THE EFFECT OF SOLAR RADIATION ON THERMOCHROMIC BUILDING COATINGS: TESTING THE PERFORMANCE AND PROPOSING METHODS FOR THEIR IMPROVEMENT

Theoni Karlessi*[1], Mat Santamouris*[1]

[1]*National and Kapodestrian University of Athens, Building of Physics - 5, University Campus, 157 84 Athens, Greece*

ABSTRACT

The improvement of the urban microclimate combined with the reduction of the energy loads is a highly important target that requires the research and development of innovative solutions with advanced thermal and optical properties. Color changing thermochromic coatings being reflective in summertime and absorptive in wintertime can address to the demand of lower surface temperatures and lower cooling loads. The interaction though with the solar radiation results in the breaking of the chemical bonds and the degradation of their performance.
The present work aims to investigate various methods and techniques for the improvement of the coatings performance. Towards this direction an important step is to identify the factors that affect thermochromism. Combinations of UV and optical filters were used on thermochromic coatings applied on concrete tiles under accelerated ageing conditions of one month period in order to isolate the parts of solar spectrum that cause the photodegradation. Covering the sample with red filter which cuts off wavelengths below 600nm protects most efficiently the reversible color change of the thermochromic coating as the solar reflectance at the dark phase remains unaffected during the whole experimental period.
The promising results of this research in addition to the advantages from the color changing properties concerning energy efficiency in buildings, indoor air environment and urban microclimate, encourages further investigation of the materials and the techniques.

KEYWORDS

thermochromic coatings, photodegradation, , accelerated ageing

1 INTRODUCTION

The materials used in the urban fabric play a very important role for the microclimatic thermal balance. They absorb solar and infrared radiation and dissipate part of the accumulated heat through convective and radiative processes to the atmosphere increasing ambient temperature. Thus, the optical and thermal characteristics of the materials used determine to a high degree the energy consumption and comfort conditions of individual buildings as well as of open spaces [1-6].
The main properties of a material that control its surface temperature are the solar reflectance and the infrared emittance [7]. New generation materials and techniques that present advanced

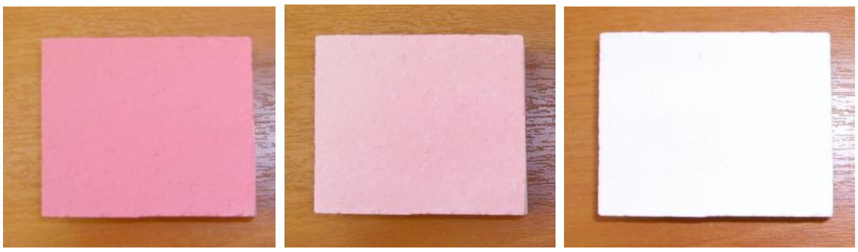
thermal characteristics, dynamic optical properties, increased thermal capacitance and a much higher heat island mitigation potential have been developed[6]. Innovative materials have the ability to be more reflective and present lower surface temperatures during the cooling period, while being more absorptive and taking advantage of the solar gains during the heating period [8]. This property can be described and analysed by thermochromism. The thermochromic effect is a change in the spectral properties of an organic or inorganic substance caused by heating or cooling. In intrinsically reversible organic thermochromic systems, heating above a defined temperature causes a change in color from darker to lighter tones. This transition is achieved by a thermally reversible transformation of the molecular structure of the pigments that produces a spectral change of visible color. When temperature decreases below the color-changing point, the system returns to its thermally stable state [11-16].
Towards this direction, thermochromic color-changing coatings have been developed and tested. Thermochromic pigments have been developed as three component organic mixtures and they were incorporated into common white coating [13, 14]. After an hour of exposure to solar radiation and for ambient temperatures below 20^{o}C the thermochromic coating could absorb almost the same amount of solar energy as an ordinary colored coating, but when the temperature was above 20^{o}C it could reflect more solar energy, presenting 4^{o}C lower temperature than the ordinary colored coating [14]. Karlessi et al. developed eleven thermochromic coatings at 30^{o}C color changing temperature by using thermochromic pigments into an appropriate binder system and tested their thermal and optical characteristics against color matching conventional and cool (highly reflective) coatings [10]. The results for the brown thermochromic coating indicate higher values for the solar reflectance (SR=0.55 for the colored and SR=0.76 for the coloreless phase) compared to the common (SR=0.18) and cool coating (SR=0.41) of the same color. Mean daily surface temperature during a hot summer was also measured and the temperature difference between common and thermochromic coatings was $\Delta T = 11.3\ ^{o}C$, and between cool and thermochromic coatings was $\Delta T = 9.2\ ^{o}C$. These results reveal the potential of thermochromic materials to avoid overheating in summertime, and absorb heat in wintertime when it is necessary.

