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FACULTY OF CHEMISTRY
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ÚSTAV CHEMIE MATERIÁLŮ

THE APPLICATION ASPECTS OF THERMOCHROMIC TEXTILE COATING
APLIKAČNÍ ASPEKTY TEXTILNÍCH ZÁTĚRŮ S TERMOCHROMNÍMI PIGMENTY

MASTER'S THESIS
DIPLOMOVÁ PRÁCE

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ABSTRACT

This paper presents a literature review of thermochromic pigments and their application into polymers. The research carried out an improved understanding of leuco dye based thermochromic pigments as well as their application in polyurethane textile coating. For the incorporation, the method floating knife was used and optimum adjustment is presented. The thermal and colour fastness properties of thermochromic coating were examined.

ABSTRAKT

V diplomové práci je prezentovaná literární rešerše na téma termochromní pigmenty a jejich aplikace v polymerních matricích. Výzkum byl zaměřen na hlubší pochopení termochromního efektu v pigmentech na bázi molekulárních komplexů. Termochromní pigmenty byly aplikovány do polyuretanového textilního zátěru a bylo zjištěno optimální nastavení podmínek zátěru. Textilní zátěry byly podrobeny termickým zkouškám a zároveň byla pozorována jejich stálobarevnost.

KEYWORDS

Thermochromic pigment, microencapsulation, polyurethane textile coating, floating knife technology, colour fastness, CIE L*a*b* colour space.

KLÍČOVÁ SLOVA

Termochromní pigment, mikroenkapsulace, polyuretanový textilní zátěr, technologie zatírání, stálobarevnost, barevný prostor CIE L*a*b*.

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DECLARATION

I declare that the diploma thesis has been worked out by myself and that all the quotations from the used literary sources are accurate and complete. The content of the diploma thesis is the property of the Faculty of Chemistry of Brno University of Technology and all commercial uses are allowed only if approved by both the supervisor and the dean of the Faculty of Chemistry, BUT.

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Student's signature

CONTENT

1 INTRODUCTION

Colour plays an extremely important role in our everyday lives. Even today the psychological and social impact of colour is not yet satisfactorily clarified. However, there has been huge progress in understanding the colour ever since Newton recognized the relationship between light and colour in the late seventeenth century. The science behind colour has been studied with great effort and its myriad applications has been increasing gradually, until it has reached today´s level of sophistication.

Thermochromism is the phenomenon of a colour change with dependence on temperature. This phenomenon is known since antiquity and in the last decades, thermochromism as a field of study has made tremendous progress. Organic thermochromic systems are widely used as a carrier in various applications such as smart packaging, security printing, toys and marketing. Thermochromic pigments and their incorporation into mass market polymers have become increasingly important in the art technology. However, even today the colour changing effect has not been fully explained yet.

With thermochromic pigments, the whole new era is opening in the field of textile materials due to development of innovative fabrics and coloration systems. This opens various opportunities and thermochromic materials occupy a unique place as they are exciting materials, not yet fully explored on textiles. One of the new sections being explored are "Smart textiles", which includes many different stimuli sensitive products. This field has opened up possibilities of new designs and applications. Textiles with thermochromic pigment come with associated problems regarding application on textile substrates. The efforts are to improve properties such as light fastness and to simplify application procedures. Wide range of thermochromic textile materials has been developed but still many innovations are waiting for commercial applications. Considerable volume of scientific study needs to be carried out in different application areas before large-scale production can become a reality.

2 THEORETICAL PART

The light rays in visible region stimulate the eye. Different wavelength ranges give rise to different colours - violet, indigo, blue, green, yellow, orange and red. In general, forming of colour can be classified into five fundamental mechanisms as shown in Table 1. [1]

***Table 1:** Different mechanisms and causing of colour generation [1].*

Mechanism	**Subdivision**	**Examples**
Physical phenomena	Dispersion or dispersive refraction	Rainbow, halos
	Scattering	Raman scattering, blue sky
	Interference	Oil slick on water
	Diffraction	Opal, most liquid crystals
Atomic/molecular vibration and excitation	Incandescence	Flame, lamps
	Gas excitation	Vapour lamps, lasers
	Vibration and rotations	Water, iodine
Transition involving ligand-fields	Transition metal (Cr, Mn, F, Co, Ni, Cu) compounds	Phosphorus, lasers
	Transition metal impurities	Ruby, emerald
Molecular orbital transition	Conjugated bond	Most dyes
	Charge transfer	Blue sapphire, many pigments
Energy band transitions	Metals	Copper, silver, gold etc.
	Pure semiconductors	Silicon, diamond
	Doped semiconductors	LED
	Colour centres	Amethyst, lasers

For the change in colour is used term chromism. Chromic phenomena involve processes such as absorption and reflection of light, absorption of energy and emission of light, absorption of light and energy transfer or a conversion and manipulation of light that leads to colour change. Reversible change of colour can result from an alteration of the electronic state, especially involving π- or d-electrons, physical change of the material or rearrangement of molecules in a matrix. By different stimuli we can categorize the type of chromism such as thermochromism – induced by heat, photochromism – induced by light irradiation, electrochromism – induced by addition and subtraction of electrons as a result of electric current flow, solvatochromism – induced by the polarity of solvent, ionochromism – induced by ions, halochromism – induced by pH, tribochromism – induced by mechanical friction, vapochromism – induced by vapours, mechanochromism – induced by mechanical activity, chronochromism – induced by time, radiochromism – induced by ionizing radiation, magnetochromism – induced by magnetic field, biochromism – induced by biological sources and piezochromism – induced by mechanical pressure. [2]

2.1 Thermochromism

Thermochromism is the phenomenon of a colour change as a function of temperature. Nowadays is known reversible and irreversible thermochromism by single compound as well as by inorganic and organic composites. The reversible thermochromic pigments are leuco dye or cholesteric liquid crystal based. Thermochromism can occur in all types of polymers such as thermoplastics, gels, inks, paints or coatings. The polymer itself, a doped thermochromic additive or a supramolecular system built by the interaction of the polymer with an incorporated non-thermochromic additive can cause the thermochromic effect. The thermochromic effect might origin in light reflection, absorption and scattering properties with temperature [2]. Table 2 displays a list of different types of thermochromic polymer systems according to the effect of light causing the thermochromism.

Table 2: *Different types of thermochromic polymer materials [3].*

Polymers thermochromic themselves		Polymer materials doped with thermochromic additives	Thermochromic through polymer-additives interaction		Thermochromic polymer systems
Absorption	Reflection	Absorption	Absorption	Reflection	Scattering
	Liquid crystalline polymers with a helical superstructure	Leuco dye-developer-solvent systems		Crystalline colloidal arrays embedded in swollen gel networks	Polymer blends
Conjugated polymers		Inorganic pigment	Dyes embedded gel networks		Thermotropic polymer gel networks
Swollen gel networks of conjugated polymers		Conjugates polymers			Thermotropic casting resin

2.2 Polymer materials doped with thermochromic additives

One way of obtaining thermochromic polymer is to incorporate thermochromic material into a polymer matrix while one phase does not influence the other. For such effect we can use microencapsulated leuco dye–developer–solvent systems, inorganic pigments or conjugated polymers. The reversible thermochromic organic systems change colour by applying heat and return back to original colour after cooling down the system. The reversible colour change results from an alteration of the electronic state, physical change of the material or rearrangement of molecules in a matrix. [3]

A comparison between the classes of thermochromic systems presented in this work in section 2.2 is given in Table 3. All given properties has to be considered with the view to application. The outstanding properties of inorganic pigments are their high thermostability and light stability compared with organic microcapsules and conjugated polymers. On the other hand those pigments are toxic which limit the application range. Organic thermochromic materials allow switching the temperature and colour can be customised. By combining several thermochromic additives the creation of multiple switching effects is allowed. This can be achieved due to the narrow absorption band. [3]

Table 3: *Comparison between organic microcapsules, inorganic pigments and conjugated polymers [3].*

