Catalytic coatings – functional coatings

Introduction : functional coatings based on sol-gel technologies

"Functional coatings" are systems which possess an additional functionality besides the classical properties of a coating (i.e., decoration and protection),. In recent years, companies were very active in the development and commercialization of coatings with additional properties like, for example, self-cleaning, easy-to-clean (anti-graffiti), antifouling, soft feel or antibacterial. Various mechanisms are used to add these new functionalities. In general, the additional functionalities take place in three distinct zones: 1) at the film-substrate interfaces (anticorrosive coatings), 2) in the bulk of the film (intumescent coating) or 3) at air-film interfaces (antibacterial or self-cleaning). Based on their functional properties, functional coatings are classified in different categories (see Figure 1).[1]

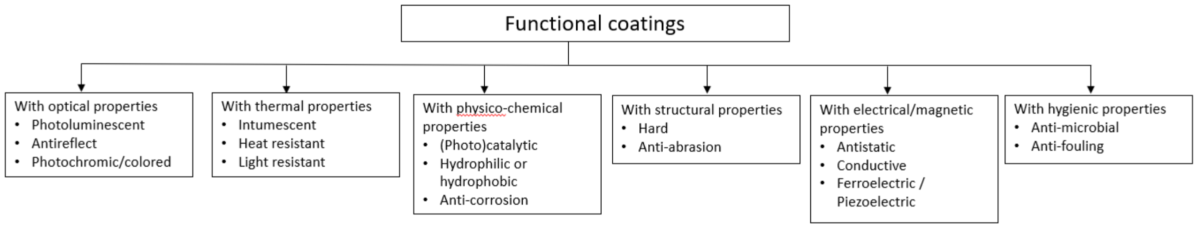

Figure 1 : Classification of functional coatings

The field is extremely broad and new functional coatings are continuously developed. This paper will focus on inventions and patents on coatings with physico-chemical and hygienic properties such as (photo)catalytic coatings and anti-microbial /anti-fouling solutions using the sol-gel production process. The goal is to highlight inventions which bring new functionalities using ceramic-like coatings or a liquid based process at low temperature to improve a production process or a cleaning procedure in an industrial environment.

The sol-gel technology

The sol-gel process is an inorganic polymerization of solute molecular precursors to form glass- or ceramic-like coatings at low temperature. It produces oxides in various forms (ceramic-like coatings, very low density material, thin films…). This fabrication process is inspired by diatoms, microalgae that can be anywhere in nature as long as there is some degree of moisture. These micro-organisms can synthesize their silica shell at room temperature by using dissolved silica from their environment. The mild conditions associated with these bio-inspired syntheses allow the formation of organic-inorganic hybrid nanocomposites in which both organic and inorganic phases are

[1] Functional Coatings and Microencapsulation: A General Perspective, Swapan Kumar Ghosh, 2006 WILEY-VCH, ISBN 3-527-31296-X

mixed at a molecular level. Even fragile bio-species such as enzymes, yeasts or whole cells can be trapped within the solid network.[2]

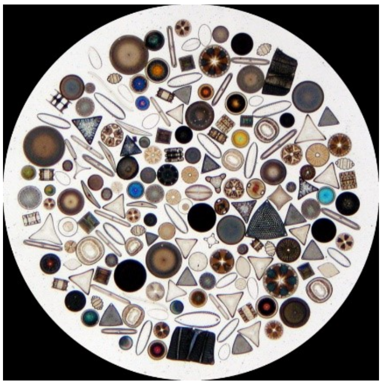

Figure 2 : Marine diatoms[3]

In summary, the sol-gel process consists in the creation of an oxide network through chemical reactions in a tri-dimensional lattice, which creates a gel, from a solution with alkoxides and inorganic atoms like Si, Ti, Zr …Finally, drying the film through an evaporation process creates a vitrified thin film. The entire process takes place at low temperature with a deposition process as easy as dip coating, spray coating... [4,5]

Applications of functional coatings

Process intensification and safety, which aim at reducing working volume with similar or increased performance, are a key area for of chemical reaction engineering. Structured reactors and catalysts are thus gaining importance each year, especially with the development of the microreactor technology. Many chemical applications for the industry require catalytically active components. The use of catalytic coatings with large surface area deposited on microreactors walls is an efficient solution to get efficient mass and/or heat transfer while keeping pressure loss low, as generally observed with micro-packed beds of powder catalysts. Various coating preparation methods exist such as sol-gel, chemical vapor deposition, anodic oxidation…[6].

