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Evaluation of the Potential of Optical Switching Materials for Overheating Protection of Thermal Solar Collectors

Final Report

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SUMMARY

Providing renewable energy for domestic hot water production and space heating, thermal solar collectors are more and more widespread, and users' expectations with respect to performance and service lifetime are rising continuously. The durability of solar collector materials is a critical point as the collector lifetime should be at least 25 years. Overheating and the resulting stagnation of the collector is a common problem with solar thermal systems. During stagnation high temperatures lead to water evaporation, glycol degradation, and stresses in the collector with increasing pressure. Special precautions are necessary to release this pressure; only mechanical solutions exist nowadays. Additionally, the occurring elevated temperatures lead to degradation of the materials that compose collectors: seals, insulation materials, and also the selective coating which is the most important part of the collector.

A promising way to achieve active cooling of collectors without any mechanical device for pressure release or collector emptying is to produce a selective coating which is able to switch its optical properties at a critical temperature Tc. An optical switch allows changing the selective coating efficiency; the goal is to obtain a coating with a poor selectivity above Tc (decreasing of absorptance, increasing of emittance).
Obtaining self-cooling collectors will allow increasing collector surfaces on facades and roofs in order to get high efficiency and hot water production during winter without inconvenient overheating during summer.

Optical switching of materials can be obtained by many ways. Inorganic and organic thermochromic compounds, and organic thermotropic coatings are the main types of switching coatings that have been studied at EPFL-LESO-PB. Aging studies of organic thermochromic paints fabricated at EPFL suggest that the durability of organic compounds might not be sufficient for glazed metallic collectors. **First samples of inorganic coatings showing thermochromic switching behavoir have been produced at EPFL.** These coatings switch from a semiconducting to a metalic state at critical temperatures around 65°C, as indicated by a resistivity change of typically three orders of magnitude.

Project Goals

The aim of the project is to investigate different ways to obtain optical switching at a chosen temperature either by organic or inorganic materials; solutions for glazing or rough collectors are presented in this report. A general overlook of work carried out in this field is presented and experimental methods from literature have been investigated in the LESO-PB laboratory.

The preferred way to proceed is to modify the selective absorber coating in order to introduce thermochromic optical switching. Adding a thermochromic function to the glazing is an alternative approach. The latter has the advantage that the basic collector components cab remain inchanged, implying only a modification on the protective glass. Both approaches, thermochromic coatings applied directly to the solar absorber, and optically switching coatings on the collector glazing, are investigated in this report.

In this study, various synthesis routes for optical switching coatings are explored in order to evaluate the feasability of overheating protection of themal solar cllectors by thermochromic materials.

Approaches:

1. Inorganic thermochromic thin films for emittance switching at critical temperature

- Literature data collection in solar range and in middle IR domain
- Simulation of emittance switching
- Efficiency simulation of selective coatings containing thermochromic layers
- Deposition of inorganic layers

2. Organic thermotropic self-shading glazing

- Efficiency study based on literature
- Thermoplastic polymer blends for thermotropic glazing
- Thermotropic glazing containing thermo-sensitive additives

3. Organic thermochromic pigments for switchable selective paints

- Producing a paint containing thermochromic pigments
- Durability study

4. Switchable mirrors on selective coatings for absorptance switching

- Concept for α switching

Description of Work and Results

1. Inorganic thermochromic thin films for emittance switching at critical temperature

The materials that have been extensively studied during this project are transition metal oxides and related compounds that undergo a semiconductor-to-metal phase transition beyond a critical switching temperature. This phase change is accompanied by a dramatic change of optical properties. As the switching temperature depends on the composition, a ternary compound that switches above 80°C has been identified.

See Confidential Appendix for further details.

Literature data collection in solar range and in high IR domain:

A thorough literature research has been conducted in order to obtain data on the optical material properties in the metallic and semiconductor state. An author has been directly contacted successfully, he sent us important data files directly by electronic mail. The collected data on the material properties allow simulating the optical behavior of the films in the solar range as well as in the middle infrared region.

