



The William Blum Lectures

#54 – Per Møller – 2017

The 54th William Blum Lecture
Presented at NASF SUR/FIN 2018
in Cleveland, Ohio
June 4, 2018

Innovative Applications of Electroplating and PVD for New Material Solutions

by
Dr. Lars Pleth Nielsen
for
Dr. Per Møller
Recipient of the 2017 William Blum
NASF Scientific Achievement Award





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Editor's Note: The following is the Powerpoint presentation for Dr. Møller's William Blum Memorial Lecture at SUR/FIN 2018, in Cleveland, Ohio on June 4, 2018. Due to Dr. Møller's serious illness, he was unable to make the journey to SUR/FIN. In his stead, his longtime professional colleague, Dr. Lars Pleth Nielsen, of the Danish Technological Institute (DTI), presented the lecture.

William Blum Scientific Achievement Award

Innovative applications of electroplating and PVD for new material solutions

*Prof. Per Møller,
Technical University of Denmark (DTU)*

and

*Dr. Lars Pleth Nielsen,
Danish Technological Institute (DTI)*



Slide 1 - Title.

Introductory material

There was great concern about the outlook for Dr. Møller's health, and Dr. Nielsen began the lecture by reporting on his current status (Slide 2). While the matter was very serious, the good news was that a stem cell donor had been found and the prognosis was good.

William Blum Lecture



Prof. Per Møller sends his regards

Per is temporary grounded and unable to present his William Blum Lecture

- Diagnosed with MDS special sub-group of bone marrow cancer
 - Low red blood cells, low platelets and low white blood cells
- Treatment will include chemotherapy and stem cell transplantation.
- The good news – a donor with optimal match has been identified.
- Per is currently being prepared for stem cell transplantation.
- The overall prognosis is good.

Slide 2 - Dr. Møller's health status.

Dr. Nielsen also shared some of the published news items, both here and in Denmark, that covered the good news that Dr. Møller had received the Scientific Achievement Award for 2017 (Slides 3-4).

William Blum Scientific Achievement Award

TEKNOLOGIPRIS

Professor **Per Møller**, Institut for Mekanisk Teknologi på DTU, har modtaget William Blum's Scientific Achievement Award.

Den prestigefulde pris uddes af NASF, som er den amerikanske brancheorganisation for overfladeteknologi (National Association for Surface Finishing).

Prisen gives til en person, hvis tekniske og praktiske brydende forskning og teknologiske fremskridt har bidraget til udviklingen af overfladeteknologi.



med åbningsceremonien på den amerikanske SURFIN-2017-konference i Atlanta, Georgia.

Det er kun ganske få forskere uden for USA, der har modtaget prisen, og professor Per Møller sætter med prisen dansk forskning og udvikling inden for avanceret overfladeteknologi på verdenskortet.

Som begrundelse for tildeling af prisen nævnte et enigt udvalg, at professor Per Møller gennem mange års virke har bidraget internationalt og ikke mindst gennem udgivelsen af 'Applied Surface Technology' til det

intertwined world of applied surface engineering".

NASF udtaler bl.a. om bogen, der er blevet til i tæt samarbejde med Lars Pleth Nielsen, Teknologisk Institut: »Det er det største og mest betydningsfulde værk skrevet inden for overfladeteknologi de sidste 40 år.

Med den ærefulde pris følger bla. William Blum Memorial Award for Per Møller sine forskning og udvikling inden for overfladeteknologi på DTU i 2018.



Slide 3 - Plaudits on the Award (1).

William Blum Lecture



SCIENTIFIC ACHIEVEMENT AWARD

DR. PER MØLLER, TECHNICAL UNIVERSITY OF DENMARK

The Scientific Achievement Award recognizes a person who has contributed to the advancement of the theory and practice of electroplating, metal finishing and the allied arts; raised the quality of processes and products; enhanced the dignity and status of the profession; or has been involved in a combination of these efforts. The first recipient of this award was Dr. William Blum, Sr., who was instrumental in the establishment of fundamental research in the Society.



This year, we were very pleased to recognize Dr. Per Møller for this prestigious award. His accomplishments in the technology of surface finishing and his contributions to our industry are both wide and in depth. Most notably, he has contributed the modern "bible" of our industry, the two-volume Advances in Surface Technology, as important to the engineer today as Blum and Hogaboom's Principles of Electroplating and Electroforming was in the 1930's.

- Highlighted:
 - Contributions to surface finishing
 - Contributions to industry are both wide and in depth
 - The two-volume Advanced Surface Technology known as the surface "bible"

I will do my very best to exemplify and underline these points

Slide 4 - Plaudits on the Award (2).

Dr. Nielsen was the perfect person to deliver the lecture in Dr. Møller's stead. The two are a very close team, and have collaborated on numerous research projects, and have published numerous papers and books together (Slide 5).

William Blum Lecture

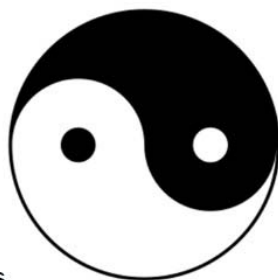


- I have known Per for more than 15 years
- We have worked extremely close together and initiated numerous projects
 - Commercial projects
 - R&D projects
- Written several books together
- Right now we are writing on a corrosion book
- We are going into energy: H₂, CH₄ upgrading, biogas cleaning, CH₃OH synthesis

"If you can't afford the "professor" you can always get the "doctor"...."



Chemist
Wet based coatings



Physicist
Vacuum based coatings

Slide 5 - Long-time collaborators Møller and Nielsen.

It was noted that Dr. Møller was dedicated to the surface finishing field, his mind constantly on the lookout for examples of metal finishing performance in the field. At SUR/FIN 2015 in Rosemont, Illinois, Dr. Nielsen pointed out that the many attractions in the Chicago area (Slide 6), were superseded by Dr. Møller's interest in examining the corrosion performance of street hardware in the city (Slide 7).

Surfin 2015, Chicago



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Stephens Convention Center, Rosemont, IL, USA

Slide 6 - Tourist activities in Chicago.

Surfin 2015, Chicago



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Stephens Convention Center, Rosemont, IL, USA

Slide 7 - Dr. Møller's activities in Chicago.

Dr. Nielsen outlined the lecture (Slide 8), which was in essence a career retrospective of the work of this very talented man. He began the lecture by noting that “surfaces are everything,” noting that surfaces, through control of their properties, are essential to everything in our world, from the scientific technologies to mundane everyday products (Slide 9). The emphasis of the talk related to current efforts in sustainable energy made possible by electrochemical technology.

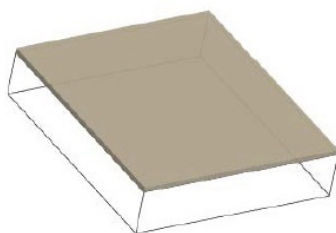
William Blum Lecture



- Examples of Per Møller’s patent portfolio
 - Some highlights
- Examples of books
 - Advanced Surface Technology
 - Our upcoming corrosion book
- Energy
 - Hydrogen - from lab to large-scale
 - Biogas - Upgrading CO₂ to CH₄
 - Ideas on methanol
- Self-cleaning paints
- Antibacterial surfaces
- Summarizing

Slide 8 - Blum Lecture outline.

Surfaces are everything



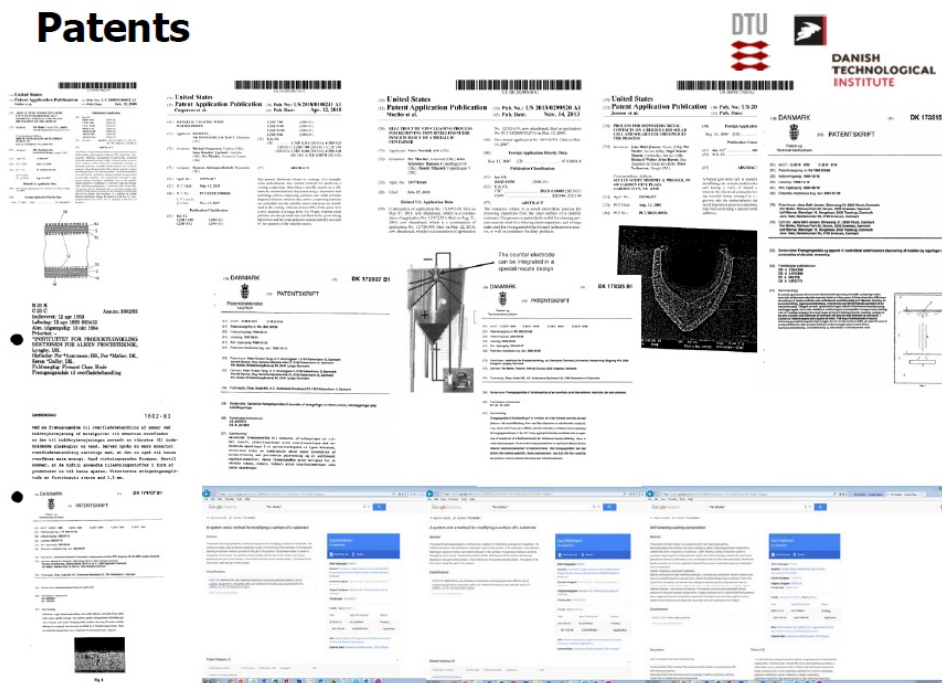
Wear resistance
 Tribological properties
 Magnetic properties
 Electrical conductivity
 Solderability/weldability
 Hardness
 High temperature resistance
 Corrosive resistance
 Biocompatibility
 Hydrophobic/hydrophilic properties
 Catalytic properties
 Self cleaning properties
 Friction properties
 Color and appearance
 Decorative appearance
 Refractive index
 Oxide formation/passivation

Slide 9 - Surfaces are everything.

Patents

Dr. Møller has been awarded numerous patents (Slides 10-15). In the patent portfolio, is a method for manufacturing implantable medical devices (Slide 11; US Patent 5,772,864 (1998)), by electroforming a prosthesis on a dissolvable mandrel. Another involves a process for electrodepositing copper wire contacts on silicon-based solar cells (Slide 12; with BP Solar; US Patent 6,881,671 (2005); European patent appl.). Another patent cites a unique slip ring, using electrodeposited rhodium for wind turbines (Slides 13-14; Vestas Wind Systems; WO/2001/061795 (2001)). Dr. Møller was instrumental in the development of a process for producing stress-free nickel and cobalt electrodeposits (EP0835335B1) for Daimler Benz Aerospace. This was the key to the use of additive layer manufacturing (ALM) of the rocket engine for the Ariane Vulcan 2 (Slide 15).

