SENSORTEX: Implementation of chromic functionalities in textile materials

Part 2: NEW THERMOCHROMICS

New developments making thermochromics useful for function-driven features (visual monitoring) in textile applications

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1. Introduction

Temperature can be considered to be the most explored stimuli in the case of chromatic sensoric functionalities. Although some milestones have been reached, most of them were design-driven on (mostly) non-textile substrates, based on novelty, gadget effects and with little emphasis on the **sensing** function, its accuracy or interpretation, durability (process stability, colour fading, fastness properties), ecological and health/toxic aspects. The lack of a knowledge background and adapted 'chromic' host-systems has until now limited their actual exploitation for textile purposes.

Therefore, the focus of a two-year Flemish collective research Sensortex-project was mainly on thermochromic systems that change colour in a controlled way when the temperature is varied. During the project we focus on FUNCTION-DRIVEN features (**visual monitoring**, the colour change can give a visual warning to the user). In the selection of the sensor the trigger can induce either a reversible colour change or an irreversible change.

Until now, this approach was still an almost unexplored issue, although the potential applications for such cost-driven or high added value textiles for niche markets are huge.

2. Conventional thermochromics – actual problems

Thermochromic encapsulated dyes were developed a number of years ago, and primarily incorporated into plastic or paper for wide commercial applications. For potential textile applications, two main systems of thermochromism have yet been explored. The first, using leuco dyes, gives rise to reversible changes between two colours (or between a colourless and coloured state) upon exceeding a temperature threshold. The second, using liquid crystals, gives rise to a continuous spectral change over a range of temperature. The high cost of liquid crystals and restriction in the effective temperature range excluded this approach in our research project.

Leuco compositions are (mostly) reversible systems whereby the spectral absorption reverts to the original following the removal of the heat source. The two-way thermochromic colour change based on leuco dyes is generally provided by a multicomponent system, consisting of a pH-sensitive colour, a developer (mostly Bisphenol A), and a readily fusible, solid, non-polar co-solvent medium. The colour development of the ternary system depends on the melting point of the solvent used. The change is in general from coloured to colourless. These three agents are generally put inside a closed system or microcapsule. This consists of a core containing the thermochromic system and a coating or shell of a polymeric material (single wall, especially made of melamine-formaldehyde based). The encapsulated thermochromic dyes undergo a colour change over a specific temperature range. The dyes currently available change from a particular colour at low temperature to colourless at a high temperature.

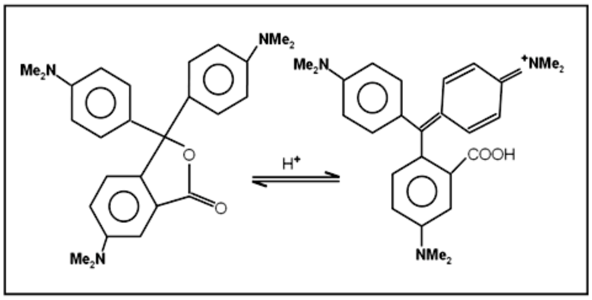

Figure 1: thermochromic dyestuff (lactone type)

In the frame of the project different thermochromics, delivered by six international suppliers were tested and evaluated on the level of the chromic sensors and textile supports treated with these chromics.

The Sensortex have revealed the multiple critical issues dealing with the application of actual microcapsules and illustrated that these commercial available chromics *cannot be* used for an accurate visual monitoring.

Critical issues are multiple:

a. On the level of microcapsules

Actual capsules suffer from weakness mainly due to a residual permeability of the capsule wall to polar solvents or other chemicals: some of them succeed penetrating through the capsule wall, and “unset” the formulation of the internal phase.

Most microcapsules suffer from a non-homogenous particle size and distribution, due to non-optimized emulsion and microcapsulation procedures (figure 2).

