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Thermochromism applied to Transportation Engineering: asphalt roads and paints

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Abstract. Thermochromic materials change their optical response to temperature reversibly. This study explores the application of thermochromism to road engineering, which is still incipient in this area, from two perspectives. The first one is about the development of functionalized road markings (FRM) working as thermochromic sensors to alert the presence of ice on the road and, in this way, to improve road safety. The second one concerns the functionalization of asphalt pavements for reversible color change at high temperatures to reduce energy absorption in the form of heat and, in this way, mitigate Urban Heat Islands (UHI) effect. For the development of the FRM, thermocapsules were added into acrylic ink, applied to an AC10 asphalt mixture, submitted to high and low temperatures, and visually characterized. For the functionalization aiming for UHI reduction, thermochromic solutions (TS) containing thermocapsules, dye, and resin were superficially sprayed at an AC10, and the Quick Ultraviolet Accelerated Weathering Test (QUV) was performed with subsequent Colorimetry Analysis, where the color coordinates defined by the *Comissione Internationale de l' Éclairage* (CIE) were measured. The results show that it is possible to functionalize road marks to work as a thermochromic sensor. Also, this property can be improved by synthesizing or using thermocapsules with TT closer to the water melting point. The results also indicate that the asphalt pavement functionalization with surface spraying of TS points out to higher luminosity results in terms of color coordinate, which is intended for the mitigation of heat energy absorption, consequently mitigating the UHI.

Keywords: road safety, urban heat island, thermochromism, smart asphalt, road engineering

1. Introduction

Smart materials (SM) modify their physical properties when submitted to external stimuli, such as pH, chemical composition, or temperature [1,2]. Chromogenic materials are SM that can reversibly change color [3] and can be grouped into various categories depending on the source of modification, such as thermochromic (temperature), photochromic (visible or UV light), electrochromic (electrical field), piezochromic (pressure), and chemochromic (chemical composition) [1].

Thermochromic materials (TM) change their optical response reversibly due to temperature changes and undergo this process at a specific transition temperature (TT) as a result of a chromogenic core [4]. TM ensure various possible applications and provide a high simplicity of implementation [1], having potential application in aerospace, military, textile, and construction fields, with some functions related to smart windows, sensors, functional coatings (paints, printing, and inks), and anti-counterfeiting technology as well [5].

TM can be classified concerning the mechanisms of revealing thermochromic behaviour in dye-based, and non-dye. The dye-based works through the proton transfer of dyes embedded in a polymer matrix or by proton transfer reactions in Leuco dyes, as seen in Figure 1. The non-dye presents a color change associated with the effects at nano-scale or molecular rearrangements by temperature change [4]. Leuco dye thermochromic systems change from the colorless to the colored state through the temperature change and consist of three components: color former (Leuco dye), color developer, and co-solvent; the melting point of the co-solvent determines the temperature at which the color change occurs [4,6–8]. They have a TT consistent with the building sector and a low cost of production [9]. The main downside to the practical application of dye-based thermochromic coatings and materials is their fast aging [4,10]. For this reason, microencapsulation is used to hold the system stable and protected [11].

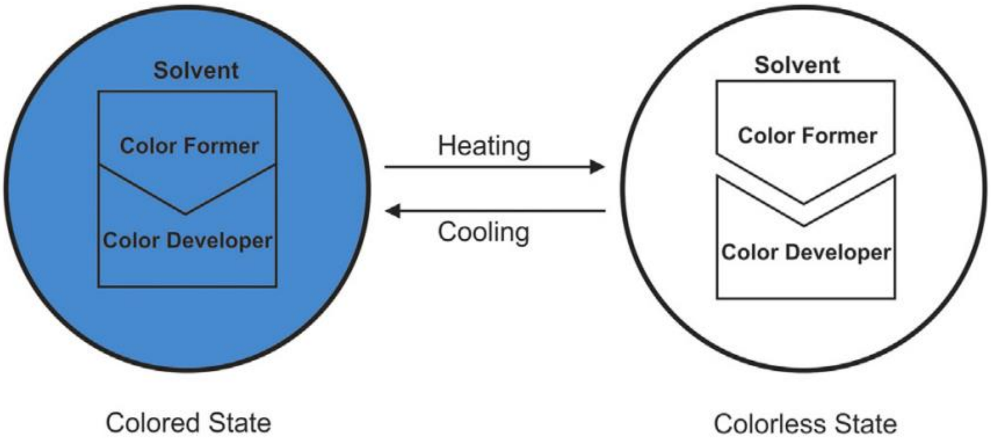

Fig.1: Thermochromic mechanism in Leuco dyes [4]

