the size and aggregates and molecular conformation (Neddermeyer 1993).

According to Drexler, in his already classic *Engines of Construction* (1986), it is the variations of atoms that distinguish them between cheap or expensive, what is ill or healthy. One can simply think of carbon and diamonds, sand and computer chips, cancerous and healthy tissues. Disposed of in a certain manner, they can compose fresh air and houses; disposed of in another, they constitute ashes and smoke. However, even though the North

American scientist praises the level we have reached today with our equipment and drugs, saving millions of lives, he signals we are still at a time when the domain over the atomic order has not yet been achieved (Drexler 1992, 57). Why? Because traditional chemical synthesis, according to him, is still a very primitive way of doing things. The chemist chooses certain reagents which are mixed in a container in the hopes that a sufficient number of molecules will eventually fall in the right place to produce the desired product. Drexler defends a radically new technology which will manipulate atoms and individual molecules, putting them together like Lego pieces and, thus, will provide complex molecular products in a clean and efficient way.

In contrast with this dream of synthesis without waste, Drexler characterizes current organic synthesis as a random and not very reliable process to build complex molecular chains. At the beginning of his book, Drexler already contrasts two types of technology. On the one hand, the current one, which deals with blocks of mass construction of matter, while, in a new era, the nanotechnology era, it will "manipulate individual atoms and molecules with control and precision". That is, on the one hand, a chemical process that is "top to bottom" and, on the other hand, a new approach that is "bottom up". Finally, genetic engineering, without a doubt, is the model adopted by the American physicist and engineer, because like molecular biologists describe ribosomes and proteins as molecular machines, nanotechnology will carry out specific molecular tasks for the industry.

However, this physical and mechanical model by Drexler was challenged by another great enthusiast of nanotechnology, chemist Richard Smalley, one of the winners of the Nobel Prize in Chemistry in 1996, for discovering fullerenes, an allotropic nanometric form of carbon. For Smalley, it is not possible to guide individual atoms with the precision required by Drexler. A crucial aspect of the controversy which has been established between both concerns the experimental viability of the notion of "molecular assemblers". According to Drexler, such assemblers would be capable of building everything with atomic precision, and he uses, as an analogy, the protein synthesis made by RNA, an example of a biological nanorobot. Smalley contests the viability of this machine model, defying the possibility of obtaining precise control of nanophenomena such as the assumptions theoretically adopted by Drexler. Smalley raises two main objections: the fat fingers and the sticky fingers issues. On the first one, the target is Drexler's mechanistic reductionism, which conceives nanorobots without taking into account that they, themselves, are also formed by atoms, in such a way that there would not be sufficient room for control with atomic precision at a nanometric scale. On the second objection, the sticky fingers issue, precise control over the positioning of atoms required by Drexler also could not be achieved with the known chemical operations since the atoms of the manipulating arms can always interact with other atoms. Finally, an epistemological analysis of this debate in the history of nanotechnology reveals that there is, in fact, a profound incommensurability between these two projects. This incommensurability occurs in relation to the concepts that are employed, the theoretical principles, for those proposed by Drexler derive from quantum physics while Smalley's concepts are bound to experimental chemistry, and also to the intended experimental goals and the proposed methods. Nevertheless, despite this incommensurability, both programs share the same scientific instruments, maybe the only possible means of communication between these two scientific, but also philosophical approaches to nanotechnology (Bueno 2004).

Beginning in the 1990s, nanotechnology started becoming part of research programs in North American and European universities. But it was in the USA that this new domain of scientific research started getting an industrial and commercial influence, above all, with the creation of the National Nanotechnology Initiative by the federal government[7]. For the historiography of nanotechnology it is pertinent to observe that Drexler became critical of the initiatives of the NNI. His objections related not only to the research programs supported by the agency, which privileged, above all, synthetic chemistry and the emergence of new material properties, but also the abandonment of Feynman's revolutionary scientific goals in favor of a solely economical and commercial orientation for research in nanotechnology (Laurent 2010, 31). In the beginning of the 21st century, other industrialized countries also implemented incentive systems for the research and application of nanotechnology products. Since then, the production of nanostructures can be observed, be it in the form of reducing existing dimensions, or by way of the formation of new molecular arrangements, with the goal of creating chemical, biological and physical effects that are applicable to industrial and technological activities.