Simulation of emittance switching:

Computer simulations of emittance have been carried out at the LESO-PB lab. Fig. 1 clearly shows that one of the thermochromic compounds becomes highly emissive in metallic state. So the thermal emittance is depending on the substrate at low temperature and then on the metallic state of the thermochromic compound after switching; the optimum layer thickness has been identified.

First calculations led to projected emittance switching values from 5% at cold state to ~40% at hot state. Considering the SPF report [1] this means that a protection of glycol, sealing, selective coating, and insulating materials can be achieved by using this kind of layer in a selective coating (T kept under 160°C).

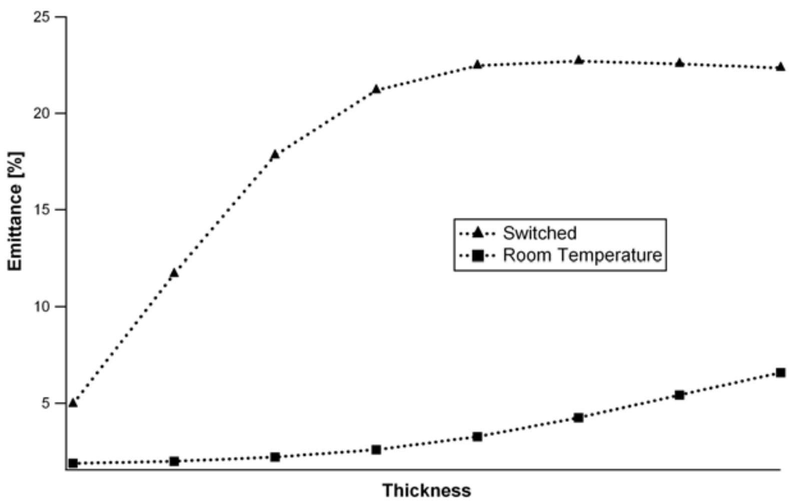

Fig. 1: Simulation of emittance switching with thickness increasing for one type of compound

Efficiency simulation of selective coatings containing thermochromic layers:

In order to predict the overall performance of the coating, a selective multilayer containing thermochromic materials has been simulated. The most important finding is that emittance switching can be obtained without any degradation of the high optical selectivity in the cold state.

Fig. 2 shows that a solar absorptance of up to 97.3% can be obtained for a selective coating switching from 5% to approximately 35% in thermal emittance.

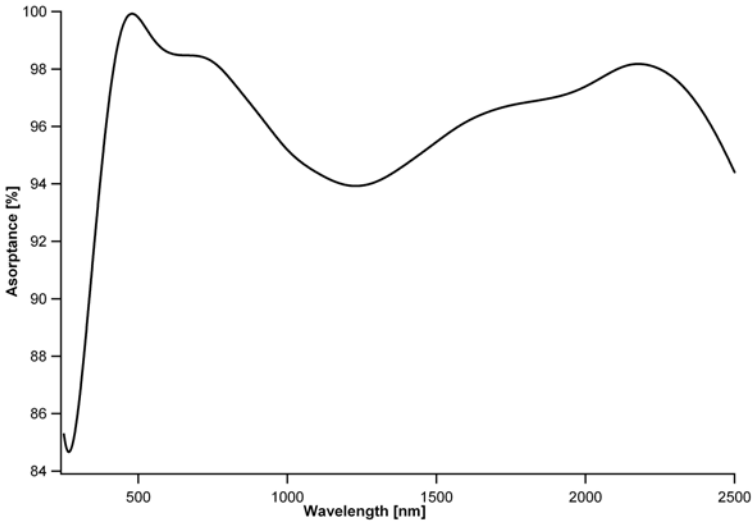

Fig. 2: Computer simulation of a thermochromic selective coating switching from 5% to 35% thermal emittance. A solar absorptance of 97.3% is achieved.

Deposition of inorganic layers:

Stable high quality layers have been obtained using three different methods: sol-gel dip-coating, DC Magnetron Sputtering, and thermal evaporation. To obtain single-phased thermochromic samples a very good control of process settings is required.