In the road engineering field, thermochromism studies are still incipient, intending to control the variation and amplitude of temperature to avoid reducing the mechanical performance of asphalt pavements [12]. However, other approaches can be given to the insertion of TM in this area, such as the application of TM to road signs to make them serve as a thermochromic sensor at low temperatures and indicate the presence of ice on the road surface; as well as the functionalization of the asphalt pavement surface to reduce energy absorption in the form of heat due to the dark color of the pavement and, in this way, mitigate Urban Heat Islands (UHI) effect.

Road signs acting as a thermochromic sensor can indicate that the pavement friction is reduced, such as in situations where there is ice on the road surface, and induce a change in driving behavior, avoiding accidents and thus improving road safety. The second approach considers the influence of the high temperatures on the pavement, which, besides negatively affecting some mechanical characteristics of asphalt mixtures, are related to UHI. This phenomenon has a high impact on the environment, human health, and electricity and fuel consumption increase to maintain thermal comfort [13]. This phenomenon is aggravated by the high rates of absorption of energy in the form of heat due to the dark coloration of asphalt pavement. Therefore, the functionalization with TM intends to mitigate this effect and its unintended consequences.

In the present work, two applications of TM in Road Engineering are presented, by functionalizing a road paint and an asphalt mixture. In both situations, temperature sensitivity leads to a color change for each intended purpose.

2. Road markings as thermochromic sensor

The production of the smart ink aimed at functionalizing commonly used inks in horizontal road signs (road marks), water-based acrylic inks, to develop the thermochromic sensor and be able to change color reversibly when the specimen reaches low temperatures.

The functionalization consisted of the volume incorporation of commercial thermocapsules (Chromazone - Colour changing, heat sensitive) within the water-based acrylic ink (5% w/w) and stirring of the blend by a magnetic stirring of 300 rpm for 30 min.

The functionalized paint was applied over an AC10 asphalt mixture and allowed to dry for 48 hours. For visual characterization, the specimen containing the smart paint was cooled to temperatures near 0 °C and then heated to approximately 25 °C. The visual characterization of the sample took place at a controlled temperature and a video of the aforementioned test can be accessed online [14].

According to the video and Figure 2, the ability to change color of the paint applied over the asphalt mixture was verified, possessing a notable and significant color change response to the temperature variation applied to the specimen, being possible to work as a thermochromic sensor to serve as alert to drivers when there is ice on the pavement surface and, consequently, reduced friction. The use of computer graphic simulation can be an ally in understanding which are the best colors to this purpose, whether this technology can be applied to other road sign elements, and their effects on drivers' behavior.

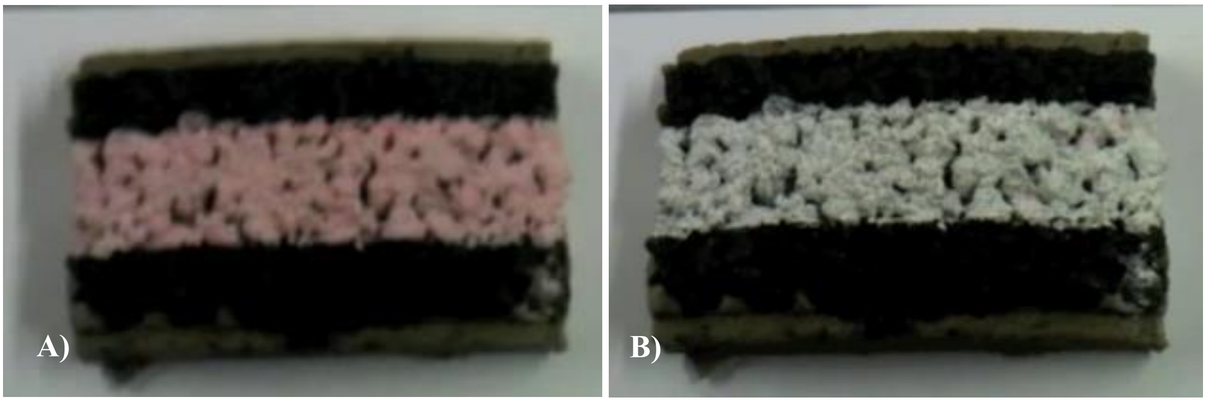

Fig. 2: Smart road signs applied to asphalt mixtures: A) 1 °C and B) 25 °C

3. Asphalt pavement as UHI avoidance

For the functionalization of the asphalt mixtures able to change color at high temperatures, the following materials were used: commercial thermocapsules (Chromazone - Colour changing, heat sensitive), yellow dye, resin, and asphalt mixture AC10.