Material property	**Organic microcapsules**	**Inorganic pigments**	**Conjugated polymers**
Switching temperature	0-130 °C	70-500 °C	–
Thermostability	<200 °C	Stability at 500 °C possible	<200 °C
Light stability	Insufficient	Suitable for outdoor application	Insufficient
Multiswitching between colours	Possible	Possible for irreversible	Possible
Switching temperature adjustment	Adjustable	Fixed transition temperatures	Fixed transition temperatures
Colour variable at constant switching temperature	Colour variable by changing dye component	Fixed colours	Fixed colours
Toxicity	Non-toxic	Toxic	Non-toxic

2.2.1 Leuco dye thermochromic systems

The leuco dye thermochromic pigments are mostly coloured in solid state and colourless above the melting temperature of solvent. In the molten state the solvent works as an inhibitor of the colour-forming reaction, while in the solid state it does not interfere with the colour formation as you can see in Figure 1. [3]

The leuco dyes exhibit following properties in contrast to other thermochromic materials:

- They have sharp colour transition, which means that leuco dyes are able to change colour over a few degrees temperature.
- By applying different solvents with specific melting points, colour changing effect can be obtained in different temperatures.
- Colour to colourless changes across whole visible spectrum available.
- By using colour formers with a secondary chromophore or pH-sensitive dyes as a base colour it is possible to obtain colour to colour changes [5].

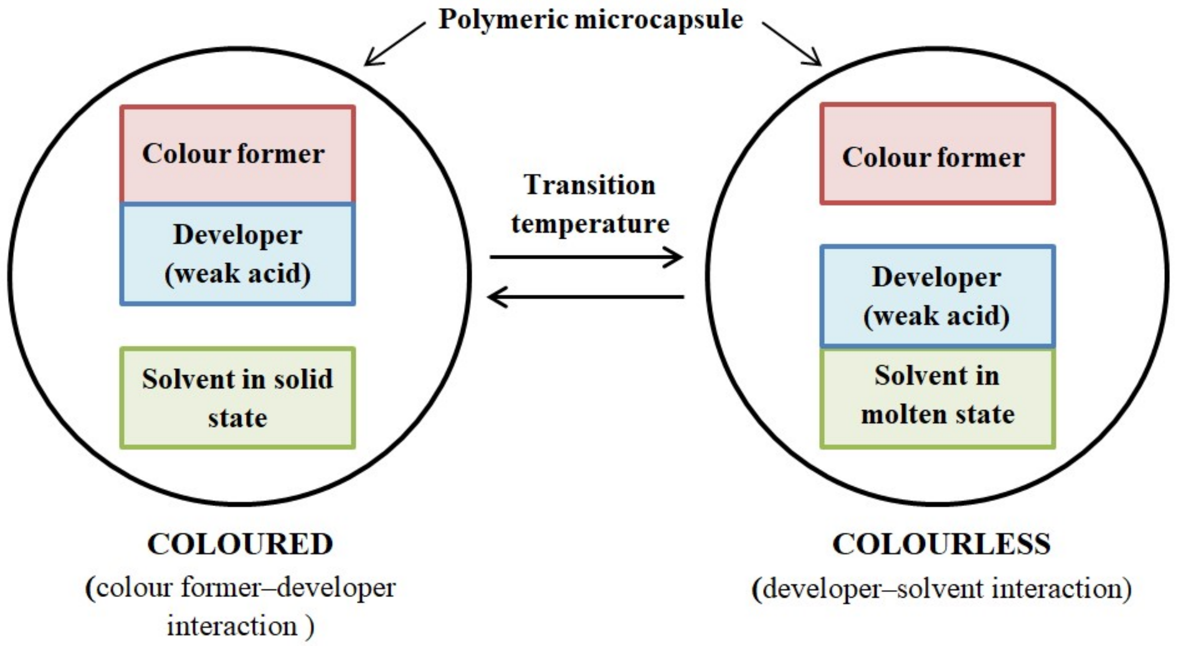
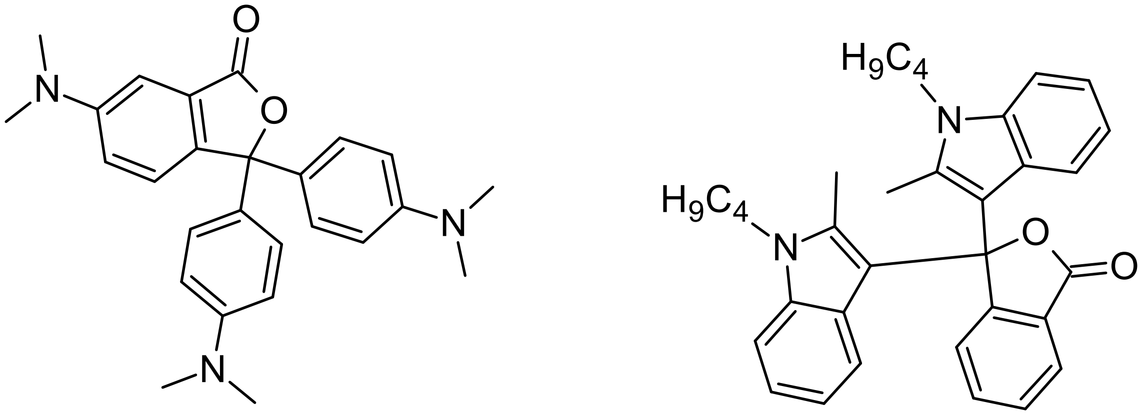


Figure 1: *Scheme of colour change principle in leuco dye thermochromic systems.*

The leuco dye thermochromic pigments consist of chromogenic compound (Figure 2), developer (Figure 3) and solvent. Chromogenic compound or in other words colour former is pH sensitive dye. The most common electron-donating chromogenic compounds are phenylmethane and fluoran derivatives with a lactone ring. While the lactone ring-closed state occur these so-called leuco dyes or colour formers are either colourless or weakly yellow coloured [7]. Developer is usually weak acid such as Bisphenol A, which works as electron acceptor. The solvent is hydrophobic compound with long aliphatic chain accompanied by polar end group. The length of alkyl chain of the solvents determines the temperature region where phase transitions of the thermochromic pigment take place. Solvents with longer tail give pigments with higher activation temperatures [4]. Some examples are 1-alcanols, 1-alcylamides and 1-alcanoic acids with chain length of more than six carbon atoms. This structure allows a disperse-disperse interaction through the polar group. Especially polar-polar interaction between the solvent and the developer can occur. The reversible thermochromic effect of these systems is explained by a competition between dye-developer and solvent–developer interactions. The melting point of solvent is set to specific temperature at which can the colour former and the developer interact with each other. Thus in the molten state solvent-developer interactions win, the dye-developer complexes are destroyed and the the decolourisation occurs. [1]

Molecular mechanism of colour forming reaction of leuco dyes is explained by proton-triggered ring-opening/ring-closing model. According to this model the acidity of the developer is a measure for its effectiveness to drive the ring-opening/ring-closing equilibrium of leuco dyes towards their ring-open coloured state. In many cases, this simple model fails to explain the experimental results [8]. The opening of lactone ring happens after reaction between electron accepting developer with colour former which results in formation of a zwitterionic structure. This results into extended conjugated π-electron system of the dye and the longest wavelength absorption peak shifts from the UV to the visible range and the dye becomes coloured. The reaction can be reversible due to addition of a suitable solvent. [3]