However, photodegradation is a major problem for thermochromic materials when exposed to outdoor conditions. Interaction with solar radiation cause the breaking and/or crosslinking of the polymer chains, leading to altered chemical and mechanical properties, and loss of the reversible thermochromic effect [15, 16].
Various techniques have been tested to decrease the degradation of the thermochromic coatings and improve their outdoor performance. Experiments proved that when UV absorbers are incorporated in the thermochromic coatings the optical efficiency is not improving and the ageing problems remain. Efficiency is improved when the UV protectors are applied on the surface of the coatings but still the problem of degradation is important. UV filters with a transmittance at the UV part of the solar radiation close to zero have also been used for the photostabilization of the thermochromic coatings [6, 17-19]. Results however showed that although the optical performance improves considerably but the problem remains. This indicates that not only the ultraviolet but also other parts of the solar radiation interact with the molecular bonds, having a negative effect on thermochromism. The advantages that can be derived from their color changing properties concerning energy efficiency in buildings, indoor air environment and urban microclimate encourages further investigation [10] and results in this work.
The following study aims at the investigation of the optical performance of a thermochromic coating under accelerated ageing conditions, using combinations of UV and optical filters in order to isolate the influence of different parts of the solar radiation.

2 PRODUCTION AND APPLICATION OF THERMOCHROMIC COATINGS

For the production of the thermochromic coating, organic water based red thermochromic pigments of powder form and color changing temperature of 25^oC were used. An appropriate binder system that should not itself absorb infrared radiation was produced for the development of the thermochromic coatings. The system composed of water (32%), thermochromic pigment red (12%), titanium dioxide (9%) in order to avoid transparency at the colorless state and other additives. With a temperature increase above 25^oC the thermochromic coating becomes transparent, revealing the color of the substrate.

The thermochromic coating was applied on concrete tiles, size of 6cm x 6cm. In Fig.1 the thermochromic sample in three different thermal phases before the exposure to accelerated ageing conditions is presented. Figure 1(a) depicts the sample in full coloration at a temperature of 10^oC, while in Figure 1(c) the sample is completely decolorized at a temperature of 35^oC. An intermediate phase is presented in Fig.1(b).



a. b. c.

Figure1(a) Full coloration, (b) Intermediate phase, (c) Full decoloration

3 EXPERIMENTAL PROCEDURE OF ACCELERATED AGING

Accelerated ageing of the samples was performed in an Accelerated Ageing Xenon Test Chamber (Q-SUN, Xe-3HS) [20] for one month period in a 24 hours basis according to the specifications and requirements of ISO 11341: Paints and varnishes -Artificial weathering and exposure to artificial radiation- Exposure to filtered xenon arc radiation [21]

In order to protect the samples from the exposure to accelerated ageing conditions optical and UV filters were used: red filter, yellow blue and green filters and UV glass filter. The filters were placed on top of the samples covering the thermochromic surface. All measurements were performed every five days of exposure for a total time period of 30 days.

The transmittance of the filters at a range of 300-2500nm is presented at Fig.2.The appropriate selection of the filters was based on their transmittance range and the aim was to cover partially the whole wavelength range, providing thus the ability to isolate the influence of the ageing conditions in each part of the spectrum and for each filter.