Dr. Nielsen pointed out that years of experience with innovation have given Dr. Møller the ability to motivate students and collaboration partners to develop components and devices which create meaningful solutions instead of focusing on useless patents.



Slide 10 - Selection of Møller patents.



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US005772864A

United States Patent [19]
Møller et al.

[11] **Patent Number:** 5,772,864
[45] **Date of Patent:** Jun. 30, 1998

[54] **METHOD FOR MANUFACTURING
IMPLANTABLE MEDICAL DEVICES**

5,328,587 7/1994 Fenske 205/73
5,352,512 10/1994 Hoffman 428/311.51

[75] Inventors: **Per Møller, Lyngø; Jørgen
Kamstrup-Larsen, Allerød, both of
Denmark**

FOREIGN PATENT DOCUMENTS

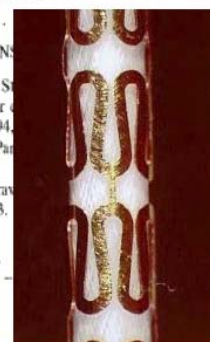
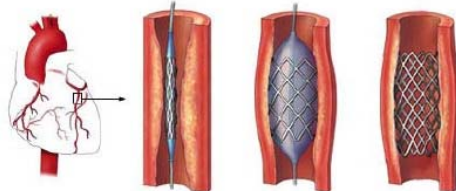
1542039 3/1979 United Kingdom

OTHER PUBLICATIONS

Traxcenter Course of Coronary S
Ruygrok and Claudia Sprenger
Netherlands, Dec. 15-17, 1994,
me for Metal Meromechanical Pat

wenheim, Electroplating, McGraw
k, 1978, pp. 426-441, 160-163.

Examiner—Bruce F. Bell
Examiner—William T. Leader



Slide 11 - Electroformed stents.



(19) **Europäisches Patentamt**
European Patent Office
Office européen des brevets

(11) **EP 1 182 709 A1**

(12) **EUROPEAN PATENT APPLICATION**

NHR139 20.0kV X1.50k 26.0um

(51) Int. Cl. 7: **H01L 31/0224, H01L 31/068,
H01L 31/18**

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(72) Inventors:

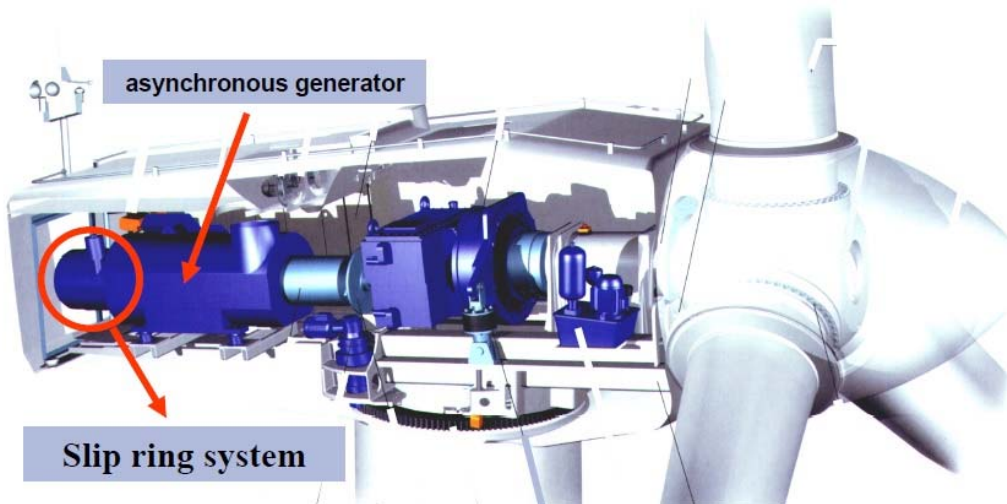
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- Møller, Per
3200 Esbjerg (DK)
- Rasmussen, Per
2800 Lyngby (DK)
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5222 BC 's Hertogenbosch (NL)

(74) Rasmussen, Per
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© 1998 The SMSS Federal "Promotion Program for PV" - TMC Consulting AG, CH-8007 München

Development of a process for depositing metal contacts on a buried grid solar cell and a solar cell obtained by the process. (2000) Patent application nr: EP 00610081.2-1235

Slide 12 - Deposited metal contacts and solar cells.



Slide 13 - Slip ring in wind turbine generator (1).

NATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY

Intellectual Property Organization
International Bureau

(10) International Publication Number
WO 01/61795 A1

MøLLER, Per (DK/DK); 20, Rishave Park, DK-3230 Grøsted (DK).

(74) Agent: CHAS. HUDE A/S; 33, H.C. Andersens Boulevard, DK-1780 Copenhagen V (DK).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, EE, EG, ES, FI, FR, GB, GR, GT, HK, HU, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, SV, TH, TJ, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(54) Title: ELECTRICAL MACHINE

(57) Abstract: Electrical machine comprising a rotor and a stator, the rotor being provided with a plurality of slip rings being provided with a hard coating having a low sputter coefficient. The rotor surface structure is reduced as a result of the material of the slip rings being provided with a hard coating. This means that the surface structure is reduced as a result of the material of the slip rings being provided with a hard coating.

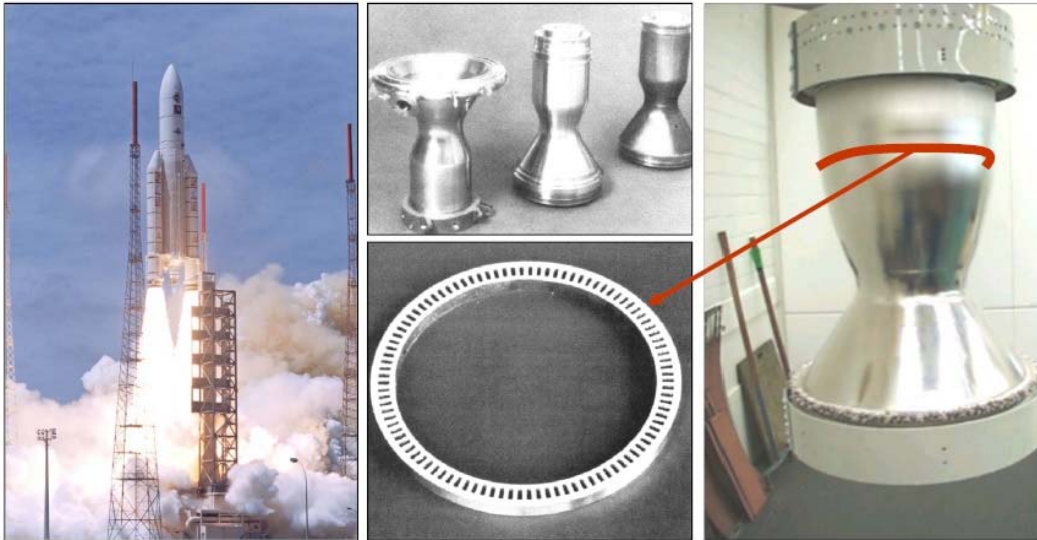
Rh-C Phase Diagram

Weight Percent Carbon

Atomic Percent Carbon

Slide 14 - Slip ring in wind turbine generator (2).

Patents; Space (Ariane)



Electroplating production method, EP 0835335B1

Slide 15 - Additive layer manufacturing for a rocket engine.

Published Books

Examples of books



Slide 16

Dr. Møller has published many papers and a number of books during his career, but the most significant one was published in 2013. Co-authored with Dr. Nielsen, the two-volume, 1240-page *Advanced Surface Technology* was lauded as the most comprehensive text on surface engineering technology published to date (Slides 17-19). Currently in development is another text which promises to be as important as *Advanced Surface Technology* - a new book on corrosion, *Understanding Corrosion from an Applied Perspective* (Slide 20). In addition to the information shown in Slide 20, for the chapter on corrosion types, topics will include (a) introductory material; (b) thermodynamics and the equilibrium potential; (c) corrosion potential, polarization and Pourbaix diagrams and (d) optimal material and surface selection for corrosion protection.

Advanced Surface Technology



2 volumes – 1240 pages

It took us 4 years to write...

Slide 17 - *Advanced Surface Technology* (1); Covers.

Advanced Surface Technology



“It is truly a **surface bible**,” VOM, association for surface finishing techniques, Belgium

“The present two-volume set of *Advanced Surface Technology* is arguably the **most comprehensive** ever to be published in the field of surface finishing. Drs. Per Møller and Lars Pleth Nielsen have devoted years of effort to provide, in their words, ‘a holistic view on the extensive and intertwined world of applied surface engineering,’ NASF, National Association for Surface Finishing, USA.

“The books are clear and the schematic setting makes the reading very pleasant and interesting even for those who are simply looking for up-to-date information and data..... the English language is not an obstacle to understanding. It is clear and linear. This **book should not miss among the technical manuals** of those who are interested in surfaces and their property. It’s definitely a good tool for those who work in technical offices or produce finishes or treatments on metals, as well as offices and, of course, included in the reference manuals, of whom teaches at the University or in Master Class dedicated to surfaces”, Enzo Strazzi, Association for Aluminum Surface Treatment, Aital Oxit, Italy.

Slide 18 - *Advanced Surface Technology* (2); Plaudits.

Advanced Surface Technology



- Wear and friction properties of surfaces
- Introduction to corrosion
- Basics of electrochemistry
- Introduction to chemical and electrochemical processes
- Guidelines for electrochemical deposits
- Electroplating of zinc
- Electroplating of nickel
- Electroplating of copper
- Electroplating of tin
- Electroplating of chromium
- Electroplating of precious metals
- Electroplating of alloys
- Electroless plating of metals
- Chemical and electrochemical polishing
- Conversion coatings
- Introduction to gas phase processes and plasma
- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD) Industrial PVD and CVD processes
- Ion-beam processes
- Thermochemistry and diffusion processes
- Hot-dip galvanizing
- Vitreous enamel
- Thermal spraying and hardfacing
- Mechanical plating
- Introduction to paint
- Classification of paints
- Special paints and special application methods
- Pre-treatment prior to painting
- Selection of paint systems
- Characterization of surfaces and materials
- Measuring hardness
- Measuring the “total visual appearance” of surfaces
- QC: Thickness and adhesion of coatings
- Corrosion evaluation and durability testing
- Thermodynamic consideration
- Pourbaix diagrams

Slide 19 - *Advanced Surface Technology* (3); Contents.