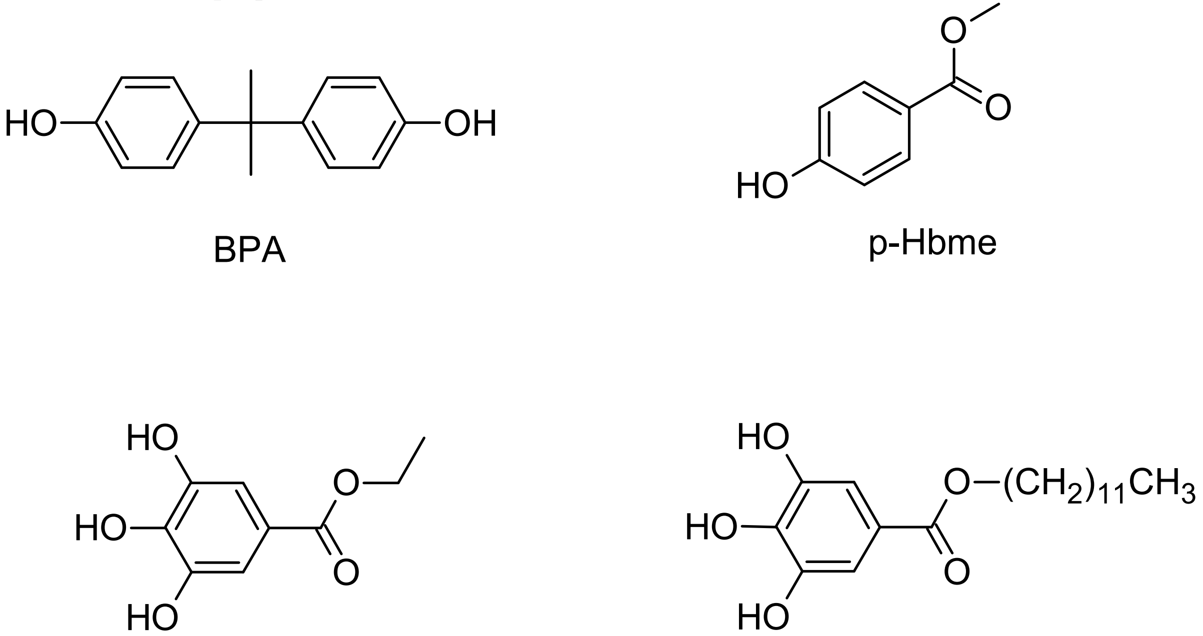


CVL

RED-40

Figure 2: *Potential structures of leuco dyes chromogenic compounds [3].*

Experimentally the colour forming reaction has been investigated on the binary system of the leuco dye crystal violet lactone (CVL) and the developer bisphenol A (BPA). This reaction is shown in Figure 4. It was revealed that leuco dye developer complexes are formed in the coloured solid state [9]. The Job method was used to determine the leuco dye-developer ratio in the complexes. It was found that one CVL molecule is associated with four BPA molecules. [10]



BPA

p-Hbme

EG

LG

Figure 3: *Possible structures of developer [3].*

An example of a reversible thermochromic leuco dye–developer–solvent system is a mixture of 1 wt% 2-chloro-6-diethylamino-3-methylfluoran, 5 wt% 2,2′-bis(4-hydroxyphenyl)-propane and 94 wt% 1-hexadecanol. On cooling below 48 °C the colourless molten state develops a vermillion colour when crystallisation takes place [1].

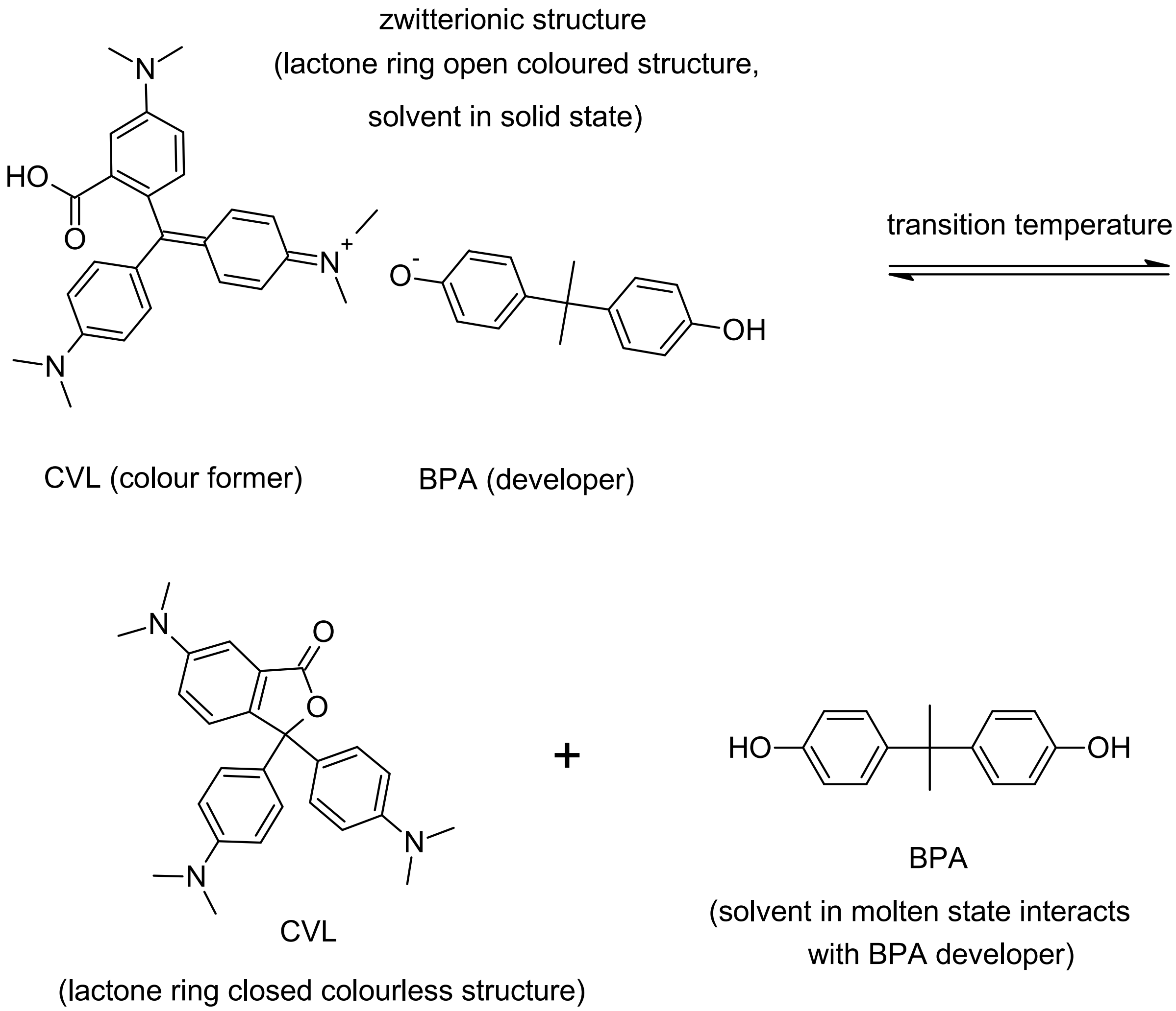


Figure 4: *Colour forming reaction of CVL leuco dye (colour former) and BPA (developer). Below transition temperature CVL interacts with BPA and ring open coloured structure occurs. Above transition temperature BPA interacts with molten solvent and lactone ring closed colourless structure occurs [14].*

Also binary system of CVL leuco dye with the lauryl gallate developer (LG) has been investigated. It was revealed that after cooling from melting state coloured complex has been formed with an equilibrium stoichiometry of $(LG)_3CVL$. Infrared (IR) and Raman spectra showed that hydrogen bonding between the carboxylate group of the ring-open CVL and the protons from LG increases in the system as the complex is formed. This leads to a stabilisation of the zwitterionic ring open state of the CVL molecule [11]. From experimental measurements it was found out that hydrogen bonding is the principal factor for the formation of the coloured complexes. The authors revealed that for the investigated developers with two or three hydroxyl groups, hydrogen bonding via two

OH groups occurs. They concluded that this stabilises the entire complex by electron delocalisation [1]. Although there are a lot of reversible thermochromic leuco dye-developer-solvent systems, only a few of them are two-component systems, which combine function of developer and the solvent. The main difference is that two-component systems are coloured in the molten state and colourless in the solid state. One example of such system is a 1:7 mixture of the fluoran leuco dye 2′-(o-chloroanilino)-6′-d n-butylaminospiro[isobenzofuran-1(3H),9′-[9H]xanthene]-3-one with octadecylphosphonic acid. [12]

The photostability of leuco dyes thermochromic systems is very poor when exposed to UV as well as to visible light. There are possible causes of photodecomposition: dealkylation of the alkylamino groups via the formation of an N-oxide, oxidative cleavage by a reaction with singlet oxygen or reduction of the excited dye cation state to a colourless leuco form. Investigations of the photo stability of leuco dyes have led to the formation of particular leuco dye-matrix-stabiliser system, in which the photofading process of the leuco dye is almost inhibited. Unfortunately, none of these systems has reversible thermochromic properties [13]. The photo stability of thermochromic systems is further discussed in section 2.5.