In this context, we witnessed the emergence of a new domain of chemical investigation: nanochemistry. The synthesis of nanostructures and nanomaterials by means of using supramolecular and biomimetic materials which make bottom-up nanostructured materials emerge constitutes the pillars of nanochemistry. It presents two important aspects: One of these is associated with gaining insight into peculiarities of chemical properties and the reactivity of nanostructured particles, which feeds the research in this domain of chemistry. Another aspect, connected to nanotechnology, consists of applying nanochemistry to the synthesis, modification, and stabilization of individual nanoparticles and also for their directed self-assembling to give more complex nanostructures (Sergeev and Klabunde 2013).

The properties of chemical substances depend on the size of the entities considered. The dependence of chemical activity in relation to the size of reagent particles is characterized by the fact that the properties of atoms and molecular aggregates (< 1nm) and nanoparticles (1-100nm) differ considerably from microparticles (> 100 nm) commonly present in laboratory samples. Besides chemists, this difference in properties due to the size also draws the attention of great philosophers of chemistry, in particular those dedicated to the study of the *emergentism* of chemical entities. Despite the varied emergentist theories, one concept prevails, that is, that the properties of a determined level of materiality, although derived from an inferior degree, are exclusive to this level. Some philosophers of chemistry support that the process of emergence for nanochemical entities differs from those of macrochemical entities, since, while the former would be ruled by quantum mechanics, the latter would follow the laws of classical thermodynamics, which would make these entities ontologically distinct (Zambon and Córdoba 2021). These important discussions give rise to reflections about the ontology of chemical entities itself.

Above we have seen some properties and the large number of applications of titanium dioxide in its natural modes of existence, whose diameter of entities is between 200 and 300nm. But could the applications of this material not be expanded if it were possible to structure them in a nanometric form? The synthesis of the first TiO_2 nanotubes was obtained in 1996 by chemist Patrick Hoyer through a process of electrochemical deposition in a porous aluminum oxide mold. These titanium dioxide nanotubes had an internal diameter between 70 and 100nm and were excellent semiconductors (Hoyer 1996). Curiously, the small dimension of nanoparticles greatly increases the relationship between the available surface area for physical-chemical activity and the volume of the material. Because the properties of titanium dioxide are mainly associated with the available crystalline surface, the investigations of its nanostructured forms then started attracting great interest from both scholars and industrialists.

[7] https://www.nano.gov/about-nni. The creation of this research agency and its development in the year 2000 by president Bill Clinton is a result of, above all, the efforts of Mihail Roco, its first director, who had coordinated the report on "Nanotechnology Research Directions" in 1999 (Roco 1999).

TiO_2 nanoparticles have been studied with the intention of knowing its mechanical and chemical properties, its effective biological and chemical inertia, its optical effects, and its resistance to corrosion. Nanocrystalline TiO_2 exists, mainly, in three polymorphs, which include rutile, anatase and brookite, and which depend on the conditions of production and thermal treatment after its production. The research indicates that TiO_2 nanoparticles could have a wide range of applications, which include nanomedicine, nanobiotechnology, solar and electrochemical cells, wastewater treatment, the food industry, soil recovery, gas detection, cosmetics, plastics, paints, paper production, production and storage of hydrogen fuel, antiseptic and antibacterial compounds, self cleaning devices, as well as many others yet to be discovered (Wu and Ren 2020).

The production of these nanoparticles can happen through a variety of experimental methods and its cost is relatively low. According to the method used (Vapor Deposition, Solvothermal Method, Electrochemical Approaches, Solution Combustion, Microemulsions Method), different variations of sizes and shapes of TiO_2NS are obtained, and may present particular biological and physical-chemical properties (Khataee and Mansoori 2012, ch. 3). It seems that here we have an interesting example of the primacy of experimental over theoretical, as mentioned by Ian Hacking, for it must be admitted that the reality of entities is related to experimental devices that act as a *cause* producing certain phenomena (Hacking 1983).