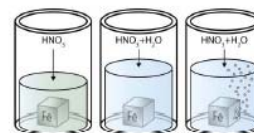
New Corrosion book



4. Corrosion types

- 4.1 Introduction to corrosion types
- 4.2 Even or uniform corrosion
- 4.3 Galvanic corrosion
 - 4.3.1 Factors influencing galvanic corrosion
- 4.4 Selective corrosion
- 4.5 Localized corrosion
 - 4.5.1 Crevice corrosion
 - 4.5.2 Pitting corrosion
 - 4.5.3 Filiform corrosion
- 4.6 Cover corrosion
- 4.7 Stray current corrosion
- 4.8 Corrosive wear
 - 4.8.1 Abrasive wear
 - 4.8.2 Adhesive wear
 - 4.8.3 Erosive wear
 - 4.8.4 Fretting wear
 - 4.8.5 Evaluating corrosive wear
- 4.9 Thermogalvanic corrosion
- 4.10 Intergranular corrosion
- 4.11 Environmentally assisted cracking (EAC)
 - 4.11.1 Stress corrosion cracking (SCC)
 - 4.11.2 Hydrogen embrittlement (HE)
 - 4.11.3 Sulfide stress cracking (SSC)
 - 4.11.4 Corrosion Fatigue (CF)
 - 4.11.5 Liquid metal embrittlement (LME)
- 4.12 Photo corrosion

UNDERSTANDING CORROSION



Understanding corrosion from an applied perspective

Theory and praxis

by Per Møller & Lars Pihl Nielsen

M&N

Slide 20 - New Corrosion book, *Understanding Corrosion from an Applied Perspective*.

Methane gas storage for renewable energy (MeGa-StoRE)

Sustainable energy is a hallmark of the power profile in Denmark. Dr. Møller's work in this area has contributed to a program called MeGa-StoRE (Slide 21), where wind energy is converted to methane gas and stored in the country's natural gas grid.

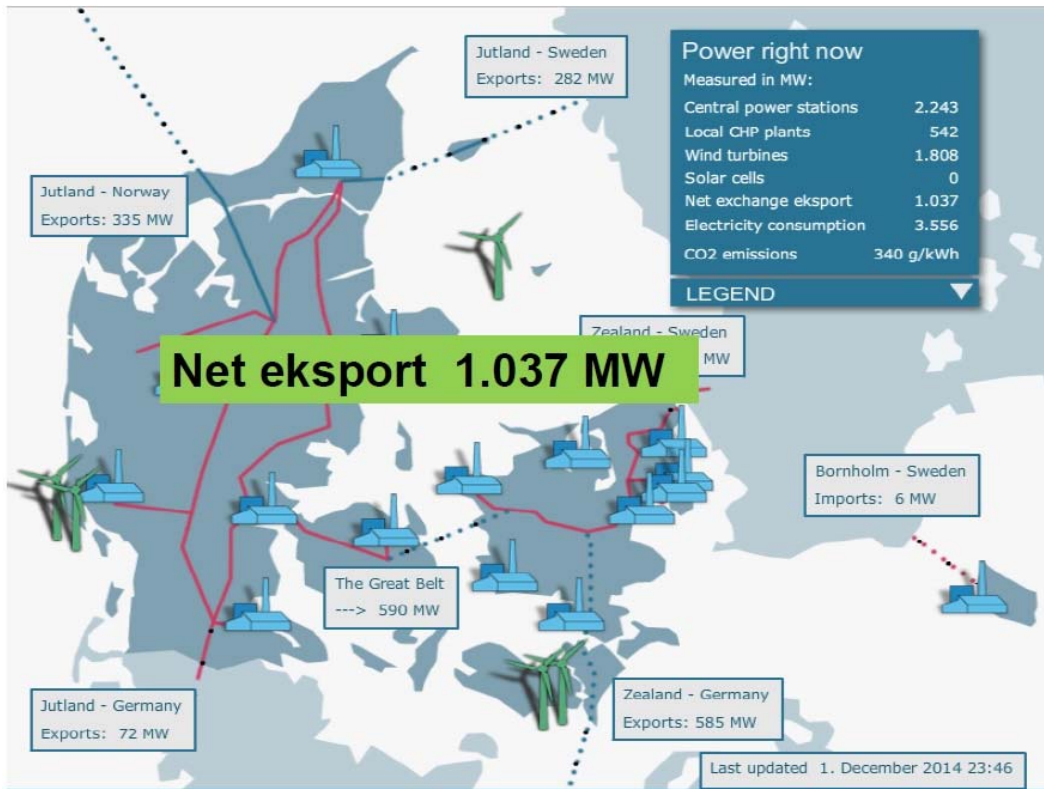
At present, about 40% of Denmark's electrical supply is provided by wind turbines (Slide 22), with plans to exceed 50% by 2020-21. Wind turbine technology has advanced over the years, with the power generated by an individual unit continuing to increase (Slide 23). Denmark is a net exporter of energy when the wind is above a certain level.

At the same time, biogas is extensively used as an energy source. Consisting of methane and carbon dioxide, thermophilic biogas is produced from waste generated by farms (manure) and industrial waste products.

Using electrocatalysis via alkaline electrolysis, Dr. Møller has developed the means of converting the wind energy from turbines into hydrogen (Slide 24). In turn, the hydrogen is reacted with the carbon dioxide in biogas to produce chemically pure methane. Virtually all of the CO₂ can be converted, and the methane is stored in the natural gas grid. Thus, excess wind energy, via hydrogen generation, is used to eliminate CO₂ in biogas and produce methane, for clean carbon-based energy. The concept has been proven at the Lemvig biogas plant, the largest in Denmark.

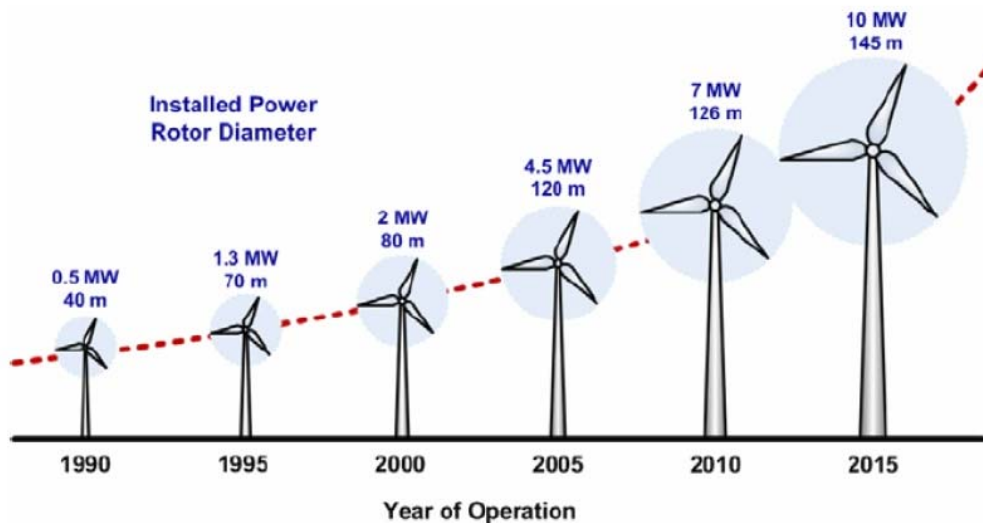


Slide 21- Methane gas storage for renewable energy.



Slide 22 - Power profile in Denmark.

Energy: Electricity, upgrading and conversion



Slide 23 - Growth in individual wind turbine power capacity (1990-2015).

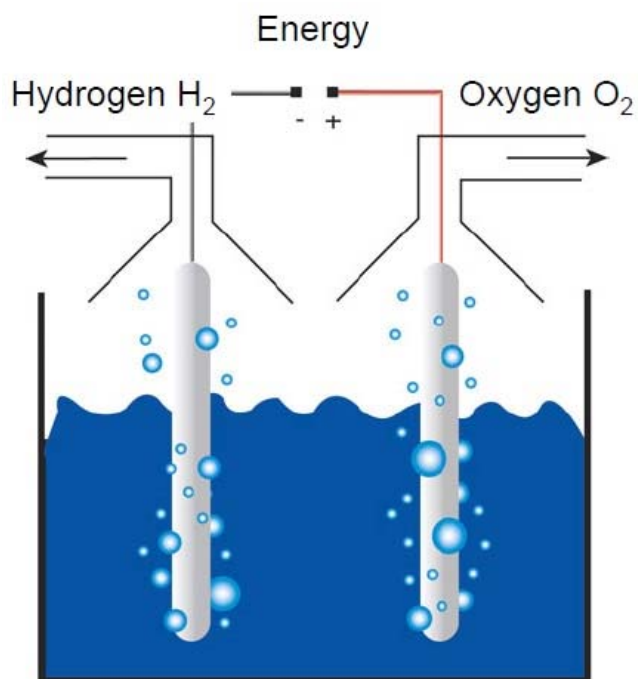
Hydrogen generation - electrode development

The key to the generation of hydrogen from wind energy (Slide 24), lay in the development of the catalytic electrode. Reaching back nearly 90 years, Dr. Møller found a 1927 patent (US Patent 1,628,190, *Method of Producing Finely Divided Nickel*), which provided the basis for the hydrogen generation (Slide 25). Finely-divided nickel, with very high surface area, was found to be extremely catalytic for hydrogenation processes. The preparation involves the mixing of nickel and aluminum, heating to form an alloy, and then selectively dissolving the aluminum, resulting in highly porous (*i.e.*, "finely-divided") nickel.

Cheap hydrogen = winning position



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25 wt% KOH at a temperature of 90°C

Slide 24 - Innovation in hydrogen generation.

Patented May 10, 1927.

1,628,190



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UNITED STATES PATENT OFFICE.

MURRAY RANEY, OF CHATTANOOGA, TENNESSEE.

METHOD OF PRODUCING FINELY-DIVIDED NICKEL.

No Drawing.

Application filed May 14, 1926. Serial No. 109,189.

This invention relates to a method of preparing catalytic or finely divided material.

The principal object of the invention is the production of metallic nickel in a catalytic state such as may be used in the hydrogenation of oils, fats, waxes and the like. To this end the invention contemplates the alloying of metallic nickel with metals such as silicon and aluminum in various proportions, and then dissolving the aluminum and silicon from the alloy by means of a solvent which will not attack the nickel, whereupon the nickel remains in a finely divided state.

In this condition the nickel may be extremely catalytic, these properties apparently being intensified by the treatment.

the invention is not to be restricted to the proportions given.