2.2.2 Inorganic pigments

The appearance of thermochromism in inorganic pigments has its origin in changes of crystal structure such as phase transitions, changes in ligand geometry, equilibria between different molecular structures and changes in the number of solvent molecules in the coordination sphere, for example involving dehydration. Thermochromic behaviour is exhibited in solids or in solution by many metals and inorganic compounds also.

Inorganic pigments are usually based on transition metals and organo-metallics. Almost all inorganic thermochromic systems are intrinsic, which means that the colour changes solely depend directly on heat. [2]

For example, colour change from red to brown of copper mercury iodide, $Cu_2(HgI_4)$, is caused by a change between an ordered and a disordered structure. In both modifications the iodide ions form a face-centered cubic cell with tetrahedral holes. These holes are partly occupied by the copper and mercury ions. In the low-temperature (below 70 °C) modification tetrahedral holes are occupied, whereas in the high-temperature (above 70 °C) modification the cations are randomly distributed throughout all of the tetrahedral holes. [3]

Considering textile application, inorganic thermochromic systems have not been used much as the change in colour occurs at high temperature or in solution. For these to be applicable on textiles, they should be reversible and solid (or encapsulated) system that is suitable for dyeing and printing application. The thermochromic systems for textile applications require colour changes at close to ambient temperatures. For ski wear is demanded temperature around -10 °C and around body temperature for smart textiles. Thus, inorganic and organometallic systems are mostly used in temperature indicating paints and crayons, to identify the temperature change and also to provide a permanent record of thermal data. [15]

Chosen inorganic pigments with their colour changes and respective transition temperatures are listed in Table 3. In most of the inorganic pigments the thermochromic effect appears at temperatures above 100 °C and is irreversible.

Table 3: *Thermochromic inorganic pigments with reversible (↔) and irreversible (→) colour change [3].*

Inorganic pigment	**Colour change**	**Temperature [°C]**
$Ni(NH_4)PO_6 \cdot 6H_2O$	Light green → grey	~120
$Cu(CNS)_2 \cdot 2$-pyridine	Green → yellow	~135
	Yellow → black	~220
$(NH_4)_3PO_4 \cdot 12MoO_3$	Yellow → black	140–160
$Co(NH_4)PO_4 \cdot H_2O$	Fuchsia → deep blue	~140
	Deep blue → grey	~500
NH_4VO_3	White → brown	~150
	Brown → black	~170
$[CoNH_3)_6]PO_4$	Yellow → blue	~200
$(NH_4)_2U_2O_7$	Yellow → grey	~200
$[CoNH_3)_6](C_2O_4)_3$	Yellow → violet	~215
	Violet → brown	250–270
	Brown → black	320–350
$Mn(NH_4)P_2O_7$	Violet → white	~400
$Cu_2(HgI_4)$	Red ↔ brown	~70
$Co(NO_3)_2 \cdot 2HMTA \cdot 10H_2O$	Pink ↔ purple	~75
HgI_2	Red ↔ yellow	~127

2.3 Thermotropic liquid crystals

In solid state, the molecules are closely packed and remain in specific shape. While being in solid state, molecules may be present in either amorphous or crystalline state. In a crystalline form, the molecules are arranged in regular three dimensional patterns, which have an influence on physical properties. Crystal is defined by the fact, that if a patter is located at a point x_0, the probability of finding an equivalent pattern at the point $x = x_0 + n_1a_1 + n_2a_2 + n_3a_3$ $(n_i = integer; i \in \{1,2,3\}$ and $\{a_i\}$ basis vectors) stays finite when $|x - x_0| \to \infty$. As a result, its X-ray diffraction pattern shows sharp Bragg reflections characteristic of the lattice. [16]

In liquid state molecules can move freely. They are not ordered in any way and they adopt specific shape of container. Due to the randomness of the orientation of the molecules, the physical properties of liquids are independent on direction. Liquids can be defined in similar way as crystals. If one has been able to locate a molecule or some pattern at a given point x_0,, there is no way to express the probability of finding a similar one at the point x far from x_0. These liquids are known as isotropic liquids. In a gas form, molecules can move freely and occupy any available space. [16]

Certain organic materials do not show only a single transition from solid to liquid, but rather a cascade of transitions involving new phase. This state of matter is called anisotropic form. The mechanical and symmetry properties of these states are intermediate between those of a liquid and those of a crystal. That is the reason, why they are usually called liquid crystals. Liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present. By anisotropy is meant that the density-density correlation function does not depend solely on the modulus $|x - x'|$ but also on the orientation of $x - x'$ with respect to macroscopically defined axes [16]. Normally, liquid crystals are narrow, rod-like molecules, but some liquid crystals are disc shape. Liquid crystals are also formed by some polymers, in chain and side chain forms, such as Kevlar [2].

Some liquid crystalline phases develop a helical superstructure if a chiral dopant is added or the liquid crystalline compound itself has a chiral molecular structure. The helical superstructure is a periodical structure on which incident light satisfying the Bragg condition is reflected. If the wavelength (λ) of the reflected light is in the visible region the liquid crystal becomes coloured. Apart from synthetic structures, several cholesteric and cellulose derivatives show selective reflection in visible region based on temperature. Thermotropic liquid crystals composed of rod-like molecules can be divided in three categories: nematic, cholesteric and smectic. [17]

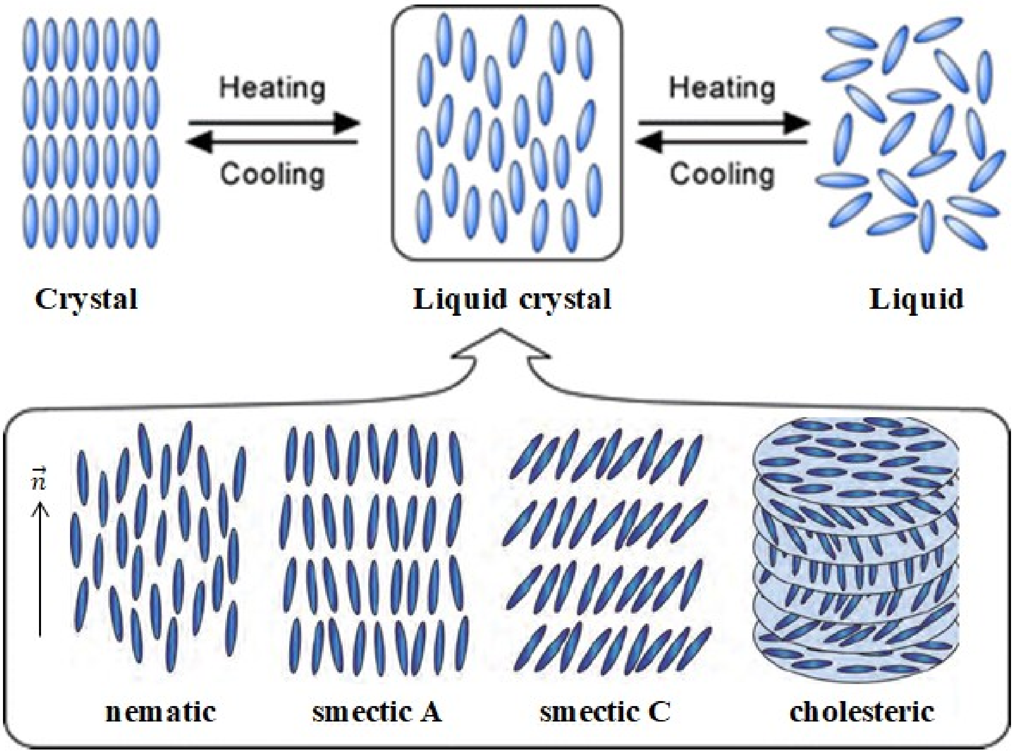


Figure 5: *Schematic representation of the molecular arrangement in liquid crystal [17].*