However, several studies have been revealing something fundamental: that in the nanometric scale new material priorities have important consequences and unexpected obstacles in their thermodynamics and their reactivity. "The properties of these new nanoparticles and nanostructures are still, in great part, unknown [...] (for example: the highly reactive surface of nanoparticles; its ability to go through membranes) and can be associated to a potentially high level of toxicity" (Riechman 2009, 267). In other words, the euphoria caused by the wonderful properties of TiO_2NS should not conceal the other side of this coin, which is: it can induce severe toxicity. These nanoparticles can be introduced in the human body through a number of different manners, including airways, the digestive, intravenous and dermal systems. Through these ways, they can easily interact with biological systems, they can also accumulate in the body over long periods of time (Dar *et. al*. 2020).

In pharmacology, for instance, nanoparticles must transport assorted substances to tissues and cells, minimizing toxic effect and increasing therapeutic efficacy. However, the interaction between substances in the organism is important for planning the drug, because, as with every medication, it can become a harmful agent, altering or destroying vital functions. From the point of view of nanoparticle inhalation, for example, there is great concern, after all, the smaller the particle, the easier it will break the barriers of our respiratory system, accumulating in the pulmonary alveolus and compromising our respiratory capacity. Once deposited in the pulmonary epithelial cells, differently from larger particles, they can migrate and reach other organs. Asthma appears here, as a disease directly linked to the inhalation of these micro particles, beside bronchitis, emphysema, and lung cancer. A 2007 study presents as well the intrinsic relationship between TiO_2 particles in the order of 10nm and significant pulmonary inflammation (Suzuki 2007).

Another area that has been growing exponentially is that of nanocosmetics, which utilizes nanotechnology to carry nanostructured active ingredients, with the clear intention of optimizing the properties and performance of the substances, when compared to the conventional ones. But TiO_2 nanoparticles used for protection against UV rays can present toxic effects such as morphological alterations, apoptosis (programmed cell death), and mitochondrial dysfunction (Zhang 2011). Besides, these nanoparticles will be fatally released in natural water environments presenting potential risks for the living organisms within these ecosystems, creating the urgent need to evaluate and understand the subsequent ecological damages (He and Hwang 2014).

This detrimental side of nanotechnology can become a great social and environmental problem, especially due to the lack of investment in investigation into its possible harmful effects. For instance, a 2006 research article points out that of the nine billion dollars spent annually worldwide with studies in nanotechnology, only between 15 and 40 million dollars are allocated to research about its risks, toxicity, safety, health effects, etc. This means that only one in every 300 dollars is spent with research related to precaution with regard to this new technoscience (Riechman 2009). Finally, it is fundamental to keep in mind that a medication, dye, capsule, cleaning agent, is always a complex object and cannot be reduced to merely a chemical substance, with certain physical chemical properties only, for it is, above all, a relational object, that is, technical, economical, social and political.

Nanostructured TiO_2 and GMOs: An Analogy about the Management of Technoscience Products

Above, we pointed out the exponential increase in the interest and research in the area of nanotechnology in general and nanochemistry in particular, and, as a direct consequence, a considerable increase of innovative products in important areas such as nanomedicine, nanocosmetics and nanopharmacology. However, as we saw in the case of titanium dioxide, the properties of many of these new nanoparticles and nanostructures are still largely unknown if we think of their highly reactive surfaces, as well as their ability to go through membranes. That means, as recent studies show, that nanoparticles can be easily absorbed by the human body, be it through circulation, inhalation or through the skin. On the other hand, regulatory measures are not following the development of said research. Well, that is, above all, an ethical problem similar, in fact, to the one that happens with genetically modified organisms (GMOs).