The asphalt mixture was functionalized by surface spraying of the thermochromic solution containing an aqueous solution of thermocapsules (3% w/V), dye (0.5% w/V), and resin (20 ml); other solutions containing only some of these elements were also tested.

When the solution is subjected to a thermal gradient, going to high temperatures (above 30 ºC), the thermocapsules, initially with a dark color, become colorless. When the dye was added, the color that the user will perceive will be the predominant color of the dye, in this specific case of Figure 3, yellow. In case of the absence of the dye, the perceived color would be the dark color from the asphalt mixture.

Figure 3 shows an example of non-functionalized AC10 and functionalized AC10 at a temperature above 30 °C, where it is possible to identify the change in surface color of the asphalt mixture due to the deactivation of the thermocapsules and perception of the dye coloration.

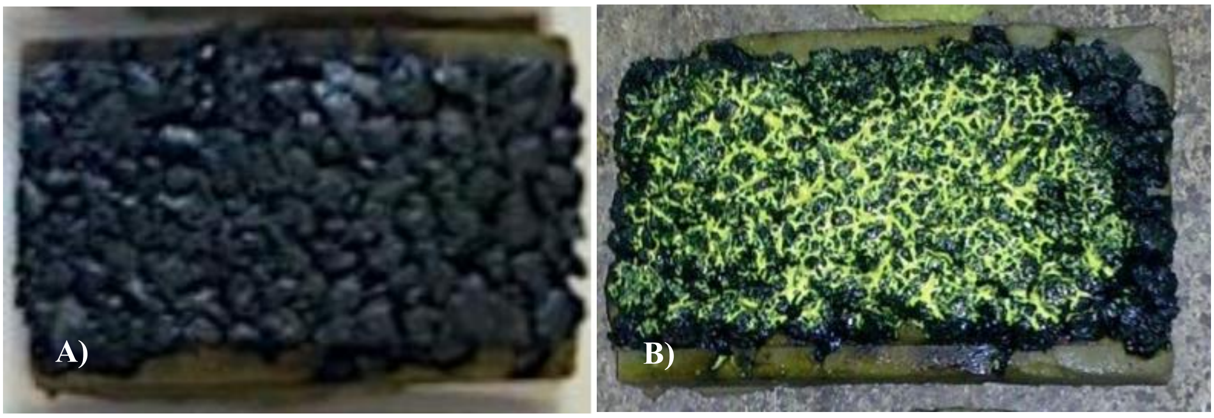

Fig. 3: Asphalt mixture, AC10, A) non-functionalized and B) functionalized at 40 °C

For the characterization of the asphalt mixture AC10, after the subsequent surface functionalization, the analysis of resistance to accelerated environmental degradation was performed through the Quick Ultraviolet Accelerated Weathering Test (QUV), with subsequent analysis of colorimetry through the color coordinates measurement for the dwell time in the QUV test. To do this, the asphalt mixture samples sprayed with the thermochromic solution were conditioned 48-hours, at 30 ºC, inside the test chamber, which simulates, through fluorescent lamps and UV lamps, the environmental conditions. The color coordinates were measured at the end of the QUV test using the Minolta CM-2600d portable Spectrophotometer equipment, providing a perception of the color values of the samples, in spatial terms L*, a*, and b*, as defined by the *Comissione Internationale de l' Éclairage* (CIE), as well as ΔE*, which works as a perceptibility factor and indicates the value of the color difference, but not the direction [15]:

$$\Delta E^{*} = \sqrt{(\Delta \mathrm{L}^{*})^{2} + (\Delta \mathrm{a}^{*})^{2} + (\Delta \mathrm{b}^{*})^{2}} \qquad (1)$$

In effect, L* represents the range from black (L* = 0) to white (L* = 100), a* the change from red (+) to green (-), and b* the change from yellow (+) to blue (-).