2.3.1 Nematic liquid crystals

The molecules in nematic phase are arranged in an alignment, which means that they are parallel to one another, but they are not separated in layers. Thus, the molecules are, on the average, oriented parallel to a mean direction referred to as the director (indicated by the unit vector $\vec{n}$ in (Figure 5). An oriented sample is optically uniaxial. The director $\vec{n}$ is apolar, thus, $\vec{n}$ and $-\vec{n}$ is equivalent and therefore the mesophase is non-ferroelectric. When exposed to heating, molecules show large changes in the direction which in turn cause variations in refractive index. The changes in refractive index caused by heating leads to increasing of the scattering of incident light and give cloudy dirty appearance. [18]

2.3.2 Smectic liquid crystals

Smectic liquid crystals exhibit layered structure. Different types of smectic liquid crystals are classified depending on the order within the layer and the interlayer correlation. In the smectic C phase, the long axis of the molecule is tilted, while in the smectic A phase, the axis is perpendicular to the layer plane. In smectic phase some molecules can transfer between the layers along the axes of columns made by single or more layers of molecules. Molecular movement is highly restricted and layers can be strongly coupled with each other. Therefore, materials in the smectic phase are close in structure to solids or soft solids. [21]

2.3.3 Cholesteric liquid crystals

Cholesteric mesophase is exhibited by optically active molecules. It is composed of nematic type, but the structure has a screw axis superimposed normal to the director, as shown in Figure 5 [20]. Due to helical structure cholesteric liquid crystal exhibits special optical properties, such as selective reflection of circularly polarized light, high optical rotatory power etc. To compare with nematic phase, cholesteric phase has sufficiently low pitch (≤ 5000 Å) and transforms into the isotropic phase via an intermediate phase, whereas nematic transforms directly to isotropic phase. This intermediate phase is called the blue phase and occurs usually over a very narrow region of temperature [19]. The cholesteric phase got its name from cholesterol derivatives (Figure 6), which originally exhibit liquid crystal phenomena.

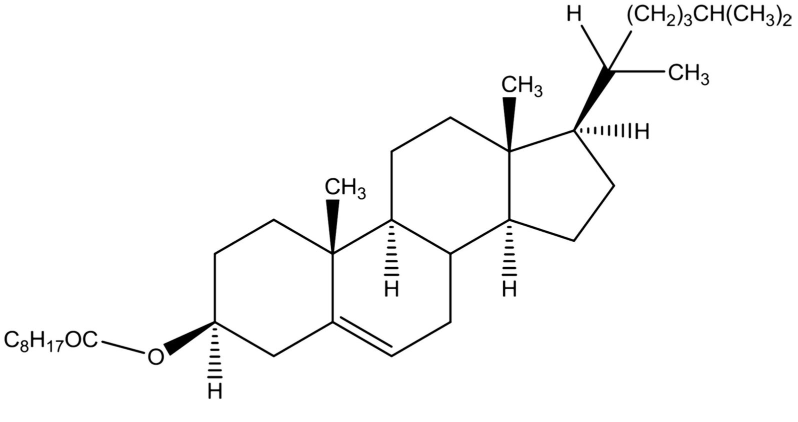


Figure 6: *Structure of cholesterol derivate [5].*

Bright, spectral colours and major optical activity is observed when the helix axis of chiral nematic liquid crystals is in alignment with the direction of incident light and the pitch length matches with the wavelength of visible light. Because the cholesteric liquid crystals exhibit ability to reflect the incident light (as discussed above), there is also change in reflected wavelength by variation of temperature. When varying the temperature, the specific wavelength of the visible light is reflected back, while the rest of the wavelengths are transmitted through (Figure 7). Generally, the pitch depends on temperature and can be tuned by an external electric field. Thus, these compounds possess thermochromic and electrochromic properties. [2]

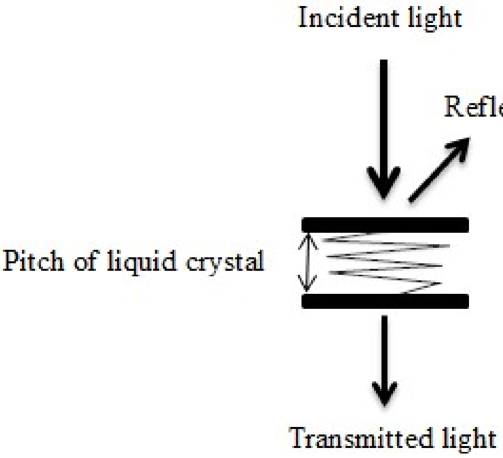


Figure 7: *Interaction with light in cholesteric liquid crystals [5].*

2.3.4 Conjugated polymer

Conjugated polymers such as polyacetylenes, polydiacetylenes, polythiophenes and polyanilines often exhibit thermochromic properties due to absorption of light in the visible range and their high reflectivity. Thermochromic properties origin in conformational changes in the polymer backbone, especially because of its planarity. The colour change can occur continuously with temperature or abruptly at phase transitions. Even a small modification of the conformational structure leads to significant colour change. Generally the colour changes of conjugated polymers are reversible. [3]

Poly(3-alkyl thiophene) exhibits thermochromism due to temperature-dependent conformational changes of the conjugated π-electron system. Their chemical structure can be modified to switch the temperature of the polythiophene pigments. By dispersing 0.1–1.0 wt% into commercially available paints, plastics and rubbers visible thermochromic effects were observed in the doped host polymer matrices. [2, 3]

2.4 Microencapsulation processes

The range of possible applications of thermochromic materials has increased dramatically with the development of the process of microencapsulation, which protects the system from unwanted reaction with the environment. Each microcapsule contains the whole system for the creation of colour, chromogenic compound, developer and solvent. Since thermochromic dyes are sensitive, they have to be microencapsulated to process a protective shield with low porosity. There are two different microencapsulation processes. One of them built melamine resin and the other an epoxy resin shell around the thermochromic core material. By controlling the degree of crosslinking, porosity and elasticity, the melamine resin shell can be adjusted within wide ranges. In comparison to the epoxy resin microcapsules smaller sizes and narrow size distributions can be obtained. On the other hand epoxy resin capsules have higher transparency of the shell and better thermal stability. [22]

Firstly the thermochromic leuco dye-developer-solvent system has to be emulsify in an aqueous solution, which determines the size distribution of the final microencapsulates. To obtain emulsion, surface-active compound has to be added. The problem is that the surfactant can interfere with the formation of complex between leuco dye and developer and also with the interface polymerisation reaction of the microencapsulation process. Some system compatible surface-active compounds have been found, but the different influences of the surfactants could not be satisfactory explained. [1]

Thermochromic coatings are a mixture of thermochromic microcapsules and binders. The functionality of thermochromic coating can be adversely influenced by the UV radiation, temperatures above 200 °C and aggressive solvents. Their poor stability when exposed to UV radiation limits the time of exposure of products to external conditions. That is why they are nowadays mainly used for applications that are not directly exposed to sunlight. [23]

Since microcapsules contain the entire system necessary for the creation of colouring, the range of possible applications of such thermochromic materials has increased dramatically. [23]