Sol-gel dip-coating is a cheap way as it does not need a vacuum during process. An expensive commercial alkoxide was first used as precursor and produced homogeneous high quality layers. Novel precursor solutions based on metal salts have been developed in the lab; these solutions also produced stable high quality layers. The samples need annealing in a reducing atmosphere after calcinations to become thermochromic. Vacuum and flowing Nitrogen have been tested and showed promising results but a good quality N_2 oven is required to achieve this annealing.

The DC Magnetron Sputtering process is already extensively used in the field of selective solar absorber coatings (Interpane™, BlueTec™, etc.); deposition parameters and substrate temperature are accurately controlled during the whole process in order to get films of precise stoichiometry. This method also shows an advantage in that only few supplementary deposition steps are added to the ones for selective layer deposition in order to get a finished thermochromic selective surface. Experiments on magnetron sputtering were performed in collaboration with Dr. Rosendo Sanjines and Henry Jotterand, Laboratory of Thin Films Physics, EPFL. **First samples of inorganic coatings showing thermochromic switching behavoir have been produced.** These coatings switch from a semiconducting to a metallic state at critical temperatures around 65°C, implying a resistivity change of typically three orders of magnitude (see Fig. 3). Ways to increase the switching temperature have been identified. The typical sample size is in the order of 2 x 2 cm^2.

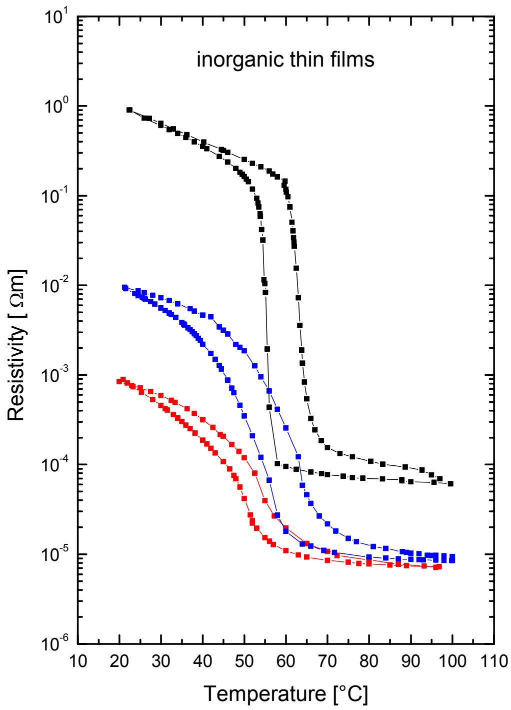

Fig. 3: Inorganic thermochromic coatings deposited by magnetron sputtering. The coatings switch from a semiconducting to a metallic state at critical temperatures around 65°C, as indicated by a resistivity change of typically three orders of magnitude (the resistivity is displayed on a logarithmic scale).The hysteresis loops are sufficiently narrow for the considered application.

A vacuum deposition machine for deposition of larger samples (up to approx. 20 x 20 cm^2) was donated to the LESO-PB laboratory by ASULAB. The first steps were to check the system and do some maintenance. Electric and hydraulic connections have been installed with the collaboration of the technical services of EPFL in order to put the device in operation. First tests used Al as evaporation material and gave good results; then thermochromic materials were tested. Vacuum evaporation is a faster and more cost-effective way to deposit thin films than sputtering, the deposition rate is higher. Additionally, due to advantageous pumping cross sections, the pumping speed of the installed machine is relatively high as compared to other laboratory installations. This vacuum evaporation process is also well established in the solar field (TiNOX™ selective absorber coatings) and is cheaper as compared to sputtering: the heating device for material deposition is simpler than a plasma system. Samples obtained by LESO-PB's deposition machine showed good and homogeneous films using higher deposition rates than sputtering; even black selective coatings have been obtained. A substrate heater system has been constructed in order to obtain a good crystallization of thermochromic films. First samples have been produced using the new substrate heating system. A special process pressure gauge has been installed in order to precisely control the oxygen partial pressure which has to be kept within a narrow range during thin film deposition.