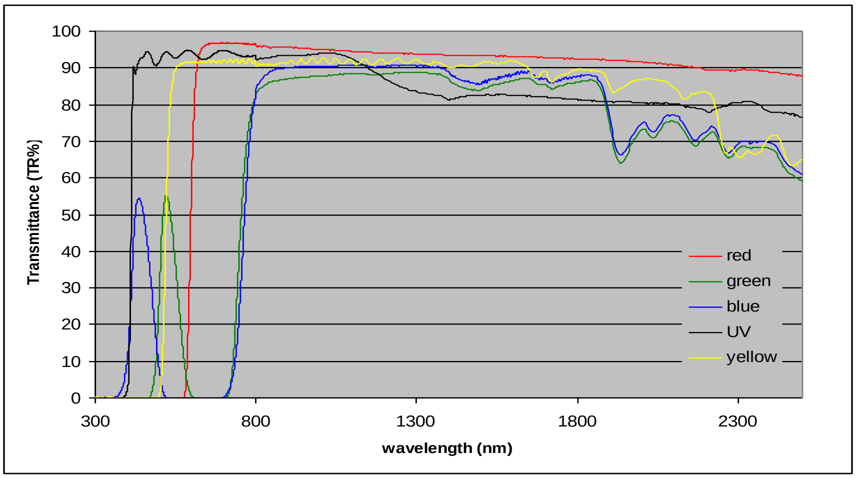
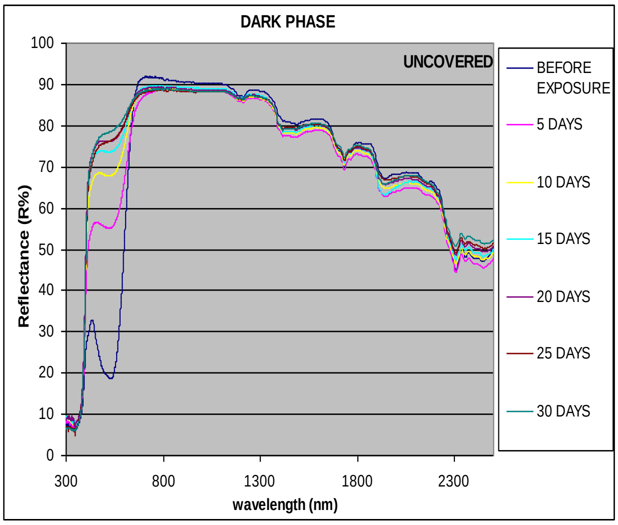


Figure 2: Transmittance of the filters at a range of 300-2500nm

3.1 Measurements of solar reflectance

The spectral reflectance of the samples was measured at a range of 300-2500nm of the solar spectrum that includes a part of the ultraviolet radiation (UV: 300-400nm), the visible (VIS:400-700nm) and the near infrared part (NIR: 700-2500nm). A UV/vis/NIR spectrophotometer (Varian Carry 5000), was used for measuring the spectral reflectance of the samples. Figure 3 presents the spectral reflectance for every five days of exposure of the uncovered and the sample with the UV and the optical red filter in the dark phase.



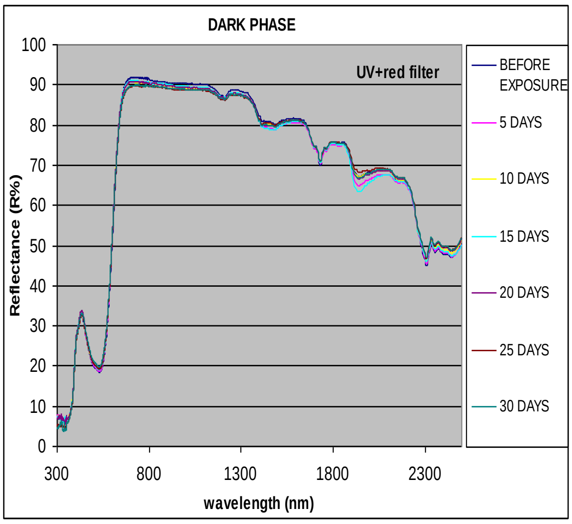


Figure 3: Spectral reflectance of the uncovered and UV+red filter sample at the dark phase

Tables 1, 2 present the calculated values of solar reflectance for the sample covered with UV+red filter for the dark and white phase respectively. Tables 3, 4 present the calculated values of solar reflectance for the uncovered sample.