2.5 Colour fastness

The light fastness is the property of a material referring to its ability to withstand exposure to sunlight or artificial light so that it retains its original form and resists degradation due to light. This may be degradation of structure, colour, physical or chemical properties. In thermochromic pigments the colour former plays the main role in the resistance to fading. Therefore, different ways of stabilizing the colour former have been investigated. [24]

The photodegradation of colour happens with prolonged exposure to sunlight. When dyes degrade, a photochemical reaction is triggered by the absorption of visible or ultraviolet light. Absorption of one or more photons of suitable energy by an organic molecule provides an electronically excited state, which is the starting point for subsequent reaction steps [25]. The energy level of loosely-held electrons in chromophores is raised so that they become more active. [24]

Degradation usually results in colour fading and is influenced by the structure of the dye, as well as by external and environmental parameters. Thus oxygen, moisture, temperature, additives such as atmosphere contaminant, wavelength of incident light and concentration of the dyes have an influence on the degradation speed and pathways as well as the surface properties, the chemical and physical structure of the substrate, residual solvent within the substrate and porosity. Photochemical degradation can occur in large variety of mechanisms and produce in result wide range of different products. [25]

Normally, three types of mechanisms occur in degradation of colours in textiles. Those are photo-oxidation through singlet oxygen, photo-oxidation through superoxide and photo-reduction through radical species [38]. In photo-oxidation through singlet oxygen the light raises the coloured molecule to an excited state, i.e., its triplet form as shown in equation 2.1. The excited triplet form sensitises the oxygen which then react with the coloured molecule to degrade it as shown in set of equations 2.2 [5].

Photodegradation of triphenylmethane dyes is accelerated by the presence of singlet oxygen sensitizers. Photooxidative cleavage of the central C-phenyl bond, probably via singlet oxygen, produces benzophenones and phenols (Figure 8) [25].

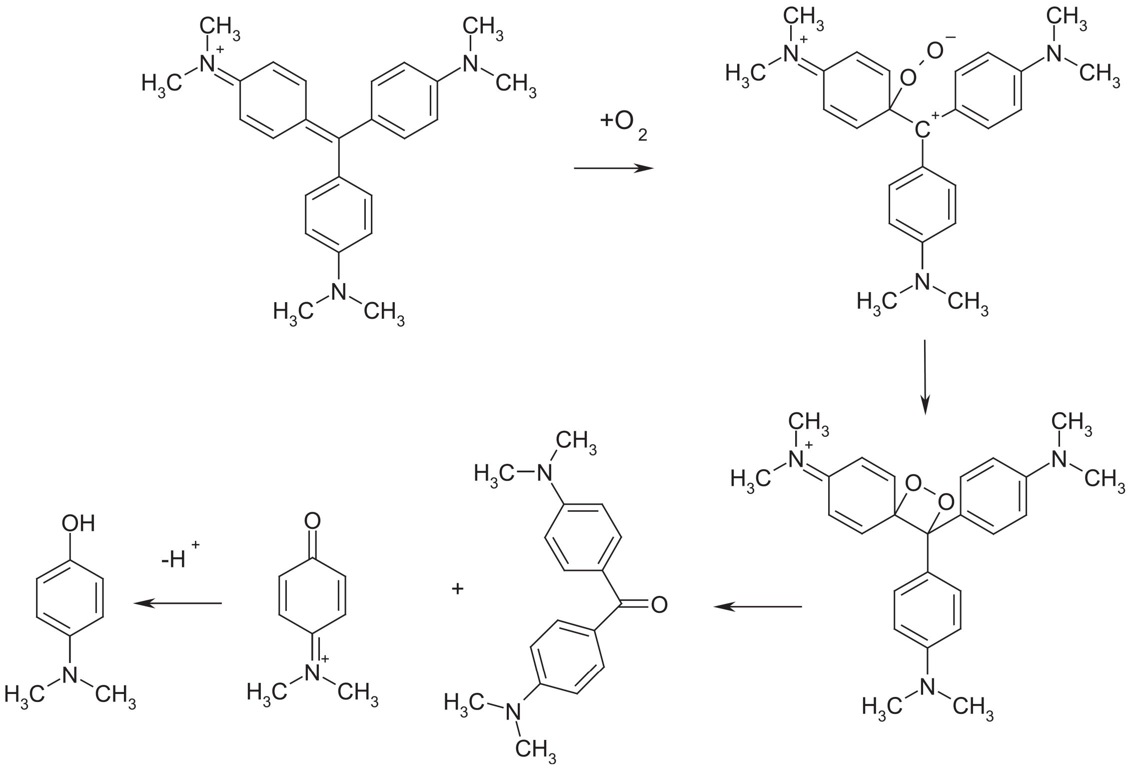


***Figure 8**: Mechanism proposed by Henriquez in 1933 and redefined by Kuramoto and Kitao for the degradation of crystal violet through singlet oxygen attack, which produces diemethylaminobenzophenones and dimethlyaminophenol [25].*

In photo-oxidation through superoxide the light raises the coloured molecule to an excited state as in photo-oxidation through singlet oxygen. Then an electron from the excited triplet form transfers to the oxygen to form superoxide which further reacts to decompose the molecule as shown in set of equations 2.3 [5].

$$Dye + hv \rightarrow {}^3Dye^* \tag{2.1}$$

$$\begin{gathered} {}^3Dye^* + O_2 \rightarrow Dye + {}^1O_2 \\ {}^1O_2 + Dye \rightarrow Decomposition \end{gathered} \tag{2.2}$$

$$\begin{gathered} Dye^* + O_2 \rightarrow Dye^{+\circ} + 0_2^{-\circ} \\ 0_2^{-\circ} + Dye \rightarrow Decomposition \end{gathered} \tag{2.3}$$

In photo-reduction through radical species mechanism, the excited triplet formed of the coloured molecule reacts with a nearby substrate, impurity etc. to abstract a hydrogen atom. This leads to the decomposition of the dye as shown in set of equations 2.4.

The presence of oxygen does not affect this process, which normally occur in presence of impurities. [5]

$$
\begin{gathered}
Dye^{*} + RH \rightarrow HDye^{\circ} + R^{\circ} \\
HDye^{\circ} + R^{\circ} \rightarrow Decmposition \\
R^{\circ} + O_2 \rightarrow RO_2^{\circ} \\
R^{\circ}/RO_2^{\circ} + HDye \rightarrow Decomposition
\end{gathered}
\tag{2.4}
$$

Usual compounds used in thermochromic additives as a colour formers are crystal violet lactone analogues and fluoran dyes. These dyes react very quickly when exposed to the sunlight. They degrade and lose their colour strength. As the use of these thermochromic pigments is increasing day by day, attempts have been made to improve their light fastness. [5]

It has been proven that some UV absorbers like hydroxyarylbenzotriazoles strongly improve the light fastness of thermochromic pigment because of their amphoteric counter-ion like behaviour. Zinc and nickel 5-(2-benzotriazolyl)-2, 4-dihydroxybenzoates, zinc and nickel 3-(2-benzotriazolyl)-2-hydroxy-1-naphthoates, zinc and nickel 2, 4-dihydroxybenzophenone-3-carboxylates and their derivatives are reported as other types of stabilizers to improve light fastness in leuco dyes. [24]

2.5.1 Hindered amine light stabilisers

Hindered amine light stabilisers (HALS) are chemical compounds containing an amine functional group that are normally used for improving resistance against photo-degradation of polymers. During photo-degradation free alkyl radicals are formed and may react with oxygen to form peroxy radicals. A hydroperoxide is formed in the reaction of peroxy radical with hydrogen. A free radical can react many times and produce large amount of hydroperoxides. These hydroperoxides then decompose forming new radicals. [27]