Fig. 4: Vacuum evaporation system (left). Black absorbing and mirrorlike film samples (right)

2. Organic thermotropic self-shading glazing

Thermotropic organic glazing changes reversibly from a clear transparent state to a white diffusing one at the switching temperature. This is due (in most systems) to the apparition of small areas of optical properties that differ from the bulk of the coating.

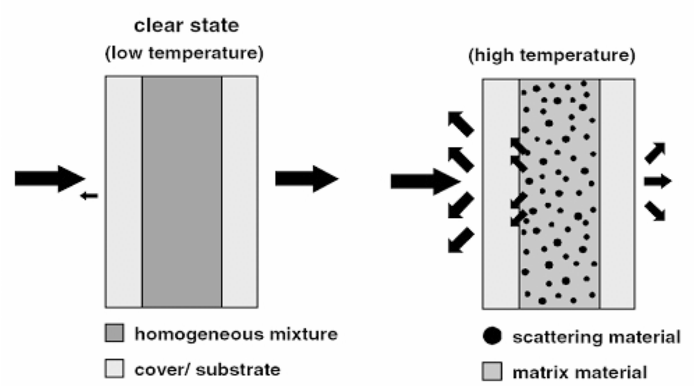

Fig. 5: General presentation of the thermotropic effect 2]

A thermotropic effect can be obtained by many different methods and materials; i.e. liquid crystals, polymer blends, hydrogels, etc [3] [4]. These coatings cannot be applied directly on a collector's surface without any protection and are therefore placed on the backside of the collector glazing.

Efficiency study based on literature:

Most improvements on this subject have been made during the 90's with great hope in the intelligent windows field. Hydrogels or liquid crystals in solution might not be suitable for the considered application as they are made of an aqueous gel that needs to be perfectly encapsulated in order to avoid evaporation. Polymer blends and additives have then been further investigated.

Thermoplastic polymer blends for thermotropic glazing:

This system is the one of the cheapest in terms of materials cost. It consists in a homogeneous mix of two polymers of different refractive indexes and a “lower critical solution temperature” (miscibility dramatically decreases at a critical temperature that depends on the system) [5]. Upon the switching temperature (cloud point), miscibility changes and the coating demixes into small droplets. Droplets coalesce to form again a homogeneous mix by cooling the coating. Literature reports values from ~80% to less than 40% in direct transmittance by heating.

PS-co-HEMA has been synthesised at the LESO-PB lab and then mixed with PPO by dissolution in a volatile solvent. Films have been obtained after spreading the mixture on substrates and removing the solvent by drying. However layers are not thermotropic yet; a lamination process would be necessary to get good switching films.

Thermotropic glazing containing thermo-sensitive additives:

Polymer Competence Center of Leoben (Austria) researchers have been working on thermotropic layers to protect all-polymeric solar collectors. They recently obtained promising results using thermo-sensisitive additives in UV-curable resins. Modelling showed that a solar transmittance of above 85% is required in clear state [6]. In opaque state a residual hemispherical transmission of 25% results in a stagnation temperature of 80°C (130°C for 60% residual transmission).

The latest article from PCCL [7] shows experimental values of 79% transmittance in clear state and 35% in opaque one. Residual transmittance in opaque state is in the range of simulated values and clear state must be enhanced to fully match the goal of thermotropic protection.

Aging tests (UV, temperature, humidity) have not been conducted yet; durability should be the main problem with these organic coatings.