The solvent may be of any desired strength, dependent upon the rapidity with which it is desired to remove the aluminum, or the aluminum and silicon. In the dissolving action a considerable amount of hydrogen is liberated, and this may be saved and used for other purposes, or not, as found convenient and expedient.

After having dissolved out the aluminum

1,628,190

the aluminum and silicon from the resultant alloy.

4. A method of preparing a catalytic material which includes the step of alloying 50% nickel, 40% silicon, and 10% aluminum and dissolving the silicon and aluminum from the resultant alloy.

5. A method of preparing finely divided nickel which includes the step of alloying nickel with aluminum and dissolving the aluminum from the resulting alloy with a solvent which will not dissolve the nickel and drying the resultant finely divided nickel.

6. A method of preparing finely divided

nickel which includes the step of alloying the aluminum and silicon from the resultant alloy with a solvent which will not dissolve nickel and drying the finely divided product.

7. A method of preparing finely divided nickel which includes the step of alloying 50% nickel, 40% silicon and 10% aluminum and dissolving the silicon and aluminum from the resultant alloy and separating the finely divided nickel from the supernatant liquid.

In testimony whereof, I affix my signature.

MURRAY RANEY.

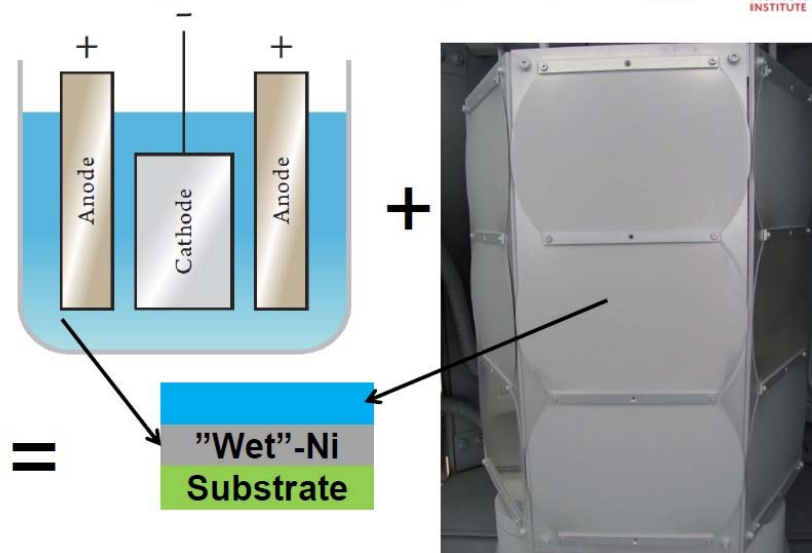
From 1926/1927

Mixing Al and Ni + heating + dissolution of Al

Slide 25 - U.S. Patent for producing finely-divided nickel.

The desired electrode was produced by a combination of physical vapor deposition and electrodeposition. Nickel was electrodeposited, followed by a PVD coating of aluminum (Slide 26). Slide 27 shows the nickel operation on a pilot scale, while Slide 28 shows the PVD operation. Alloying the layers at about 620°C produces a multitude of Ni-Al intermetallics, as in the phase diagram of Slide 29. The annealing process yields a distribution of Ni-Al phases, with Ni₂Al₃ constituting the primary intermetallic in the bulk of the deposit near the surface (Slide 30). Finally, the aluminum was selectively leached from the Ni₂Al₃, resulting in an extremely porous nickel, ideal for electrocatalysis (Slides 31-32, by optical and electron microscopy, respectively)). Recent developments have improved the electrodes even further and a new solution based on electrodeposition only is being explored (Slide 33).

Combining PVD and Electroplating



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Slide 26 - Production of catalytic electrode by PVS and electroplating.

Combining PVD and Electroplating



Slide 27 - Electrodeposition of nickel.

Combining PVD and Electroplating

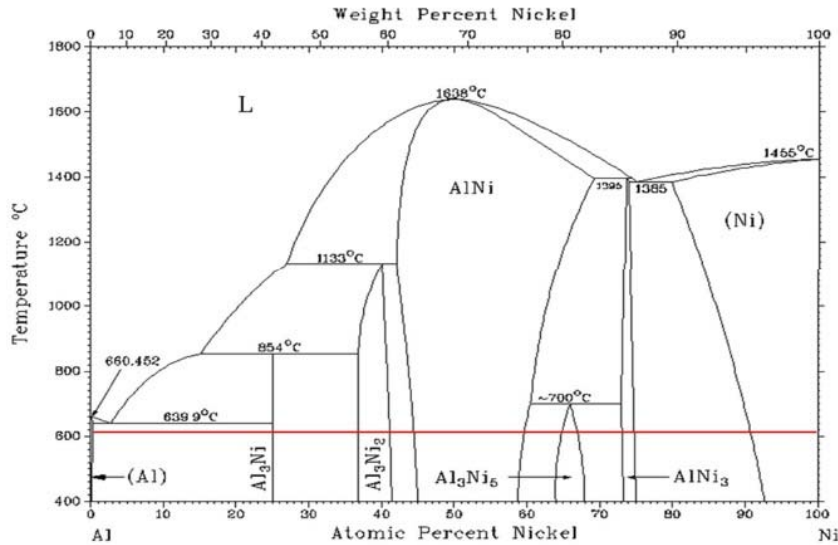


Slide 28 - Physical vapor deposition of aluminum.

Combining PVD and Electroplating



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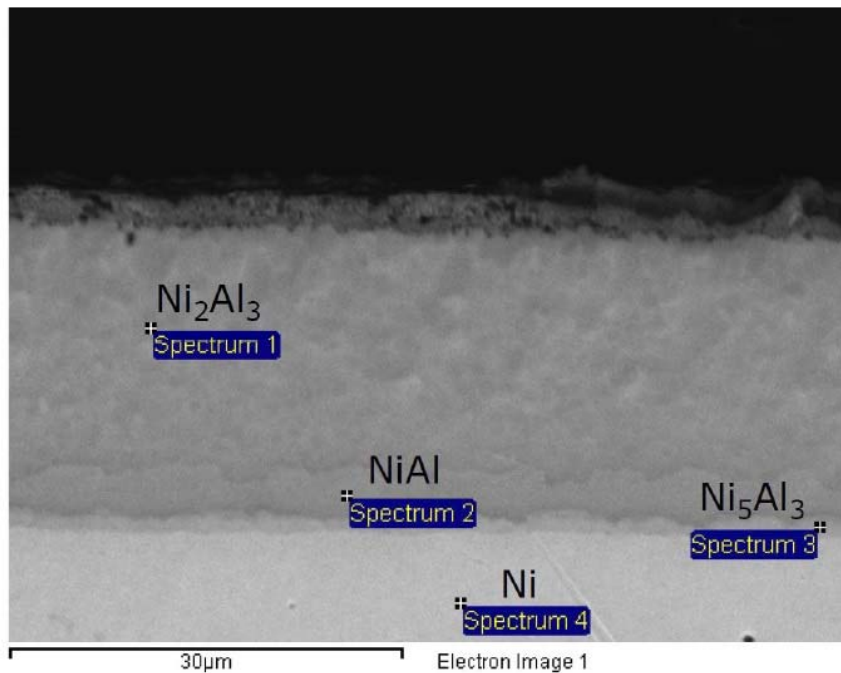


Slide 29 - Nickel-aluminum phase diagram.

Combining PVD and Electroplating



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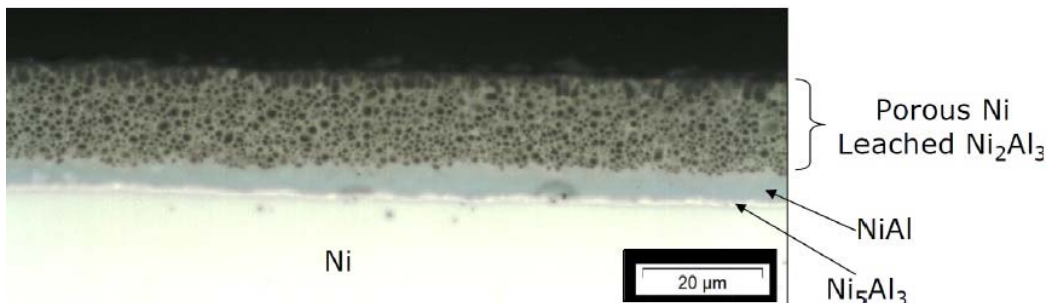
Slide 30 - Phase distribution in alloyed nickel-aluminum.

Combining PVD and Electroplating

- Aluminum was selectively leached from the Ni-Al phase



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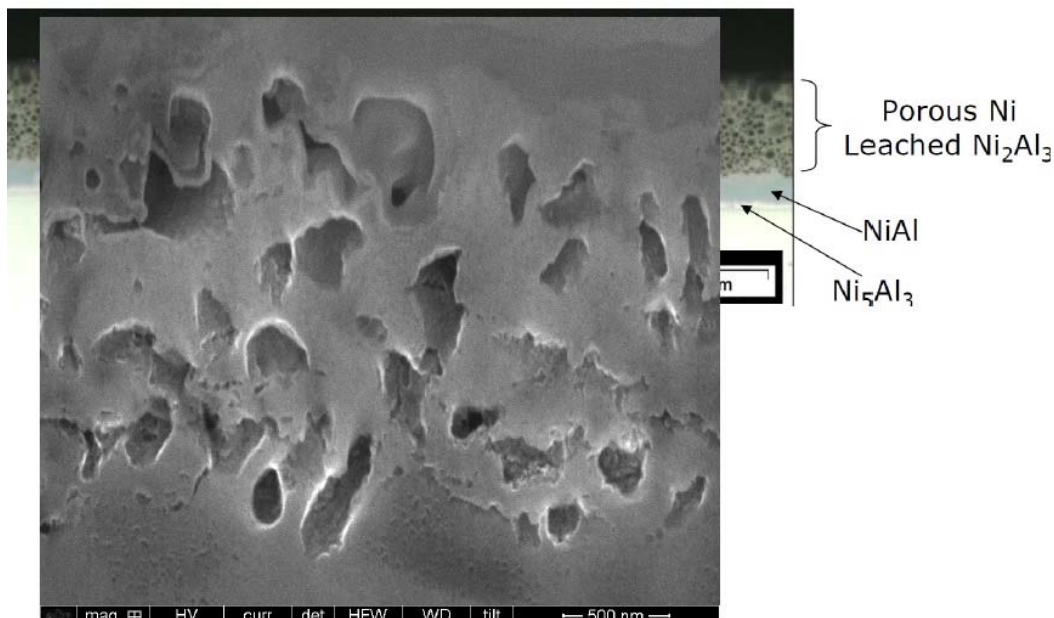
Slide 31 - Optical microscopy: Aluminum selectively leached from Ni_2Al_3 .