One of the main problems of an epistemological nature involving GMOs is based on the discussion about the scientificity or not of the so-called concept of substantial equivalence, frequently presented in opposition to the ethical precautionary principle. The concept of substantial equivalence has its history beginning in 1993, when it was first introduced by the Organization for Economic Co-operation and Development. Broadly speaking, according to the reports, this principle must include the following aspects: 1) evaluation of the new food source at a molecular level; 2) comparison of phenotypic characteristics of the genetically modified plant to a conventional plant; 3) composition analysis — that is, an analytical comparison — of the genetically modified plant and its derivatives and the composition of traditional analogs (FAO/WHO, 1996). Thus, based on this principle, if a genetically modified organism has a chemical composition equivalent to the traditional one, both would be safe. Well, what does it mean to be equivalent? The strange thing is that genetic modification has as its main objective the "introduction of new characteristics in the respective organism" and, thus, the outcome will necessarily result in a different composition of the initial genes and proteins. In fact, this is the reason why the organism can be patented, because it is different from its natural variety. The proposed equivalence refers to the chemical and molecular composition between the natural and the modified products. But the GMOs are and were synthesized with the clear objective of being distinct, different from their products of origin. Countless studies, then, show the difficulty in operating with the concept of substantial equivalence, due to its lack of scientificity, a lack that was pointed out in 1999 by *Nature*[8]. The core issue in the epistemic and scientific limit of

[8] "Substantial equivalence is a pseudo-scientific concept because it is a commercial and political judgement masquerading as if it were scientific. It is, moreover, inherently anti-scientific because it was created primarily to provide an excuse for not requiring biochemical or toxicological tests. It therefore serves to discourage and inhibit potentially informative scientific research", (Millstone et al., 1999).

such concept is that, however effective the chemical analysis (the comparison of the phenotypic characteristics, molecular level evaluation and analytical comparison), they are not able to reveal, as it is beyond of chemical and microscopic experimental apprehension, the presence of toxic components or unknown allergens.

And here we reach an important point in our discussion. The epistemic problem of the concept of substantial equivalence finds itself precisely in its limitation to reductive analysis parameters, not taking into consideration the necessary plurality of strategies, such as the ones of a biochemical, pharmacological and even biological nature. Nowadays, by distancing itself from deterministic and reductive modern science, contemporary chemistry must take into consideration the important interaction between genes and the lives of organisms, that is, take into consideration qualitative aspects of the analyzed structures, approaching "gene ecology", namely, research in which the regulation of metabolic function of organisms is in direct relationship with the wide network of interdependent genomic sequences, interacting, moreover, with environmental factors. This is necessary because the proposed chemical analyses cannot, by themselves, relate the possible effects of a biochemical, toxicological and immunological nature in genetically modified food, because, as we saw, they only take into consideration analyses of chemical, molecular and analytic composition of GMOs. Thus, the sought equivalence refers more specifically to quantity, or something measurable that can be technically compared. In comparative terms, the genomes of a natural plant and of a genetically modified organism are not equivalent. They would only be equivalent if one had originated from the other by means of vegetative reproduction. By the techniques used, genetic construction inserted in the plant has distinct elements from those found in the original plant, which can provide new gene products, which in turn can trigger serious pleiotropic effects. The challenge presented is in understanding the influences of cellular organization and macromolecular associations over the function of individual enzymes and other biomolecules (Zaterka and Mocellin 2022, ch. 5).

Something similar, as we saw, occurs with research in the area of nanotechnology, or yet, with the lack of research, after all, scientists postulate in a quick manner and without due public responsibility that natural substances and the ones that are nanoproduced possess equivalent properties. However, nanostructured titanium dioxide was built with the goal of acquiring new properties, after all, its microscopic size favors a small number of atoms and, therefore, electrons. These electrons in a nanoscale act in a manner that is very different from the traditional one, because here, they do not possess mobility, they are 'confined' to the material, following the model of quantum theory. These characteristics provide optical, electrical, transportation, and electromagnetic properties that are completely distinct, and can result in, as emphasized above, important pharmacological and toxicological issues. Therewith, we can clearly observe distinct modes of existence, with capillarizations and, therefore, unique biographies.