Patents using sol gel processes

An overview of recent patents in this domain can be found in the Appendix. Here, we highlight some of the most interesting ones:

Christophe Remy from Corning Inc.[7] has filed a patent describing the manufacture of a microstructure for chemical processing. The microstructure is composed of microchannel walls defining at least one microchannel for accommodating chemicals to be processed. On the walls, an active element is disposed using a catalyst support

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[2] S. Cassaignon et al. *"From living light to living materials"*, Materials Today: Proceedings 1S (2014) 209 – 215 Diatoms are among the most important and prolific microscopic sea organisms and serve directly or indirectly as food for many animals - https://www.britannica.com/science/diatom

[3] https://en.wikipedia.org/wiki/Diatom

[4] http://www.critt-mdts.com/Site_hybriprotech/images/documentations/05-CERTECH.pdf

[5] F. Collignon - Cahier technologique Sol-Gel du Certech - http://docplayer.fr/10621637-Cahier-technologique-sol-gel.html - Technological watch sol-gel Certech

[6] L.N. Protasova *et al.* Recent Patents on Chemical Engineering, 2012, 5, 28-44

[7] C Remy, Coated microstructures and methods of coating - US20050170142A1

powder and a sol-gel binder. The deposition process is performed by filling these microchannels with the sol-gel, then by removing it to leave a layer on the microchannels walls. The sol-gel is then cured at a specified temperature during a fixed time. These parameters depend on the sol-gel formulation used. The coated micro-channels significantly improve the reaction rate. Hence, in addition to the lack of drop in internal pressure observed with packed-bed, the coated micro-channels provide homogeneity of fluid flow and temperature which eliminate "hot-spots". The small size of the channel also provides greater control over variables such as temperature control and flow rates. Moreover, the gas/liquid, liquid/liquid and liquid/solid mass transfer coefficient can be greatly enhanced due to the flow regime control provided inside the narrow reaction channel. A few examples:

A durable alumina coating was deposited on the interior channel walls of a glass microreactor. This coating was performed using aluminum isopropoxide with nitric acid and high-surface-area alumina powder to produce a coating slurry for application to the microchannel walls. To form the alumina coating, the microreactor channels were filled with the alumina slurry and then drained using, for example, forced air circulation. The residual coating layer was then dried and cured by heating the microreactor and coating to a temperature of about 450 °C. The filling, draining, drying and curing steps were then repeated to deposit two additional coating layers onto the walls of the channels. The author presented similar process examples for Pt catalyst or NiO catalyst on alumina coating glass microreactor or coatings incorporating molecular sieve, such as zeolites, for the acceleration or control of selected catalytic reactions.

Functional sol-gel coatings also allow the deposition of an inert coating transparent to UV light. It allows the use of a photoactive catalyst to develop coatings with air or water decontaminating properties. This type of invention was developed by Karl Gross et al. at Sandia with air or water treatment using reactions initiated with UV light.[8] This technology is useful for sanitization processes which entail microbial destruction and total organic reduction. Various oxides have been tested and TiO_2 was shown to exhibit the highest photocatalytic activities to efficiently kill viruses, bacteria, fungi and algae. Within this patent, the photoactive catalyst is supported by an inert substrate matrix transparent to UV light which can be formed using sol-gel process. This later process can also be used to synthetize TiO_2 particles with mean diameters below 100nm, this reduced size enhances the photocatalytic performance. It is also known that oxide mixtures which incorporate aluminum oxide are much more dispersible in water or organic solutions making them amenable to coating surfaces by wetting and evaporation. Finally, commonly owned U.S. Pat. No. 6,188,812, herein incorporated by reference, describes a process for coating optical fibers with thin layers of a sol-gel.

Within their patent, D. Jackson et al. from Milliken & Co, developed sol-gel based films coating with durable antimicrobial properties.[9] This invention provide a low-temperature deposition method to obtain a durable coating on hard surface substrate with excellent and durable antimicrobial activity using silver-based ion-exchange

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[8] K. Gross et al., Method and apparatus for decontaminating water or air by a photolytic and photocatalytic reaction - US20030211022 A1 – 2003

[9] D. Jackson at al. Antimicrobial sol-gel films comprising specific metal-containing antimicrobial agents - US20030118624A1 - 2003

compound, oxide or zeolite compound. Especially, it provides antimicrobial films that retains a high degree of activity in presence of highly caustic solvents without any aesthetically displeasing discoloration over time. Using sol-gel processes to produce a film with a three-dimensional network of high strength. The preparation process allows the use of small colloidal particles, in the order of one nanometer or less, as glass precursors, thereby ensuring a high degree of homogeneity and purity in the final film product. The desired antimicrobial component is added as particles or powder. After mixing, the mixture can be applied through a standard procedure like dip coating, spraying … The film is then heated to generate the desired film. As example, the thin film can be produced using silica oxide, alumina oxide, titania oxide or zirconia oxide and by adding, within sol initial solution to prepare the gel, either silver oxide, RC 500, ION-PURE ®, silver sulfadiazine or ZEOMIC ® to add the antimicrobial properties. After production, such film-coated substrate were tested for antimicrobial activity using the plate-contact method to calculate the log kill rate after 22h exposure test of Klebsiella pneunomiae.

Conclusions

Sol-gel processes provide a new range of coatings bringing functionalities like excellent abrasion resistance and inertness to a surface. The liquid-based process allows to work at low temperature which broadens the range of possible substrates. In addition, the homogeneous mix of the precursors at molecular level allows for a fine distribution of the active material within the matrix. Combined with organic precursors, this innovative technology can generate an extremely large combination of possibilities to functionalizes surfaces within the coming years.