Combining PVD and Electroplating

- Aluminum was selectively leached from the Ni-Al phase

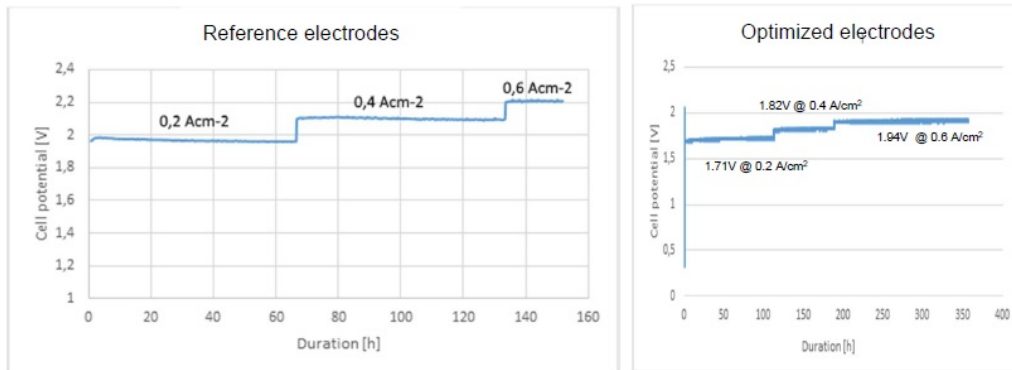


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Slide 32 - SEM: Aluminum selectively leached from Ni_2Al_3 .

New solution based on electroplating only...



0.2 A/cm²: ΔU app. 0.2 V
 0.4 A/cm²: ΔU app. 0.3 V
 0.6 A/cm²: ΔU app. 0.3 V

Slide 33 - Electrode manufacture via electrodeposition only.

Hydrogen generation - scale-up

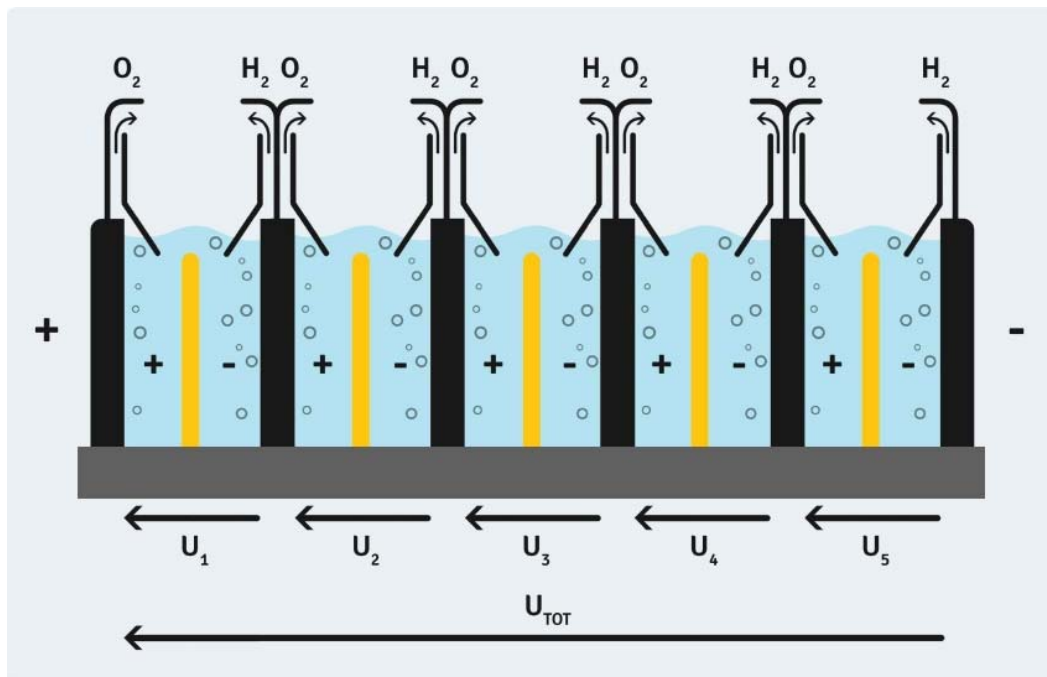
Recent work has been involved in scaling up the hydrogen generation process. The nickel electrode plating operation shown in Slide 34 illustrate the scale of operation currently achievable.

Upscaling based on electroplating



Slide 34 - Electrode scale-up.

Using a bipolar principle, an array of electrodes connected in series allows production of hydrogen at significant rates (Slide 35). A full-scale unit (Slide 36) will be ready for testing in September 2018.



Slide 35- Schematic diagram of a full-scale hydrogen generation unit.

Testing will be initiated in September



HydrogenPro

Up to 100 Nm³/h and up to 50 bar

Elplatek Electroplating technic

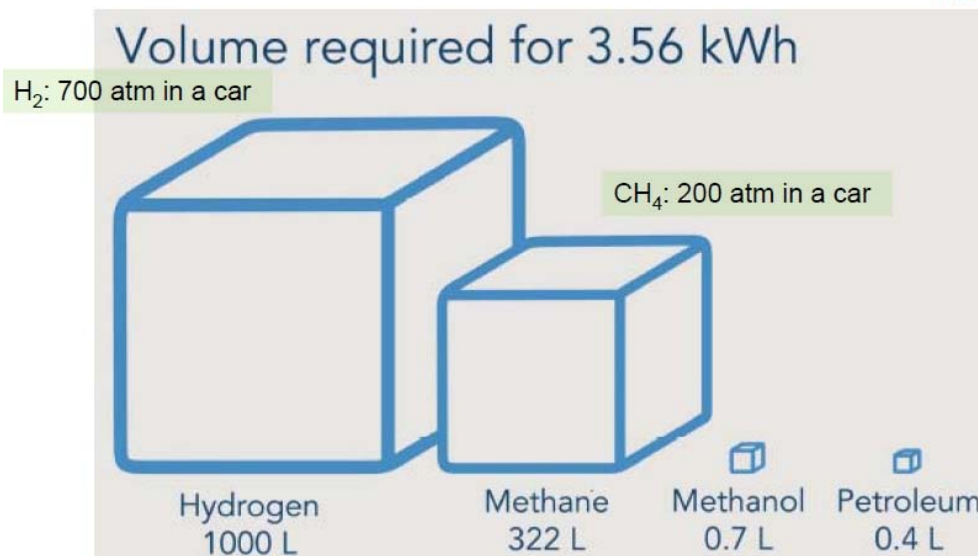
Slide 36- Elplatek/HydrogenPro hydrogen production unit to be tested in September 2018.

Potential for fuels

There are many aspects to the wind power-hydrogen-methane-biogas scheme that could be exploited. Among these was the potential for sustainably synthesizing fuels. If one considers the energy density of the substances considered here, it is obvious that the storage volume is critical for vehicles (Slide 37). Using an energy yardstick of 3.56 kW/hr between refueling, hydrogen would occupy 1000 L, requiring 700 atmospheres of compression to fit into a car realistically, a concept not too realistic in itself. Similarly, the methane equivalent would be 322 L, requiring 200 atmospheres of compression. However, methanol (not the ethanol used in cars in the United States) derived from methane, would occupy 0.7 L at one atmosphere. This compares with 0.4 L for petroleum at one atmosphere. Methanol would not be unrealistic.

In this way, Dr. Møller and his team envisioned the hydrogen produced by electrocatalysis from wind energy, being used to clean the biogas, thereby producing methane by reacting with the CO₂ in the biogas. The methane could then be converted to methanol by dry/wet reforming (Slide 38). He calculated that the energy content in the original biogas could be increased by 50% with this system (Slide 39).

Energy densities



Optimal to go for methanol production

Slide 37 - Comparison of potential sustainable fuels.

Modularized fuel factories



- Hydrogen production

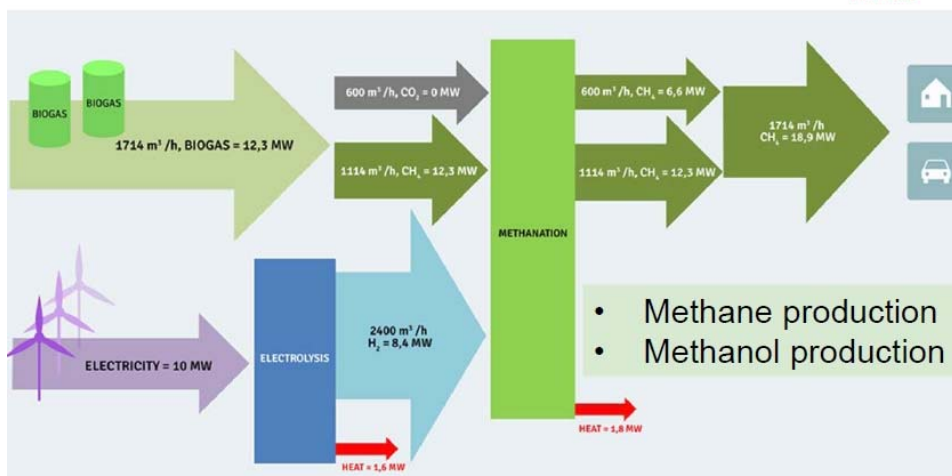


- Biogas cleaning



- Making methane by upgrading CO_2 in biogas to CH_4
 - Making methanol by dry/wet reforming
- Slide 38 - Modularized fuel factories.

Cheap hydrogen = winning position



Upgrading biogas with hydrogen produced from wind turbines, the energy content in biogas is increased by 50%.

Slide 39 - Energy enhancement of biogas to produce methane and methanol.

Electrocatalytic cleaning of biogas

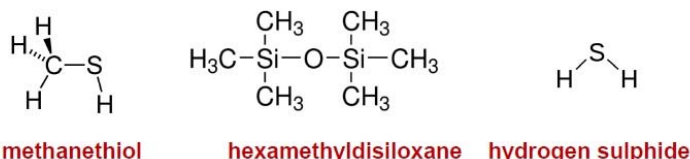
Given its origins, *i.e.*, farm and industrial waste, biogas is not pure in any sense. Although it consists of 65% methane and 35% CO₂, there are significant impurities (Slide 40). Of significant note is sulfur, in the form of 2000 ppm of hydrogen sulfide and, to a lesser extent, 50 ppm of methanethiol. To be useful for further catalytic conversion, the sulfur must be removed. In conventional cleaning of biogas, there are still waste considerations (Slide 41). Although the H₂S is effectively reduced from 2000 ppm to about 10 ppb, the sulfur is tied up as a metallic sulfide, which must be hauled away.