The results of the color coordinate measurements are shown in Table 1, where the first row indicates the samples tested. The functionalization conditions of these samples were the following:

- AC10+T: asphalt mixture sprayed with aqueous thermocapsules solution.
- AC10+T+D: asphalt mixture sprayed with the aqueous solution of thermocapsules and dye.
- AC10+T+D+R: asphalt mixture sprayed with an aqueous solution of thermocapsules, dye, and resin.
- AC10+D: asphalt mixture sprayed with an aqueous solution of dye.
- AC10+D+R: asphalt mixture sprayed with an aqueous solution of dye and resin.
- AC10+T+R: asphalt mixture sprayed with an aqueous solution of thermocapsules and resin.

The results for sample AC10+T showed the lowest values of ΔE*, which was already expected, since the thermocapsules have a dark color at room temperature and the surface where they were sprayed (asphalt mixture). Therefore, if there is the degradation of the thermocapsules, the phenomenon cannot be gauged through this analysis since the ΔL* value is relatively low (around zero) due to the equally dark color of the thermocapsules and the bitumen.

Table 1: Color coordinates at the end of the QUV test.

Color coordinate	AC10+T	AC10+T+D	AC10+T+D+R	AC10+D	AC10+D+R	AC10+T+R
ΔL*	0.58	1.54	4.69	-2.33	-10.93	-3.29
Δa*	-2.12	-0.51	1.62	0.25	0.11	-2.09
Δb*	0.5	0.17	4.5	-1.55	-3.24	3.09
ΔE*	1.2	1.54	8.66	2.36	10.93	7.26

For sample AC10+T+D there is a small increase in the ΔL* parameter, which is due to the partial degradation of the thermocapsules and thus the partial exposure of the dye. As for sample AC10+T+D+R, a considerable increase in the ΔL* parameter and a high value of the perceptibility factor, ΔE*, are observed. This sample is distinguished from the previous one only by adding resin. The addition of resin contributed to greater degradation of the thermocapsules and, consequently, greater dye exposure. However, sample AC10+D, which contains only dye on the asphalt bitumen surface, shows a significant decrease in the ΔL* parameter, indicating that the QUV test also promotes dye degradation. Samples AC10+D+R and AC10+T+R show a greater decrease in the ΔL* parameter, which may mean that the QUV test can trigger photochemical reactions between the resin and the other components and, consequently, contribute to their degradation.

4. Conclusions

In the present work, asphalt mixture substrates were modified through the application of smart paints and solutions at the surface containing TM for road safety and UHI reduction purposes, respectively. Subsequently, they were subjected to visual characterization and tests to analyze the optical characteristics promoted by the functionalization. The following conclusions were reached:

- The visual characterization of the samples with the smart paint containing thermocapsules showed that by applying a temperature gradient on this sample at low temperatures (where ice is likely to occur on the pavement surface), the paint on the asphalt mixture takes on a pinkish coloration. As the temperature on the surface of the sample approaches the ambient temperature, the color of the road paint takes on the original white color.
- To evaluate the behavior of the asphalt mixtures functionalized by spraying a thermochromic solution on the surface, exposure to the real environment was simulated from QUV tests with subsequent measurement of the color coordinates of the samples. Some aspects can be emphasized: the samples that contained aspersed solutions with thermocapsules, dye, and resin showed high values of ΔE* (a perceptibility factor that quantifies the color difference) and the highest increases of ΔL* (color coordinate variation that indicates the values from black to white), pointing to higher brightness results, which is intended for the mitigation of heat island effects. The performance of the sample containing only dye on the asphalt bitumen surface indicates that the QUV test also promotes dye degradation.

In summary, it is inferred that it is possible to functionalize horizontal road paints as a thermochromic sensor, thereby alerting drivers to the presence of ice on the road surface. Thus, they will receive the necessary feedback to change their behavior and improve road safety. Furthermore, this property can be enhanced by synthesizing or using thermocapsules with TT closer to the melting point of water. Concerning the asphalt mixtures surface-sprayed with thermochromic solutions, they showed that there is color change capability, thus that functionalization has the potential to contribute to the reduction of energy absorption in the form of heat by asphalt pavements, mitigating the heat island effect. However, a better immobilization of the solution on the bituminous substrate needs to be studied, and the assessment of the pavement surface temperature with and without functionalization in a real-world application.

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