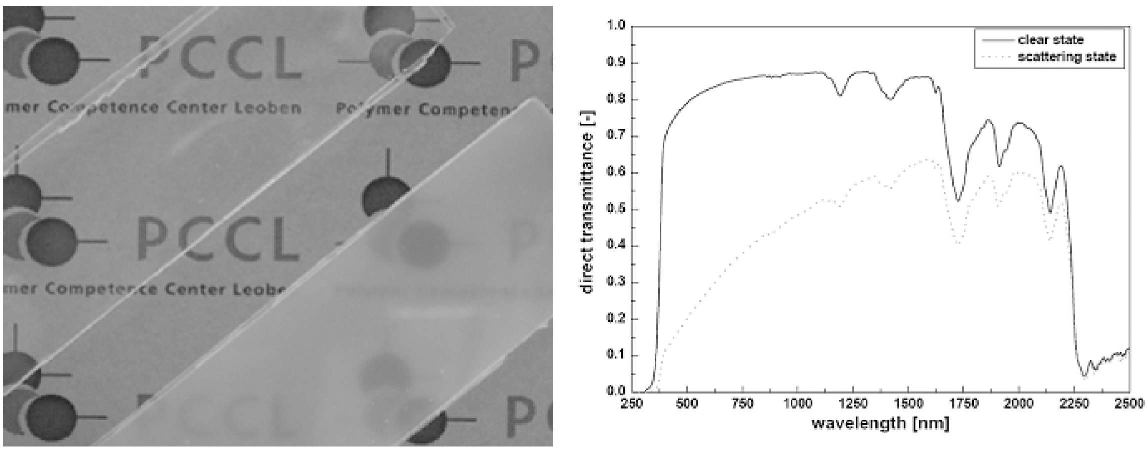

Fig. 6: Clear and opaque state of samples produced at PCCL (left) and their transmittance (right) [7]

3. Organic thermochromic pigments for switchable selective paints

Organic pigments and dyes are mainly used for safety inks and packaging but also for decorative use or road lines (which change color when the ground temperature is below zero). A change of the molecule's configuration happens at the switching temperature and it turns from colored state to white. Two types of pigments have been studied at the LESO-PB lab: magenta (Tc: 31°C), and black UV-treated (Tc: 81°C).

Producing a paint containing thermochromic pigments:

Two kinds of matrix paint have been tested: an acrylic water-based paint and a polyvinyl organic solvent-based one. Pigments were mixed with the matrixes to obtain switching paints that have been spread on aluminium plates.

The paint containing organic solvent shows a good white hot state but many pores due to fast drying of the solvent; the wettability on metal is also poor so this kind of matrix is not suitable. The aqueous paint shows a very good wettability on substrate and no apparent pores; this paint is of good quality. However it shows a remaining slight pink coloration at hot state; this comes from the acrylic paint and this small problem might be overcome by choosing another colour-neutral matrix.

Fig. 7: Thermochromic paint samples at 25, 40, and 90°C

Durability study:

A simple durability test consisting in exposing the samples to high temperatures for long periods has been carried out. High degradation of pigments has been observed at temperatures beyond 160°C instead of 130°C (manufacturer's data); this indicates that encapsulation of pigments in a paint can improve their stability in a hot oxidizing environment. Samples shows a good stability of the pigments even after 64 hours at 140°C aging but the paint matrix becomes yellow and does not resist the heat treatment. Using a better matrix and Al flakes (to reduce emissivity) might lead to stable thermochromic selective black paints for low temperature applications.

Fig. 8: 2h aged black samples at 150, 160, 165, 170, 180 and 200°C

The manufacturer indicates that this kind of pigment, even if UV-treated by encapsulation, is very sensitive to UV exposure which degrades weak chemical bonds in organic molecules. Selective thermochromic paint could then be obtained by adding UV stabilizers and metallic flakes.

4. Switchable mirrors on selective coatings for absorptance switching

Switchable mirrors, that switch from reflective to transmitting states, exhibit exciting switchable optical properties. These materials show a metal-to-insulator phase transition by hydrogen absorption of rare-earth and some other elements. The most common systems are based on Magnesium [8] or Yttrium [9] in combination with Pd that is a catalyst; most of lanthanides exhibit the same properties. Such materials could be deposited with the equipment for vacuum deposition recently installed at LESO lab.