An electrocatalytic process was developed by Dr. Møller and his colleagues, which converts the sulfide in the biogas to pure sulfur, which can be used commercially (Slides 42-43). There is no resultant waste. Instead, the sulfur impurity can be put to use.

Electrocatalytic cleaning of BioGas



What is biogas?
 About 65 % methane CH₄
 About 35 % CO₂
 About 2000 ppm H₂S
 About 50 ppm methanethiol (CH₃S)
 About 30 ppm hexamethyldisiloxane C₆H₁₈Si₂O



Slide 40 - Composition of biogas.

Conventional Cleaning of Biogas – what about waste?



Slide 41 - Waste considerations in conventional cleaning of biogas.

Electrocatalytic cleaning of BioGas



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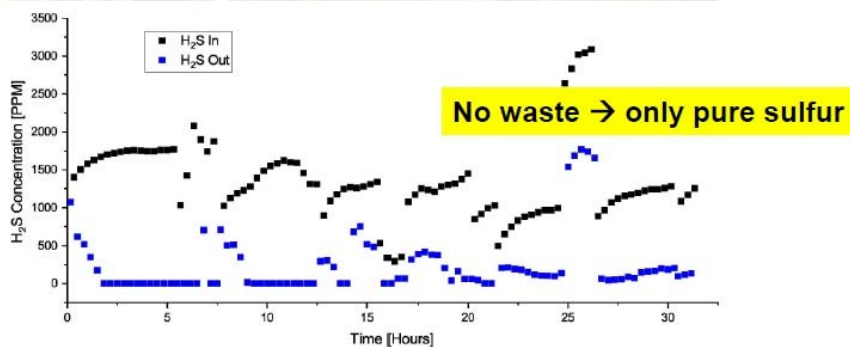


Slide 42 - Unit for electrocatalytic cleaning of biogas.

Electrocatalytic cleaning of BioGas



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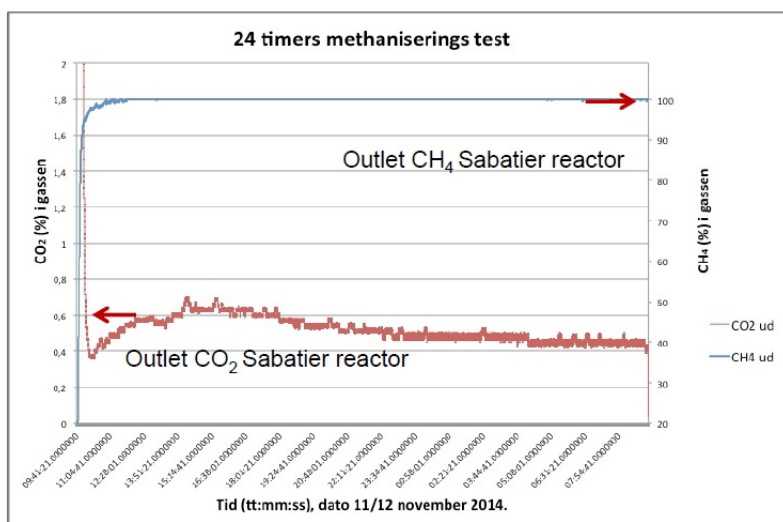


Slide 43- Impact of electrocatalytic cleaning of biogas.

Production of methane and methanol

As noted earlier (Slide 39), the next phase of this renewable energy system is the conversion of CO₂ to methane. The process uses the Sabatier reaction. Once again using the hydrogen from the wind-driven electrocatalysis, reaction with the carbon dioxide in the biogas produces methane and water. This requires a nickel catalyst (Slide 31) at a reaction temperature of 300 to 400°C (Slide 44). Such reactors, shown in Slides 45-46, are available on a commercial scale. Ultimately, the methane is converted to methanol fuel (Slide 47).

Upgrading CO₂ to CH₄ – 1 step Sabatier reactor



Slide 44 - Upgrading CO₂ to methane - Sabatier reactor.

Upgrading CO₂ in Biogas to CH₄



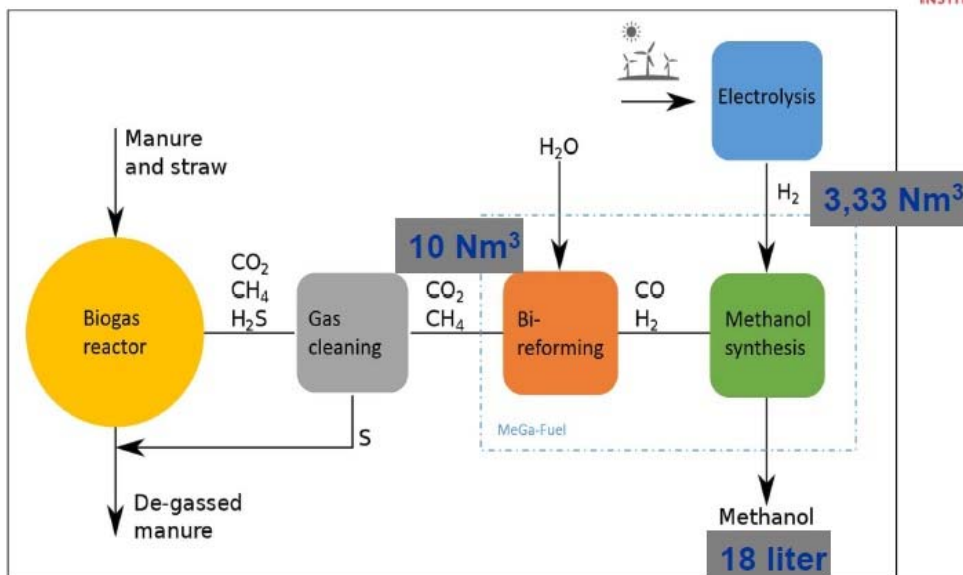
Slide 45 - Upgrading CO₂ to methane - Pilot reactor.

Upgrading CO₂ in Biogas to CH₄



Slide 46 - Upgrading CO₂ to methane - Commercial reactor.

In summary, the overall strategy for this renewable energy concept is shown in Slide 47. The biogas derived from organic waste, once cleaned for sulfur (in pure form), yields CO₂ and CH₄. The hydrogen derived from wind-driven electrolysis is then combined to synthesize methanol.



Slide 47 - Overall concept of extracting sustainable energy from wind power and biogas.

Methanol as a fuel

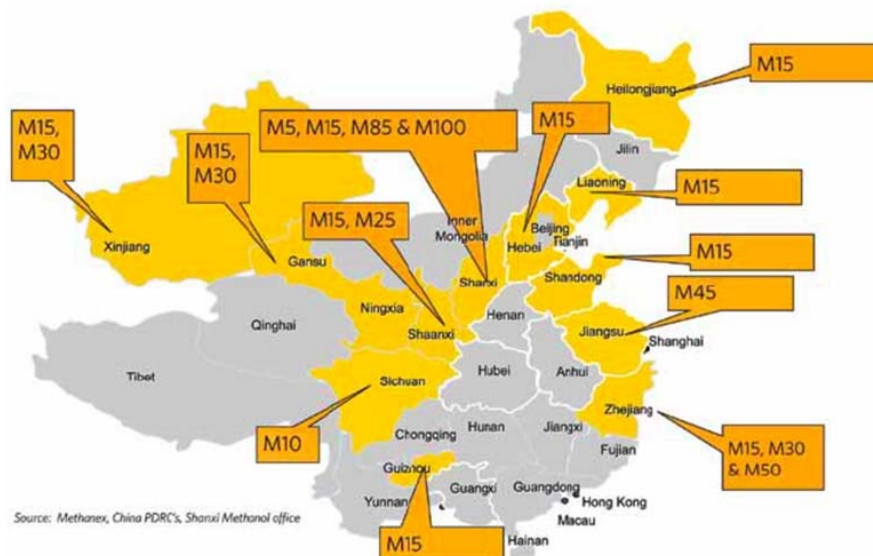
In North America, attention on alternative automotive fuels has been focused on ethanol. However, methanol has often been used in automotive racing, and is the focus in other areas of the world (Slide 48). Indeed, methanol is widely used in China (Slide 49). It is entirely reasonable to expect that wider use of this fuel offers a sustainable alternative fuel for the future.

Driving on methanol



Slide 48 - Commercially-available methanol fuel.

Methanol used in China



Slide 49 - Distribution of methanol fuel in China.

Dr. Møller's work in this area has been rather significant. Indeed, it has gotten play in the newspapers in Denmark (Slide 50). In English, (via a loose computer translation), the headline reads, "How to get a jumbo jet to fly on wood alcohol."

Politic commitment and action



Slide 50 - Reaction to Dr. Møller's work in Denmark.

Self-cleaning paints

Another avenue of surface research has led Dr. Møller to look at self-cleaning paints. Such a paint would be hydrophobic and oleophobic, repelling both water and oils, respectively. The paint would continue to maintain this property even after scratching or scuffing. It would keep pollen, insects, stains, etc., from sticking to the surface.

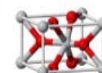
It was found that titanium dioxide is widely used as a pigment in paints, cosmetics, etc. Anatase, a tetragonal form of TiO_2 - the others being rutile, the most common form, and brookite, an orthorhombic form - possesses photocatalytic surface properties. Photoactive titania in the form of anatase was seen as a means of forming a self-cleaning surface, in addition to several other applications (Slide 51).

Slide 52 shows the performance of a normal paint, and a self-cleaning one, containing anatase, before and after exposure to 28 hr of UV. As can be seen, the blue stain on normal paint is unaffected, while it disappears from the surface of the self-cleaning paint.

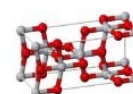
Self-cleaning paint, TiO₂



- Polymorph material: rutile, anatase, brookite
- Widely used as pigmentation in paint, cosmetics, food, ...
- Photocatalytic properties (anatase) discovered in 1967
- Possible industrial applications of photoactive titania coatings:
 - ‘Self-cleaning’ surfaces
 - Water purification, air cleaning
 - Antibacterial, antimicrobial, fungicidal properties
 - Hydrophilic surfaces
 - Photovoltaics



rutile



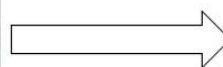
anatase

Slide 51 - Basis for titania in self-cleaning paints.