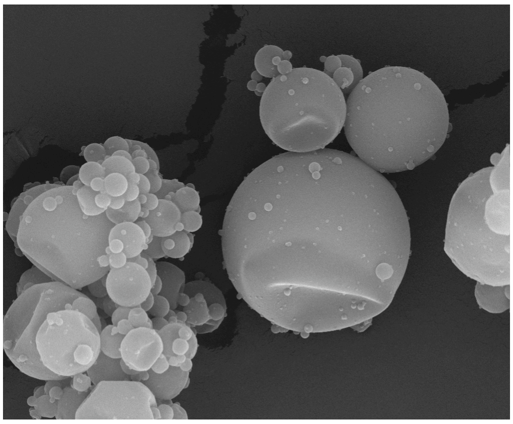

Figure 2: SEM picture of commercial available microcapsules

And above all, actual microcapsules have a not well-defined clearing or critical point (temperature at which reversible colour change take place in response to the temperautre stimuli). This is particularly important because the end use application of the thermochromic dyes will depend primarily on the critical temperature. Indeed, the majority of microcapsules show a ‘broad’ T-window dependency (a few degrees, often > 4 degrees) and this is not suitable for most of the intended end-uses (for example: use of chromic sensor for the accurate measurement of body temperature as fever). Moreover, the reversible change is in most cases too slow and after a certain number of reversible changes there is a shift in critical point.

And finally most commercial microcapsules contain Bisphenol A as acid activator. However, this product is toxic and is already forbidden in some countries. Therefore, the selection of new acid activators is quite important in view of toxicity and to preserve the durability of a thermochromic dye as it may cause an irreversible colour change in due course of time and during application.

> On the level of the host-system and textile supports

The actual microcapsules cannot be used on textiles as such but they must be compounded in an adapted ‘host-system’. *The host-systems must provide in a better durability and at the same time they must sustain the efficiency of the chromic effect, which is not an easy job!*
In the Sensortex-project especially *waterborne, thermocurable host-systems were examined. The host-system usually consists of* a binder (or mixture), a catalyst and other processing additives (dispersant, wetting agent, thickener). After application (impregnation, coating/printing) of the compound, the textile material is dried and heated at high temperature (≥ 150 °C during a few minutes) in order to fix the chromics properly

onto the fibres.

However, the project revealed that a lot of the actual thermochromics are sensitive to high temperature. Moreover the interaction of components in the host-systems with the microcapsules can have an adverse affect. If not properly chosen, the host-system can be harmful to the thermochromic dyes during high temperature applications (read: drying and fixation) or during end-use and storage. Reducing the shelf life of the thermochromic dyes makes the reuse of residual compounds after an application also impossible, resulting in a higher cost, a waste of relative expensive products and increased water pollution.

As a consequence also UV-curable systems (100 %) were examined as host-systems giving extra possibilities, allowing a broader scope of useful thermosensitive chromics (indeed, curing is done at nearly room temperature).

Furthermore water, some chemicals, abrasion… can limit their use. The Sensortex-project revealed that these fastness properties are mainly *'host-system' dependable*.

Finally, not be neglected is the influence of the textile support itself on the durability and efficiency of the chromics. During the study we noted that some textile supports, depending on type, chemistry and presence of additives can influence these items. One of the reasons is the impact of additives on the permeability and hardness of the microcapsules, resulting in "unsetting" the formulation of the internal phase.

3. New thermochromic systems

Based on these findings, TO_2C started collaboration with national and international companies in order to counteract these disadvantages and restrictions and to develop new thermochromics for *function driven* purposes.

Key drivers for this collaboration were:

- To develop new chromic microcapsules based on modified emulsion and microencapsulation procedures and at the same time avoiding the ecological, toxic properties of the actual microcapsules (read: use of less toxic products as building components for the microcapsules)
- Incorporation of the chromics in adapted and engineered host-systems (compounding, waterbased and UV-curable systems)
- Finally, the chromic compounds must be applicable within an acceptable economic and ecological context (competitive cost and with low impact on the pollution) using existing application technologies (coating, conventional and valve-jet printing) and with respect to especially healthy and non-toxic issues.