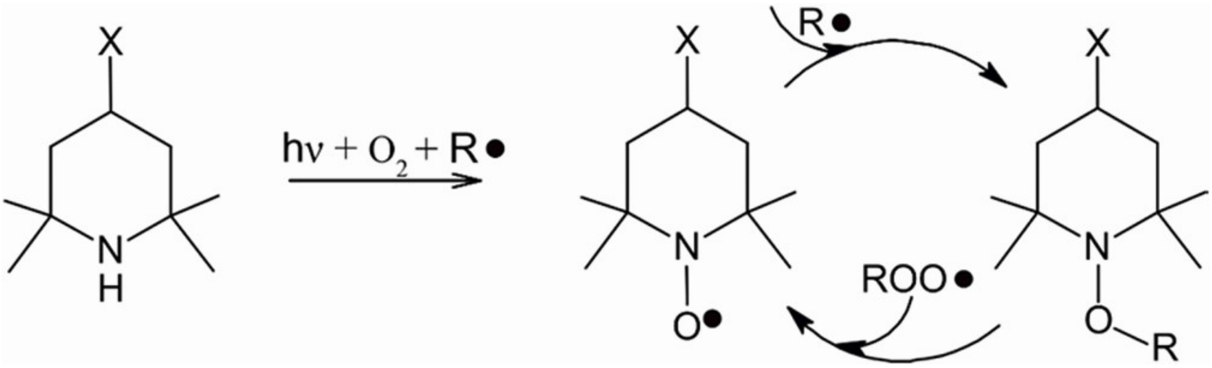


Figure 9: *HALS mechanism called Denisov cycle after Evguenii T. Denisov.*

HALS do not absorb UV radiation as UV absorbers, but act to inhibit degradation of the polymer by continuously and cyclically removing free radicals that are produced by photo-oxidation. The cyclic reaction of HALS is given in the following steps (Figure 9):

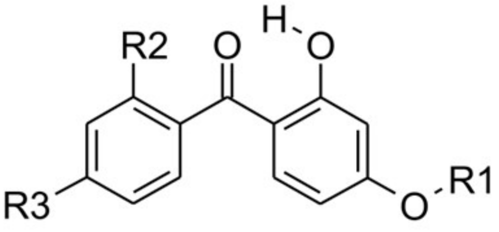
- Oxidation of HALS occurs to form radicals i.e., >NO•;
- >NO• and free radicals R• react to form non-radical amino ethers >NOR;
- reaction of >NOR with peroxy radicals to form >NO• radicals again [5].

Thus, HALS are able to return to their initial amine form via a series of additional radical reactions. Their high efficiency and long life are due to this cyclic process wherein the HALS are regenerated rather than consumed during the stabilization process.

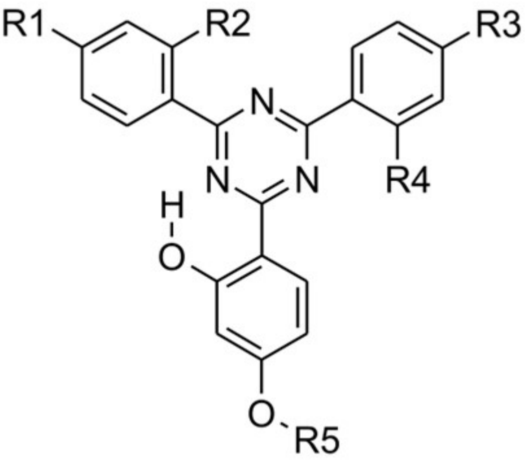
2.5.2 UV absorbers

The ultraviolet light causes photo-degradation of colours. Thus, one way of controlling photo-degradation is to reduce the content of UV light in the incident light. In chromogenic molecules a photochemically induced change in the structure causes a significant alteration of the absorption characteristics [5]. These molecules absorb incident UV radiation very efficiently, typically in the range 300–400 nm and dissipate it in the form of heat (Figure 11). As this happens in tautomeric forms of UV absorbers, these additives have a long life function. Classical UV absorbers are benzophenones, benzotriazoles and triazines with ortho-hydroxyphenol substituents (Figure 10). [26]

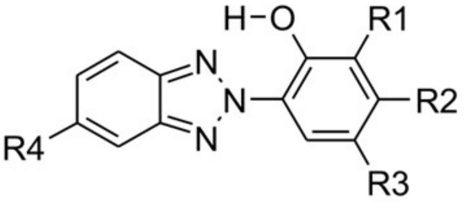
UV absorbers are normally used in polymers to protect them against photo-degradation but they have also been used in coatings and fabrics. In textiles, they have been used to enhance the lightfastness of disperse and dyes. [5]



2-hydroxyphenyl benzophenone



2-hydroxyphenyl triazine



2-hydroxyphenyl benzotriazole

Figure 10: *Types of 2-hydroxyphenol UV absorbers.*

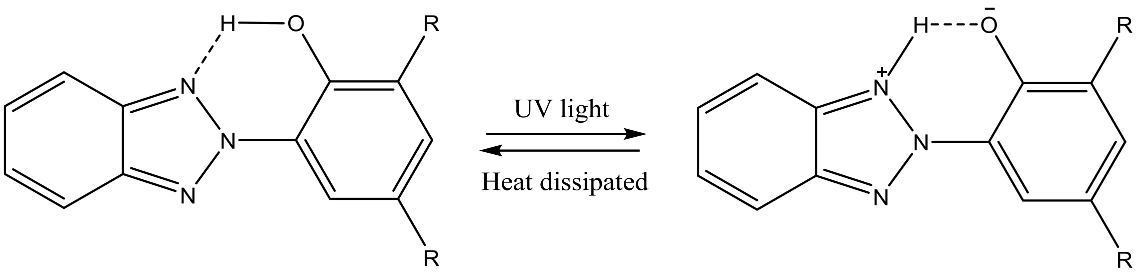


Figure 11: *Mechanism of benzotriazole class UV absorber [5].*

2.6 Application of thermochromic pigments

Thermochromic materials have become increasingly important for various applications in graphic art such as smart packaging, security printing, textile applications and marketing activities in which value or uniqueness of a product is desired.

Thermochromic pigments are often used as temperature indicators for measuring the body temperature, e.g. sportswear for detection of physical exhaustion. In medicine are used for thermography diagnosis purposes, in the cosmetic industry for moisturizing and also as a carrier for vitamins etc. In thermal mapping of engineering materials to diagnose faults in product design and in mechanical performance. If a small component is heated then defects can be identified by variation in thermal conductivity. The method has been used in the air craft industry in identifying blockages in coolant channels. By thermochromic materials can be also identified stress or strain, because heat is produced. This technique can also be applied to locate weld flaws. Electronic circuits generate a large quantity of heat while working. The abnormalities or variation in temperatures indicate underlying problems, such as short circuits overheating due to design or construction flaws, poor electrical joints or non-operative areas. Some thermochromic materials are very sensitive towards variation in heat so they can be used to rule out microelectronic flaws. Further examples are memory devices, where thermochromic pigments are used in batteries for life indication and in the architecture field for decoration or its functionality. In addition they are used to determine the temperature in food containers or history of the food storage. The hysteresis in the change in colour of cholesteric liquid crystals, which happens due to texture, is used in frozen food to indicate if the frozen food has been thawed and refrozen. As the organic thermochromic pigments are proved to be health safe they are often used in in toys, ornaments, kettles, umbrellas etc. Nowadays, the thermochromic materials are also being used in architecture as well as coating on walls for decoration or more importantly for its functionality to determine temperature and absorbing and reflecting the sunlight and ultimately using the data to save energy. [29-33]

Another large field of application are printing inks. The colour properties of such inks are usually based on chromogenic functional polymers as organic compositions can be made in many colours and display colour change at desired temperatures. One example is intelligent paints that turns the roads pink in icy conditions [3, 14]. Thermochromic printing ink is a mixture of thermochromic pigments and a binder, while the phases are separate and have no influence on each other. The size of microencapsulated thermochromic pigment ranges typically between 3 and 5 mm, which are more than 10-times larger than conventional pigment particles. The decolourisation/colourisation reactions can be reversible and it is believed that the process can be repeated several thousand times. All major ink types such as water-based and photocuring for application on paper, plastics and textile have been studied. [14]