Table 1 Solar reflectance (%) of the sample covered with UV+red filter at the dark phase

UV+red filter	BEFORE EXPOSURE	5 DAYS	10 DAYS	15 DAYS	20 DAYS	25 DAYS	30 DAYS
SR	68	67	68	68	68	67	67

SRir	**86**	**85**	**85**	**85**	**85**	**85**	**85**
SRvis	**45**	**45**	**45**	**45**	**45**	**45**	**45**
SRuv	**7**	**7**	**7**	**7**	**7**	**6**	**6**

Table 2 Solar reflectance (%) of the sample covered with UV+red filter at the white phase

UV+red filter	BEFORE EXPOSURE	5 DAYS	10 DAYS	15 DAYS	20 DAYS	25 DAYS	30 DAYS
SR	**84**	**84**	**84**	**84**	**84**	**83**	**83**
SRir	**85**	**85**	**85**	**85**	**85**	**85**	**84**
SRvis	**88**	**89**	**89**	**88**	**88**	**86**	**85**
SRuv	**7**	**8**	**8**	**8**	**8**	**6**	**6**

Table 3 Solar reflectance (%) of the uncovered sample at the dark phase

UNCOVERED	BEFORE EXPOSURE	5 DAYS	10 DAYS	15 DAYS	20 DAYS	25 DAYS	30 DAYS
SR	**68**	**74**	**78**	**79**	**80**	**80**	**80**
SRir	**86**	**83**	**84**	**84**	**84**	**84**	**84**
SRvis	**45**	**64**	**73**	**77**	**79**	**78**	**80**
SRuv	**7**	**8**	**8**	**9**	**9**	**7**	**7**

Table 4 Solar reflectance (%) of the uncovered sample at the white phase

UNCOVERED	BEFORE EXPOSURE	5 DAYS	10 DAYS	15 DAYS	20 DAYS	25 DAYS	30 DAYS
SR	**84**	**77**	**80**	**80**	**78**	**76**	**75**
SRir	**85**	**83**	**84**	**84**	**85**	**84**	**83**
SRvis	**88**	**73**	**78**	**80**	**73**	**69**	**68**
SRuv	**7**	**8**	**8**	**9**	**7**	**5**	**5**

3.2 Measurements of color coordinates

The Carry Color Calculations application is an module which allows to perform calculations on data collected by Varian Carry 5000. Calculations are performed for tristimulus values X, Y, Z, chromaticity coordinates x, y, z and color coordinates for CIE L*a*b*. Color difference ΔE^*_{ab} is also calculated. The set-up is for a selectable wavelength range of 380-780nm at an interval of 1nm, with a D65 illuminant and a CIE (1964) 10° degrees observer. Figure 4 shows the color difference the last day of exposure for each sample for the dark and the white phase.

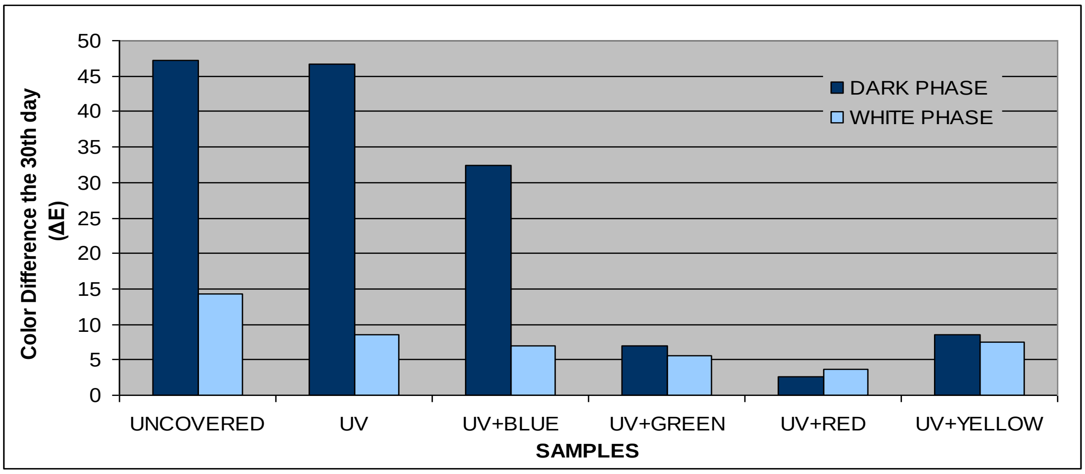


Figure 4: Color Difference (ΔE) the 30th day for each sample

Figures 4, 5 present the variation of brightness L* for the whole experimental period for the uncovered sample and the sample covered with UV and red filter respectively.