As a result of this successful collaboration ***new thermochromics*** were developed, consisting of :

a. New thermochromic microcapsules with alternative 'neutral' capsule walls resulting in adapted mechanical hardness, non-permeability for chemicals and transparency.
b. More uniform particle size and distribution of the microcapsules (average size of the new microcapsules is between 3-5 µm, figure 3)
c. The engineering and optimization of chromic compounds (microcapsules and host-systems), result in unique microcapsules characterised with an accurate controllable colour change temperature: the colour-change can take place at different temperatures from -15 ° till 80 °C (critical point) in a narrow window (**max. 1 °C**) (e.g. just below a person's external body temperature so that a colour change occurs in response to a human touch). Moreover, the thermochromics in combination with the incorporation within a suitable host-system enables us to manipulate the critical temperature for the desired colour change.
d. Engineered waterborne- and UV-based host-systems for the chromics adaptable and expendable to use on nearly every textile, where performance properties may be required to maintain functionality in use. In other words, one of the main targets was finding the right compromise and balance between the efficiency and the durability of the sensoric functionalities during application process and use, offering an excellent

resistance to repeated washing cycles, rubbing, water and UV-solar exposure are prerequisites for commercial applications.

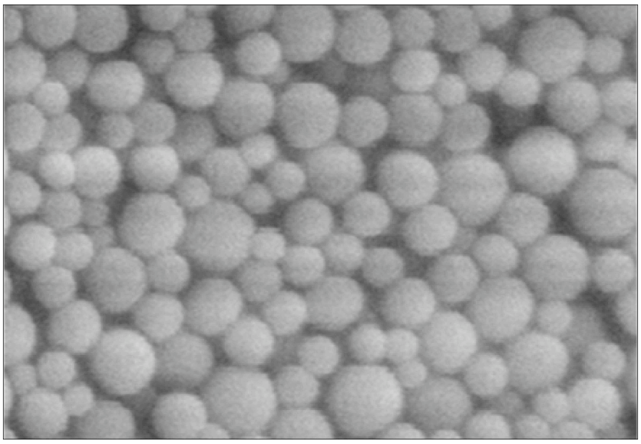

Figure 3: new developed thermochromic microcapsules

4. Conclusion:

On the one hand the increasing awareness among the consumers of textiles paves the pathway for novel developments quite apart from the conventional research focus. The thrust is emphasized on sensoric functionalities for general and special applications like medical, health care and sports applications. They can be implemented through various ways. In the last decade, a large body of work has been undertaken in flexible sensors, wearable electronics and the miniaturisation of sensors and actuators, leading to significant progress on responsive and interactive textiles supported by flexible electronics. While not precluding such future scenarios, the emphasis of the Sensortex project deals with sensoric functionalities (chromics) that do not necessitate external components and power sources to minimise weight addition for the intended applications (clothing, attributes).

An important research item during this IWT-project was the development of new thermochromics and adapted host-systems with focus on function-driven features. We succeeded in the development of new thermochromics with increasing shell-life of the thermosensoric systems – reducing their sensibility in relation to temperature. The engineered microencapsulation and production techniques, guarantee a high stability during processing and end-use and a accurate clearing point (colour-change can take place at different temperatures from -15 ° till 80 °C (critical point) in a narrow window (**max. 1 °C**).

In contrast to the actual thermochromics, the use of these new thermochromic sensors can indeed result in important new designing possibilities and in the development of new smart textiles with visual monitoring, taking care of the safety of the user.
Furthermore, an important advantage is the washability of the new systems (up to 30 washing cycles at 30 °C are possible), whereas built in electronics cause problems during maintenance.

So the new thermochromics make it possible that temperatures can easily be indicated in a visible way to warn people both for heat and cold. The thermochromic characteristics have a warning and safety function. Possible general applications are numerous: in the (para) medical, health care sectors, sensoric fabrics can indicate fever with elderly people, children or hospitalised patients, requiring different degrees of surveillance or they can be used as warning hot spots or as a record for heat history. And there are so many other useful applications.
Also the thermochromics can be used as indicators for individual security (counterfeiting, traceability) and marketing purposes.

However, light fastness properties still have to be improved. The enhancement of light fastness for especially outdoor uses is, therefore, being sought at the present time.

To be followed …

For part 1, see UNITEX nr2/2009, 17-20

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