Self-cleaning paint



Normal paint

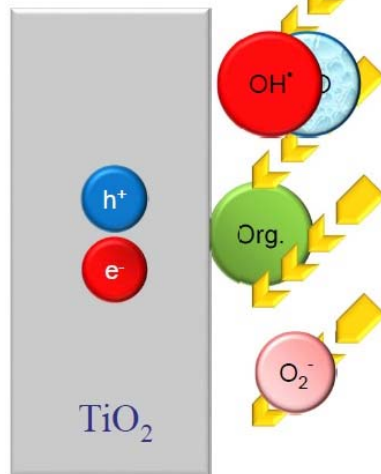


Self cleaning paint



Slide 52 - Laboratory performance of self-cleaning paint.

Integrating TiO₂ into paint



- TiO₂ mixed into paint

- Anatase/TiO₂ absorbs energy from the sunlight and creates electron/holes and OH radicals
- OH radicals break down organic matter
- What happens to the paint?



Slide 53 - Integrating titania into paint: (1) the concept.

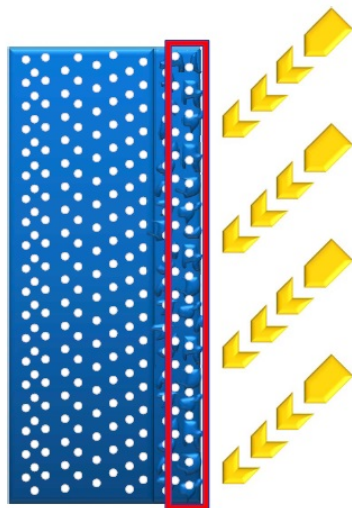
When anatase is mixed in with the paint, its photoactive surface absorbs the energy from the sunlight, creating electron holes and OH⁻ radicals (Slide 53), which in turn break down the organic matter forming CO₂ and H₂O.

When nano-sized TiO₂ particles are mixed into the paint (Slide 54), the contact area between the organic binder material and the particles is extremely high. At the surface, the binder is affected by the photocatalytic reaction, resulting in a massive release of TiO₂ from the surface. Thus, an organic binder cannot be used, as it leads to poor durability, and the usual unsightly chalking occurs.

The solution to this problem was the use of TiO₂-coated glass beads (Slide 55). The beads are deeply imbedded into the film and do not fall out. There is considerably less direct contact between the TiO₂ and the binder. As a result, minimal organic binder is affected by the photocatalysis, and a long lasting, self-cleaning film is obtained.

Dr. Møller has worked with a commercial paint manufacturer to perfect the incorporation of TiO₂ in the matrix via a patented process (Slide 56-57). An atomic layer deposition (ALD) process in a specially constructed reactor converts titanium chloride (TiCl₄) to TiO₂ at exceedingly small thicknesses on the glass bead surface (20-30 nm). The result is a self-cleaning paint of high durability.

Integrating TiO₂ into paint

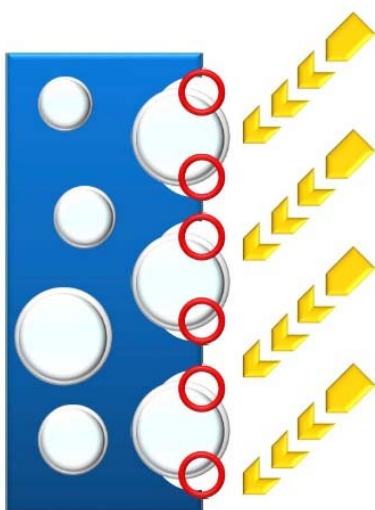


- TiO₂ mixed into paint
 - Contact area between binder and TiO₂ nano-particles extremely high
 - All the binder at the surface is affected by the photocatalytic reaction
 - High release of TiO₂ particles
 - Impossible to use organic binder
 - Poor durability
 - Chalking and loss of gloss/color



Slide 54 - Integrating titania into paint: (2) by mixing.

TiO₂ coated spheres into paint



- TiO₂ coated spheres:
 - Much less contact between binder and particles
 - Small amount of binder at the surface is effected by the photocatalytic reaction
 - Glass beads are embedded deeply in the film and do not fall out
 - No release of nanoparticles
 - Long lasting film with long lasting self cleaning effects



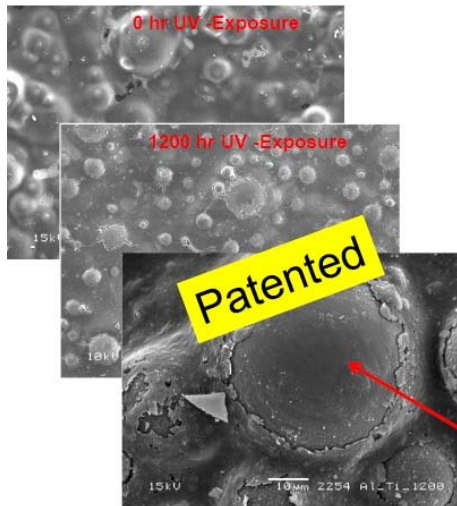
Slide 55 - Integrating titania into paint: (3) using TiO₂-coated spheres.



High durability & self-cleaning

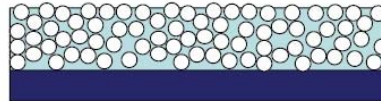
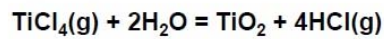


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ALD (Atomic Layer Deposition)

Made by a cyclic process in a specially constructed reactor

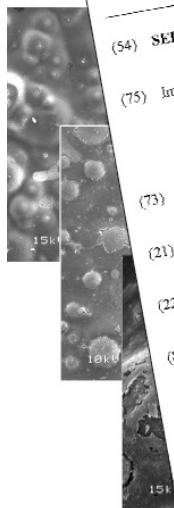


20 - 30 nm TiO₂ at the surface

Slide 56 - Integrating titania into paint: (4) commercially available.



High



(19) **United States Patent Application Publication**
 (12) **Hillebrandt Poulsen et al.**

(54) **SELF-CLEANING COATING COMPOSITION**

(75) **Inventors:** Soren Hillebrandt Poulsen, Roskilde (DK); Per Moller, Græsted (DK); Sverre Grønner Gunnarsson, Copenhagen K (DK)

(73) **Assignee:** DYRUP A/S, Soborg (DK)

(21) **Appl. No.:** 13/140,088

(22) **PCT Filed:** Dec. 16, 2009

(86) **PCT No.:** PCT/EP09/67293
 § 371 (c)(1), (2), (4) **Date:** Jan. 31, 2012

(60) **Provisional application No. 61/122,870, filed on Dec. 16, 2008.**

(30) **Foreign Application Priority Data**
 08171810.8

(10) **Pub. No.:** US 2012/0118318 A1
 (43) **Pub. Date:** May 17, 2012

Publication Classification

(51) **Int. Cl.** C09D 7/12 (2006.01)
 C09D 175/04 (2006.01)
 B08B 7/04 (2006.01)
 C09D 167/03 (2006.01)

(52) **U.S. Cl.** 134/L3; 106/436; 524/605; 524/590; 134/1

ABSTRACT

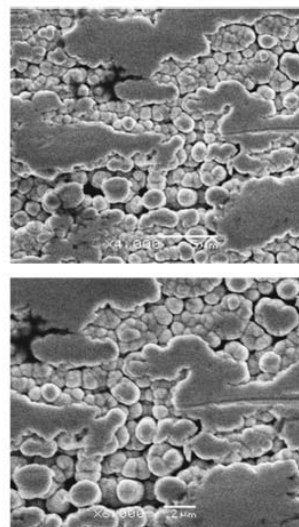
(57) The present invention relates to compositions with self-cleaning properties. More particularly, the invention concerns coatings or paints comprising particles coated with a catalytically active composition. In particular, a self-cleaning coating composition (paint) is provided, comprising micro-sized particles coated with a functional layer, wherein the micro-sized particles are hollow or solid beads, or any combination/ratio of hollow and solid beads, wherein the beads comprise one or more material(s) selected from ceramic material(s); polymeric material(s); cermet material(s); metallic material(s); pigmented material(s); light-absorbing and/or light reflecting material(s); including any combination thereof, wherein said layer is covalently bound to said particles, wherein the photocatalytic layer comprises TiO₂ in the crystal form of anatase; and wherein the coating composition (paint) comprises less than 0.1 anatase particles derived/released from the micro-sized beads, determined as weight/weight of released anatase/total amount of anatase. The invention provides paint essentially without presence of unbound anatase crystals which is highly undesired, as it is believed that their presence has a negative influence on essential components of the paint, such as binder, pigment and/or additives and furthermore, anatase may cause eye, skin, and respiratory tract irritation.

Slide 57 - Integrating titania into paint: (5) patented process.

Antibacterial Ag-Cu surfaces

Another part of Dr. Møller's work involves the development of antibacterial surfaces. Consider the common door handle in a public building, e.g., a hospital, with hundreds of hands, containing oils and bacteria of unknown origin, ready to raise a public health issue at a moment's notice. The solution was a silver-copper alloy finish known to possess anti-bacterial properties (Slide 58). And again, news of this work became well known in the local papers (Slide 59). In English, (via another loose computer translation), the headline reads, "Door handle gives bacteria a fight to the finish."

Antibacterial Ag-Cu surfaces



Elplatek Electroplating technic

Ciacolich N. et al., Surface & Coatings Technology 2018

Slide 58 - Morphology of antibacterial Ag-Cu surface.

Antibacterial Ag-Cu surfaces



Dørhåndtag giver bakterier kamp til stregen

Virksomheden Elplatek og DTU samarbejder om bakteriedræbende dørhåndtag

Af Lotte Brechmann

OVERFLADEBEHANDLING: Et tre-årigt projekt har fokus på at mindske spredning af bakterier på hospitaler. Det er virksomheden Elplatek og Danmarks Tekniske Universitet, DTU, der nu er gået sammen om at udvikle en bakteriedræbende belægning til dørhåndtag.

Det er en kobber og sølvbelægning. Kobber og sølv er kendt hver for sig som stoffer, der kan have gode effekter, man ved, at kobber har bakteriehæmmende egenskaber, og så kom tanken, hvad hvis man kombinerer kobber og sølv, fortæller Jan Boye Rasmussen, administrerende direktor i Elplatek.