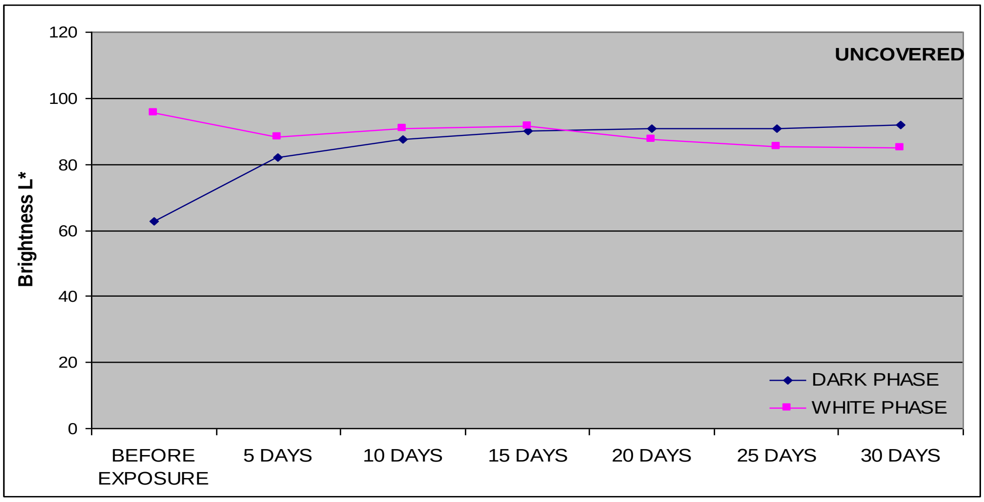


Figure 4: Variation of brightness L* for the uncovered sample

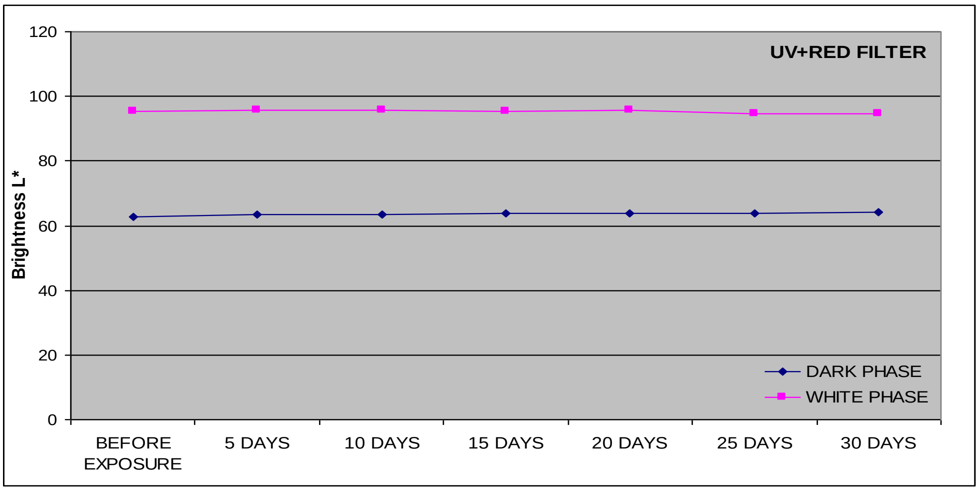


Figure 4: Variation of brightness L* for the sample covered with UV+red filter

4 ANALYSIS OF THE RESULTS

Solar reflectance for all the samples tested increases in the dark phase, while in the white phase decreases. The variation of solar reflectance is mainly in the visible part of the spectrum. The uncovered sample, 30 days after the exposure to accelerated ageing conditions has increased SR value by 8% and SRvis by 16% at the dark phase compared to its condition before exposure. At the white phase, the reduction of SR is 7.6% and of SRvis is 17.6%. The use of UV filter did not improve significantly the dark phase of thermochromic effect. Thus, the cut-off of the ultraviolet radiation does not ensure the improvement of the thermochromic behaviour of the samples. The results of the use of optical filters prove that besides the UV part of the radiation, there are parts of the visible that also affect and degrade the thermochromic properties. The greatest degradation is presented to the sample with the blue filter. Covering the sample with red filter which cuts off wavelengths below 600nm protects most efficiently the reversible color change of the thermochromic coating as the solar reflectance at the dark phase remains unaffected during the whole experimental period. The white phase presents the lowest change compared to the other samples, 0.8% for SR and 2.6% for SRvis.

The results are confirmed by the color measurements. Brightness L* at the dark phase increases, while at the white increases. For the uncovered sample and the sample with the UV filter the biggest change in brightness is remarked during the first 10 days of exposure. Afterwards, the brightness in both phases matches as the thermochromic properties are lost and the color change is irreversible. At the sample with the red filter that provides the best protection of thermochromic characteristics the change of brightness is 2.5% for the dark and 1% for the white phase. The results of color change ΔE are in accordance with the previous results. As observed in Fig.4, the higher values until the last day of exposure are remarked for the uncovered sample and the sample with the UV filter, equal to 47 in both samples at the dark phase and 7 and 8.5 in the white phase respectively. The results for the combination of UV and red filter present the lowest ΔE equal to 2.6 at dark phase and 3.6 at white. The variation of ΔE at the sample with the red filter is minor.

5 CONCLUSIONS

Thermochromic systems can contribute to the improvement of the urban microclimate and the decrease of energy loads. For high temperatures, during summertime thermochromic coatings have the ability to reflect solar energy, reducing the surface's temperature, while in wintertime absorb solar energy, increasing the surface's temperature as reversible color change takes place.