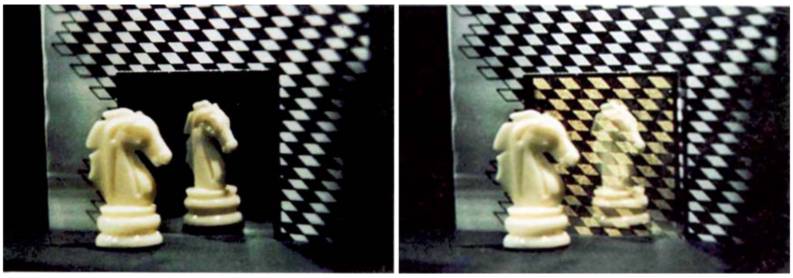

Fig. 9: Yttrium based switchable mirror in reflective (left) and transmitting (right) states [9]

Concept for α switching:

See Confidential Appendix for further details.

Gasochromic [10], electrochromic [11], chemochromic, photochromic and thermochromic [12] transitions are reported in literature. A concept has been developed in the lab for such materials to obtain an absorptance switching with temperature.

Conclusions

Promising results have been obtained concerning thermochromic inorganic layers. Computer modeling and SPF report [1] show that using an emittance switching material (5 to 35%) is sufficient to keep the temperature of thermal solar collectors under 160°C. This would protect glycol, seals, insulation materials, and the selective coating. Coupling this layer with an inorganic absorptance switching layer would fulfill the requirements for a 100°C protection of collectors. Three ways to obtain thermochromic films have been investigated and showed high quality films. **First samples of inorganic coatings showing thermochromic switching behavoir have been produced by magnetron sputtering at EPFL.** These coatings switch from a semiconducting to a metallic state at critical temperatures around 65°C, implying a resistivity change of typically three orders of magnitude. Further experiments must be carried out in order to optimize the thermochromic properties of these films, especially by adapting the switching temperature.

Samples obtained by LESO-PB's installation for vacuum evaporation showed good homogeneity. The deposition rate is higher than for sputtering; samples exhibit even optical selectivity. A substrate heater system has been constructed in order to obtain a good crystallization of thermochromic films. First samples have been produced using the new substrate heating system. A special process pressure gauge has been installed in order to precisely control the oxygen partial pressure which has to be kept within a narrow range during thin film deposition. This will enable us to produce larger thermochromic samples in a faster process.

The existing experimental infrastructure, collaborations with other groups, and the know-how of LESO-PB in thin films deposition will lead to a rapid progress concerning inorganic thermochromic materials. Not many complementary laboratory devices will be needed.

Thermotropic systems also show a good perspective. The results of PCCL come close to the optical requirements, but the organic coatings presumably not suitable for metallic collectors in terms of durability. However, for all-polymeric collectors such thermotropic coatings might become an interesting option.

Selective black paints for low temperature applications might be feasible using thermochromic organic pigments. The choice of the right matrix is critical in terms of durability, low reflectance and UV resistance. Already developed selective paints show an emissivity up to 40%; that is why this solution is not suitable for this project but for low temperature unglazed collectors.

Switchable mirrors technology is really promising concerning absorptance switching and more investigations on this subject must be done.

Technical Support

Pierre Loesch

Industry Contacts

- Collaboration with GLAS TRÖSCH for magnetron sputtering on industrial scale, novel coatings on solar collector glazing.
- ASULAB (SWATCH GROUP) donated equipment for vacuum deposition of thin films, suitable for multilayer deposition.
- A new CTI project on sol-gel deposition of nanostructured selective solar absorber coatings is in preparation with the Swiss solar collector manufacturer ENERGIE SOLAIRE SA
- Collaboration with the French company GEMINNOV which provided the thermochromic pigments.

National Collaborations

- Collaboration with Dr. Rosendo Sanjines and Henry Jotterand, Laboratory of Thin Films Physics, Prof. Laszlo Forro, Institute of Complex Matter Physics, EPFL. Experiments on magnetron sputtering and X-ray diffraction analysis
- Within EPFL, access to electron microscopes and to the facilities of TEM sample preparation is provided by the Interdepartmental Center of Electron Microscopy CIME.
- The research group of Prof. Libero Zuppiroli (LOMM at EPFL) provides access to their new ellipsometer. This contact will be useful for future measurements of the optical properties of thermochromic coatings.
- Collaboration with the research group of Prof. Peter Oelhafen, Institute of Physics, University of Basel.