Og de foreløbige resultater er gode. Laboratorieforsøg har vist, at kobber- og sølvbelægningen reducerer bakterier med mere end 99,9 procent allerede efter to timers eksponering på kobber- og sølvoverfladen.

” Det er virkelig noget, der gør en forskel

Jan Boye Rasmussen

Her i løbet af foråret bliver det bakteriedræbende dørhåndtag afprøvet i en lægepraksis. Og næste skridt er test på hospitaler.

Vi vil gerne lave feltstudier på et hospital, hvor vi kan vurdere kvantitativt, hvor meget det kobber- og sølvbelagte dørhåndtag reducerer bakterier i virkeligheden sammenlignet med almindelige dørhåndtag i rustfrit stål. Og vi forventer, at resultaterne fra vores laboratorieforsøg vil blive bekræftet af feltstudierne, fortæller ph-d-studerende på DTU og

Elplatek, Nicole Ciacolich. Projektet er i øjeblikket på udikig efter hospitalsafdelinger, der kunne tænke sig at være med til at teste dørhåndtaget.

Store perspektiver
Hvad ser I af perspektiver i projektet?

Perspektiverne er efter vores opfatelse ganske store. For hvis lidt større og lidt mere udtredte tests fortsætter med at udvise de samme resultater, så er det en forholdsvis billig og overkommelig måde at gøre en stor indsats på, lyder det fra Elplateks administrerende direktør.

Projektet har i første omgang fokus på hospitaler, men man kunne også forestille sig røkke andre områder, hvor et dørhåndtag med antibakteriel virkning kunne være interessant, fortæller han.

Elplatek og DTU er begge en del af Fast Track-partnerskabet, der også tæller Teknologisk Institut, For-

ce Technology, Aalborg Universitet, Siemens, Hempel og Terna.

Partnere i Fast Track-sektoren har så mange kompetencer, som vi aldrig selv ville kunne komme i nærheden af som mindre virksomhed, og vi kan hurtigt få sparring, når der er behov for det, det har virkelig været en styrke for os, og det er også med til at kunne drive det her projekt hurtigere frem, siger Jan Boye Rasmussen.

Det tre-årige projekt, der løber frem til sommeren 2019, er støttet økonomisk af Innovationsfonden.



Dørhåndtaget med kobber- og sølvbelægning er et led i et ph.d.-projekt, fortæller Nicole Ciacolich. Fotos: DTU.

Slide 59 - News article on antibacterial-coated door handles.

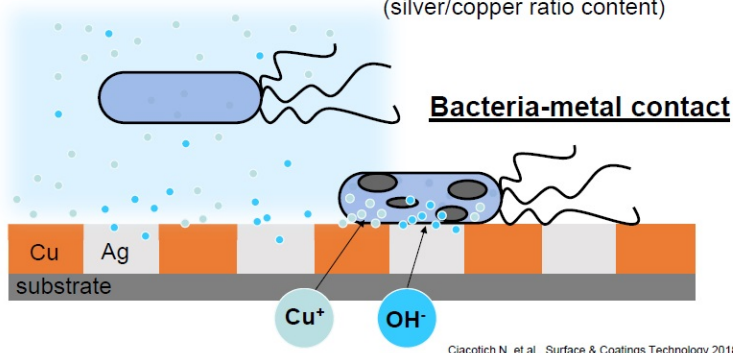
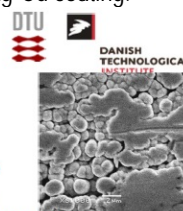
The mechanism whereby the antibacterial action takes place depends on the alloy content and the presence of a porous microstructure capable of retaining moisture. When a bacterium makes contact with the Ag-Cu deposit, oxidation of the copper and the corresponding reduction of silver produces copper ions and hydroxyl ions on the surface, killing the organism (Slide 60).

Testing involved the exposure of Ag-Cu coated test slides to a number of very common bacteria species to the contact killing mechanism (Slide 61). Dry conditions were specified, and re-inoculations of the bacteria on the test surface were undertaken every three hours for up to 21 hours, *i.e.*, multiple times. Success was defined as a minimum of 90% reduction in numbers of bacteria at all recovery times. The results were compared with tests on an uncoated 316 stainless steel reference surface. The results shown in Slide 62 indicate the effectiveness of the Ag-Cu surface in eradicating all types of bacteria tested with a killing rate of six to eight orders of magnitude. Slide 63 shows visual evidence, with the color changing from green (live bacteria) to red (dead bacteria) indicating extermination of the bacteria after 25 min. exposure to the Ag-Cu coating.

Antibacterial Ag-Cu surfaces

Galvanic coupling

- oxidation of Cu
- reduction on Ag
- porous microstructure
- cathodic/anodic area (silver/copper ratio content)



Ciacotich N. et al., Surface & Coatings Technology 2018

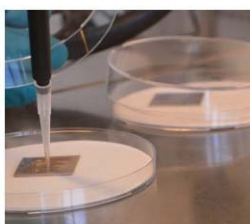
Slide 60 - Antibacterial mechanism.

Antibacterial Ag-Cu surfaces



Staphylococcus aureus (ATCC 6538)
Enterobacter aerogenes (ATCC 13048)
Pseudomonas aeruginosa (ATCC 15442)
 MRSA (ATCC 33592)

- Dry conditions
- Contact killing mechanism



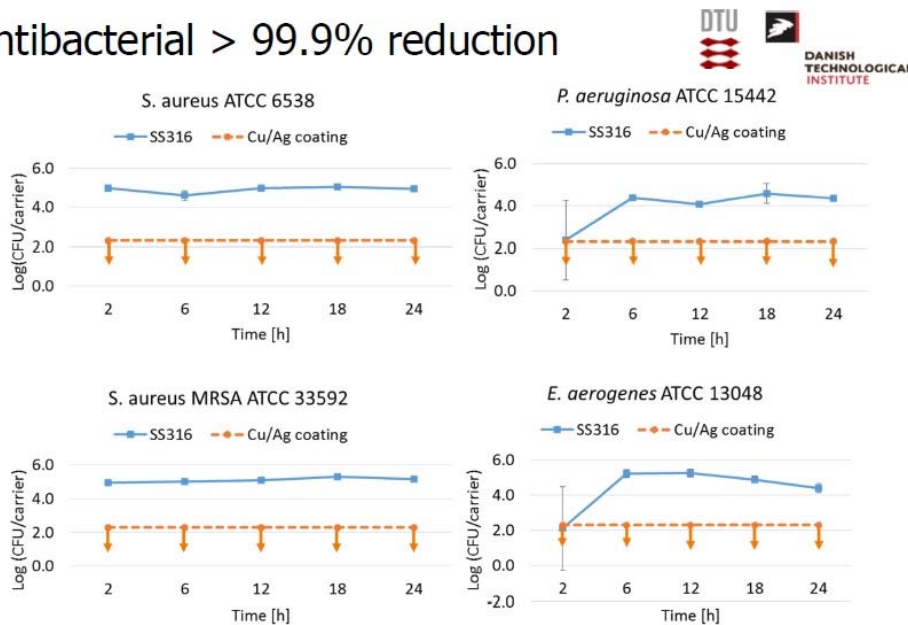
Re-inoculations after 3, 6, 9, 12, 15, 18 and 21 hours (1, 2, 4, 6 and 8 times)

Test performance criteria:
 Minimum of 90% reduction in numbers at all recovery times

Ciacotich N., Tesdorpf J. et al., manuscript in preparation

Slide 61 - Antibacterial test protocol.

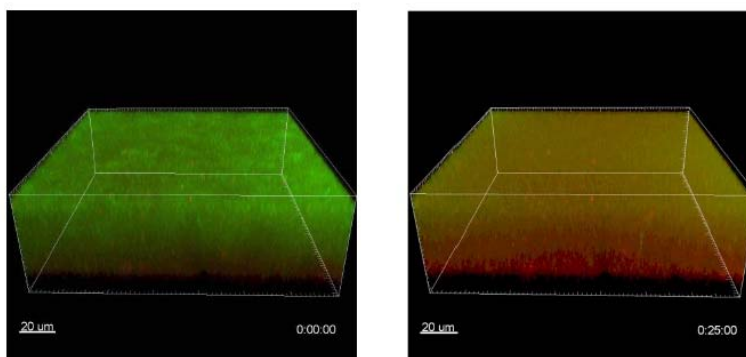
Antibacterial > 99.9% reduction



Ciacotich N., Tesdorpf J. et al., manuscript in preparation

Slide 62 - Antibacterial test results (1).

Antibacterial Ag-Cu surfaces



0 min

25 min

Slide 63 - Antibacterial test results (2).

Summary

To sum up (Slide 64), Dr. Per Møller's work has covered a multitude of applications where surface technology is critical to success. In concert with his longtime colleague, Dr. Lars Pleth Nielsen, he has documented this work through patents, papers and renowned books. The scope of his work goes beyond the more common applications found in deposition. The sustainable energy scheme described on these pages, using the principles of electrocatalysis, promises to leverage the maximum amount of

energy from wind power and biogas, the latter a resource that would otherwise be considered as pure waste in other times. The work with self-cleaning paints and antibacterial surfaces are other examples of novel applications requiring an understanding of electrochemistry and surface technology in real applications outside laboratory conditions which is indeed one of Dr. Møller's many skills.

William Blum Lecture



Highlights of Prof. Per Møller's contributions to surface finishing:

- Patent examples
- Book examples
- New ideas connected to energy
- Electrodes for alkaline electrolysis, generating hydrogen
- Electrolytic cleaning of Biogas
- Methane and methanol formation
- Self-cleaning paints
- Antibacterial surfaces

We would like to invite you to collaborate with us

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Slide 64 - Summary

About the lecturers



Professor Per Møller has a Ph.D. in surface technology from the Technical University of Denmark (DTU), in Lyngby, Denmark. During the past 30 years, he has been engaged in contract research with industry covering nearly all aspects from micro-plating, under cleanroom conditions, to the design and implementation of industrial-scale electroplating lines. He is author or co-author of more than 135 scientific papers and holds more than 25 patents in the field of surface technology and electrochemistry. Currently, he is Professor in corrosion and surface technology at the MEK-DTU Section for Materials and Surface Engineering.



Dr. Lars Pleth Nielsen has a Ph.D. in Surface Science from Aarhus University (Denmark) and a managerial degree in Organization Management and Innovation from Copenhagen Business School. He has been employed as a Research Scientist at Haldor Topsøe and in the Photonic Group at NKT Research and Innovation A/S. Currently, he leads the Tribology Center at the Danish Technological Institute.