Different from conventional ones, nanoparticles have a larger potentiality for biological interactions. For instance, if nanotechnological medications can favorably act on targets with more precision and efficacy, on the other hand, the same properties make reaching places that were unthinkable before by conventional products. In this sense, more research in relation to the possible effects in the areas of toxicity, stability, dosage and efficacy is clearly necessary. For example, a 2008 study shows that the ingestion of nanosilver, which possesses physical, chemical, and biological characteristics that are considerably uncommon when compared to silver in a macro scale, was linked to argyria, a disease which causes irreversible skin darkening, besides pro-inflammatory lung effects (Chen 2008).

As the use of nanomaterials, from an economic standpoint, proves itself a promising strategy, the manufacturing of these products is increasing, which will result in a growing appearance of nanomaterials in air, water, soil and organisms (Mueller and Nowack 2008). This environmental issue related to the application of nanotechnology makes it necessary to pay more attention to the industry, which is largely responsible for a wide range of environmental impacts due to the inadequate use of its materials and the improper disposal of residues, assuring the guarantee of development and compliance with sustainability tools and minimizing potential impacts that nanoparticles are capable of causing, due to being microscopic and carrying chemical substances with higher efficacy, able to generate high degrees of toxicology. The applicability of nanobiotechnology in several areas requires a deeper investigation, as it alters the biological environment, possesses greater accessibility to permeate physiological barriers, and the physical-chemical properties of these new reagents are more complex, becoming more challenging than conventional products (Florence 2012; Muthu 2010).

This discussion allows us to emphasize the use of the precautionary principle (PP) in these kinds of analysis, where risk, indeterminacy and uncertainty appear, connected to nearly non-existing regulation. When researchers do not have conditions of making definitive judgments about the potential risks, "the precautionary principle recommends taking special precautions and, depending on the way appropriate research about risks is conducted, postponing final decisions about, and under which conditions, implementing innovation effectively" (Lacey 2006). Incorporated, since 2005, to the French constitution by means of the Charter for the Environment, the PP affirms that: "When the occurrence of any damage, albeit unpredictable in the current state of scientific knowledge, may seriously and irreversibly harm the environment, public authorities shall, with due respect for the precautionary principle and the areas within their jurisdiction, ensure the implementation of procedures for risk assessment and the adoption of temporary measures commensurate with the risk involved in order to preclude the occurrence of such damage" (*Charte de l'Environnement* 2004).

The precautionary principle introduces a fundamental perspective in the application of science, which consists of rejecting incomplete studies based on insufficient or inconclusive reports. This seems to be the case, as no rigorous methodologies that can establish the real differences between the properties found on a macro scale and on a nanoscale exist yet. Many of the nanochemical particles can involve new interactions, new modes of absorption and a capillarization capacity that are unique and, because of that, result in complex environments where unexpected new properties can emerge.

The philosophy of chemistry, by working with the autonomy of chemical entities, points to the complex interactions of molecules with their means. In this sense, we can better map out and diagnose the modes of existence of these substances and their consequences for humans and the planet. By handling this 'molecular ecology', we can never forget about Hans Jonas' Imperative of Responsibility and thus take into consideration the principle of responsibility, besides the precautionary principle. Obviously, this does not mean immobilizing the progress of humanity, science, or the economy, but on the contrary, proposing durability of the quality of life for human generations and all existing nature on the planet. After all, is that not why our first humanists established modern science?

Conclusion

Materials have histories, and humanity's history is intrinsically connected to them. Our goal in this article was to approach some biographical aspects of metallic titanium and titanium dioxide. Although multidisciplinary, our investigation also pointed out some issues that are particular to the philosophy of chemistry, the history of technoscience and nanotechnology brought on by the different modes of existence of titanium dioxide. The historiography of some of the modes of existence we have evoked reveals that the materials are not only a set of physical and chemical properties but also a social existence and a hybrid cognitive identity. In fact, the existence of titanium dioxide, both natural and in its nanostructured forms, means more than its discovery or its invention, for they only become possible because of society's demands. We emphasized that these demands are accompanied by industrial, economic, cultural, and environmental, but also philosophical and historiographical implications, which allow us to point to the need for multiple and permanent investigations about these modes of existence to serve as a reference for decision-making processes for governments, industries and civil societies.

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