However, photodegradation is a major problem for thermochromic materials when exposed to outdoor environment. Various methods have been tested by applying different UV absorbers with different techniques in the thermochromic coatings, in order to photostabilise the color changing effect of the material. The results though show that the performance of the thermochromic material was not improved and the degradation problems remain. This indicates that not only the ultraviolet but also other parts of the solar radiation interact with the molecular bonds, having a negative effect on thermochromism.

The scope of this work is to detect the parts of solar radiation that damage thermochromism. For this reason six samples of red thermochromic coating applied on concrete tiles were prepared and covered with different combinations of UV and optical filters. The samples were submitted to accelerated aging conditions for one month period and their optical characteristics (reflectance, color coordinates and color difference) were periodically measured.

Variation of SR is mainly detected at the visible part of the spectrum. The uncovered sample, 30 days after the exposure to accelerated ageing conditions has increased SRvis value by 16% at the dark phase compared to its condition before exposure. At the white phase, the reduction of SRvis is 17.6%. The degradation of thermochromic properties was observed mostly at the samples were the filters are transparent at the parts of the visible spectrum closer to the

ultraviolet, mainly in blue, green and yellow, while the sample with red filters remained unaffected at the dark phase and changed slightly at the white.
The results of color change ΔE are in accordance with the reflectance results. The higher values until the last day of exposure are remarked for the uncovered sample and the sample with the UV filter, equal to 47 in both samples at the dark phase. The results for the combination of UV and red filter present the lowest ΔE equal to 2.6 at dark phase and 3.6 at white. The variation of ΔE at the sample with the red filter is minor.
The stabilization of one thermochromic sample under intense and prolonged weathering conditions that is accomplished in this work is a breakthrough in the field of thermochromism. Considering also the advantages that can be derived from the color changing properties concerning energy efficiency in buildings, indoor air environment and urban microclimate encourages further investigation.

6 REFERENCES

[1] Doulos, L., Santamouris, M., Livada, I., Passive cooling of outdoor urban spaces. The role of materials. Solar Energy 77 (2001), 231–249.

[2] Synnefa, A., Santamouris, M., Apostolakis, K., 2007a. On the development, optical properties and thermal performance of cool colored coatings for the urban environment. Journal of Solar Energy 81, 488–497.