International Collaboration

Collaboration with Polymer Competence Centre PCCL, University of Leoben, Austria,

- Theory and modelling of thin film optics, group Dr. Dieter Gruber.
- Discussion about polymeric materials for solar collectors, group Dr. Gernot Wallner. Discussion with Katharina Resch (same group) about thermotropic systems.

Invited talk

A. Schüler, ***Nanostructured Materials in Solar Energy Conversion***, Seminar of Condensed Matter Physics, Institute of Physics, University of Basel. October 2007.

Dissemination

Documentary ***NZZ Format: Sonne - Zukunftsenergie und Wirtschaftsmotor***, on Swiss German television channel **SF2**, 09/09/2007, 21.30h.

A considerable part of the documentary was shot in our laboratory, concerning the topics of novel colored glazing for solar thermal facade collectors, and on quantum dot solar concentrators.
The movie is available on DVD from SF2.

Awards

ABB Innovation Award 2007

Andre Kostro, ***Photonsim: development of a Monte Carlo ray tracing software for the simulation of photoluminescent solar concentrators***

Solar Energy Journal Best Paper Award 2005 – 2007

ISES world congress 2007, Beijing, China

Best Full Length Paper in Energy Conversion:

Nanostructured materials for solar energy conversion

Peter Oelhafen and Andreas Schüler

Solar Energy Vol. 79, No.2, pp.110-121

References

1. S. Brunold, P. Vogelsanger, H. Marty, 2007. ***Beurteilung der Möglichkeiten von thermochromen Schichten als potenzielle Überhitzungsschutzmassnahme für solarthermische Kollektoren***, SFOE project #43729.
2. P. Nitz, H. Hartwig, 2005. ***Solar control with thermotropic layers***, Solar Energy 79, 573-582
3. H. R. Wilson, W. Eck, 1993. ***Transmission variation using scattering/transparent switching films***, Solar Energy Materials and Solar Cells 31, 197-214.
4. H. Watanabe, 1998. ***Intelligent window using a hydrogel layer for energy efficiency***, Solar Energy Materials and Solar Cells 54, 1998.
5. A. Raicu, H. R. Wilson, P. Nitz, W. Platzer, V. Wittwer, E. Jahns, 2002. ***Facade systems with variable solar control using thermotropic polymer blends***, Solar Energy 72, 31-42.
6. K. Resch, G. M. Wallner, R. Hausner, 2007. ***All polymeric flat-plate collector – Potential of thermotropic layers to prevent overheating***. Not yet published.
7. K. Resch, G. M. Wallner, 2007. ***Thermotropic resin systems: relationship between formulation parameters, material structure and optical properties***. Not yet published.
8. B. Farangis, P. Nachimuthu, T. J. Richardson, J. L. Slack, B. K. Meyer, R. C. C. Perera, M. D. Rubin, 2003. ***Structural and electronic properties of magnesium-3D transition metal switchable mirrors***, Solid State Ionics, 309-314.
9. J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, N. J. Koeman, 1996. ***Yttrium and lanthanum hydride films with switchable optical properties***, Nature 380, 231-234.
10. I. A. M. E. Giebels, J. Isidorsson, R. Griessen, 2004. ***Highly absorbing black Mg and rare-earth-Mg switchable mirrors***, Physical Review B 69, 205111.
11. K. Tajima, Y. Yamada, S. Bao, M. Okada, K. Yoshimura, 2007. ***Durability of all-solid-state switchable mirror based on magnesium-nickel thin film***, Electrochemical and Solid-State Letters, J52-J54.
12. I. A. M. E. Giebels, S. J. van der Molen, R. Griessen, 2002. ***Thermochromic effect in*** $YH_{3-\delta}$ ***and*** $Mg_{0.1}Y_{0.9}H_{2.9-\delta}$, Applied Physics Letters 80, 1343-1346.