[3] Synnefa, A., Santamouris, M., Akbari, H., 2007b. Estimating the effect of using cool coatings on energy loads and thermal comfort in residential buildings in various climatic conditions. Journal of Energy and Buildings 39, 1167–1174.

[4] Akbari, H., Davis, S., Dorsano, S., Huang, J., Winert, S., 1992. Cooling our Communities – A Guidebook on Tree Planting and White Colored Surfacing. US Environmental Protection Agency, Office of Policy Analysis, Climate Change Division.

[5] Santamouris, M., Adnot, J., Alvarez, S., Klitsikas, N., Orphelin, M., Lopes, C., Sanchez, F., 2004. Cooling the Cities. Eyrolees, Paris, France, ISBN: 2-911762-54-1.

[6] Santamouris, M., Synnefa, A., Karlessi, T., Using advanced cool materials in the urban built environment to mitigate heat islands and improve thermal comfort conditions, Solar Energy, Volume 85, Issue 12 (2011), 3085-3102

[7] Akbari, H., Bretz, S., Taha, H., Kurn, D., Hanford, J., Peak power and cooling energy savings of high albedo roofs. Journal of Energy and Buildings – Special Issue on Urban Heat Islands and Cool Communities, 25(2) (1997), 117–126.

[8] Karlessi, T., Santamouris, M., Apostolakis, K., Synnefa, A., Livada, I., Development and testing of thermochromic coatings for buildings and urban structures, Solar Energy, 83 (2009), 538–551.

[9]White, M.A., LeBlanc, M., 1999. Thermochromism in commercial products. Journal of Chemical Education 76, 1201–1205.

[10] Ma,Y., Zhu, B., Research on the preparation of reversibly thermochromic cement based materials at normal temperature, Cement and Concrete Research 39 (2009) 90-94

[11] Ma, Y., Zhu, B., Wu, K., Preparation and solar reflectance spectra of chameleon-type building coatings, Journal of Solar Energy 70 (2001), 417–422.

[12] Ma, Y., Zhang, X., Zhu, B., Wu, K., Research on reversible effects and mechanism between the energy-absorbing and energy-reflecting states of chameleon-type building coatings. Journal of Solar Energy 72 (2002), 511–520.

[13] Lopes, F., Neves, J., Campos, A., Hrdina, R., Weathering of Microencapsulated Thermochromic Pigments, Research Journal of Textile and Apparel 13 (2009), 78-89

[14] Bamfield, P., 2001. Chromic phenomena, technological applications of color chemistry. Royal Society of Chemistry, 33–41.

[15] Pospisil, J., Nespurek, S., Photostabilization of coatings. Mechanisms and performance. Progress in Polymer Science 25 (2000), 1261–1335

[16] Berdahl, P., Akbari, H., Levinson, R., Miller, W.A., Weathering of roofing materials – an overview, Construction and Building Materials 22 (2008), 423–433.

[17] Pospısil,J., Pilar,J., Billingham, N.C, Marek, A., Horak Z., Nespurek,S., Factors affecting accelerated testing of polymer photostability Polymer Degradation and Stability 91 (2006) 417-422

[18] ODA, H., PHOTOSTABILIZATION OF ORGANIC THERMOCHROMIC PIGMENTS: ACTION OF BENZOTRIAZOLE TYPE UV ABSORBERS BEARING AN AMPHOTERIC COUNTER-ION MOIETY ON THE LIGHT FASTNESS OF COLOR FORMERS DYES AND PIGMENTS VOLUME 76, ISSUE 1 (2008) 270–276

[19] ODA, H., PHOTOSTABILIZATION OF ORGANIC THERMOCHROMIC PIGMENTS. PART 2: EFFECT OF HYDROXYARYLBENZOTRIAZOLES CONTAINING AN AMPHOTERIC COUNTER-ION MOIETY ON THE LIGHT FASTNESS OF COLOR FORMERS DYES AND PIGMENTS VOLUME 76, ISSUE 2,(2008) 400–405

[20] Q-Lab http://www.q-lab.com/products/q-sun-xenon-arc-test-chambers/q-sun-xe-3

[21] ISO 11341: Paints and varnishes -Artificial weathering and exposure to artificial radiation- Exposure to filtered xenon arc radiation.