Other applications that are currently under development are smart windows, tunable light filters, large-area displays as well as sensors that can visualise local surface temperatures. All of them are based on thermochromic polymers. One of the examples is thermochromic plastic films and injection molding parts (Figure 12). Most of thermoplastics can be processed by using extruder technology into films and injection molding parts. During processing the raw materials are subjected to thermal, as well as high degree of mechanical stress, which thermochromic pigment has to withstand. Currently can be achieved technology-compatible production of thermochromic polymer films and injection molding parts where the thermochromic dye is homogenously distributed throughout the entire volume of the polymer. The temperature is tunable between 0 °C and 70 °C and with reversible and irreversible colour change. Thermochromic pigments can be also added into hydrogels. Their thermochromic behaviour is based on the interaction between the dye's molecules and the hydrogel's micro-environment. These materials are extremely suitable for use in hybrid light- and heat-regulating solar protection glazing. Such demo windows of up to 1 m² are currently being tested under practical conditions. For all these innovations, laboratory prototypes demonstrating the effect have been presented to the public but almost none of them have reached readiness for market. [28]

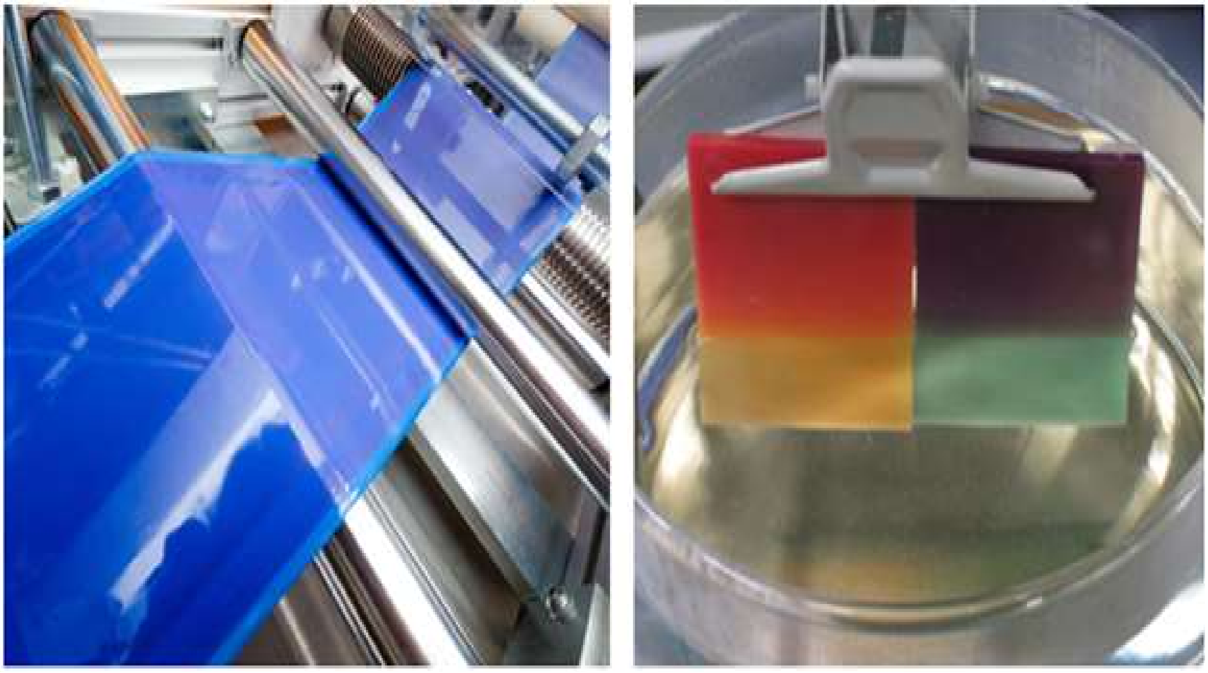


Figure 12: *A photo of thermochromic foil and its colour change under the influence of heat [28].*

2.6.1 Thermochromic materials in textiles

Use of thermochromic materials in textile is increasing in recent years. Mostly two types of thermochromic materials are applied, leuco dye based thermochromic pigments and liquid crystals. The application of thermochromic materials onto textile fibres experiences difficulties due to lack of affinity and water insolubility. That is why they are normally applied as pigments with some binder systems on the surface of the fabrics and therefore need microencapsulation prior to application. [15]

The colour strength of these pigments is lower compared to other commercially available pigments. This is due to a small amount of dye being presented in the final formulation which is about 2 % in weight prior to microencapsulation and even less in the final product. Therefore, to avoid pale shades, these pigments are used at 15-30 % by weight in the coating. [15]

Because of difficulties with dyeing due to of lack of affinity for textile filaments, a dyeing method has been developed by cationization of cotton fabric. In this method, the cotton is first treated with a cationic compound and then this fabric is poured into the dispersion of reversible thermochromic materials presented in a high polymer compound [34]. It has been used in T-shirts, children clothing, jeans, electronic heat profiling circuitry, incorporated in man-made cellulose fibres and acrylic fibres. For cellulose fibres, the wet spinning technique was used for filament formation during which the thermochromic pigments were incorporated [37].

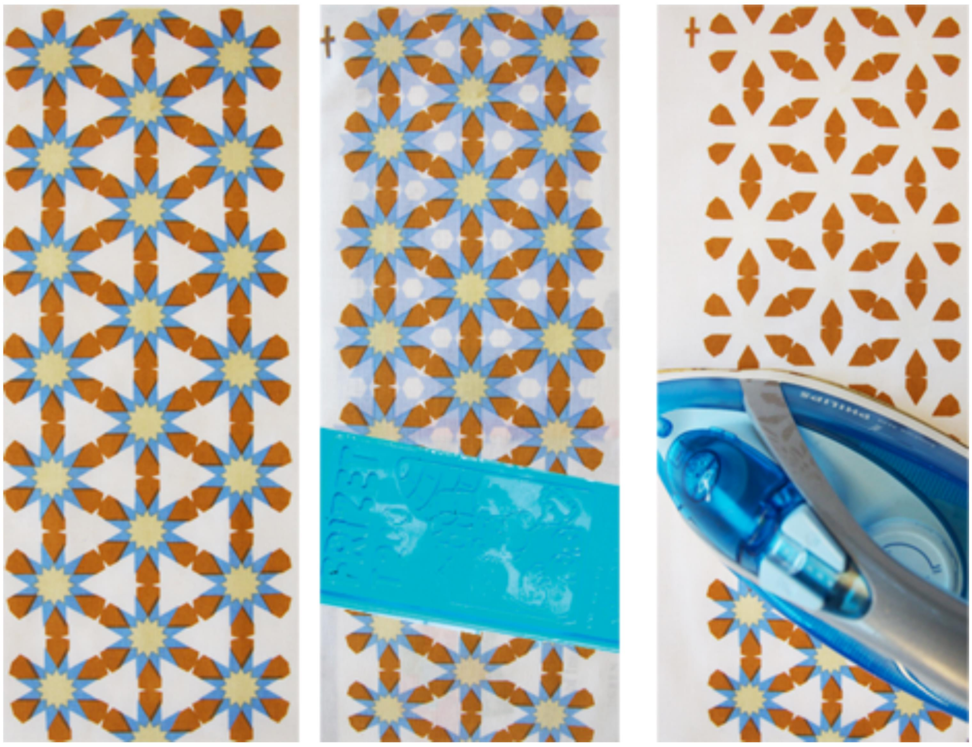


Figure 13: *From left to right: The printed fabric produced by the inks with activation temperatures 27 °C and 15 °C, the effect of cooling the printed fabric and the effect of heating the printed fabric [35].*

From a textile designer’s point of view, an investigation has also been carried out based on the potential of thermochromic materials in textiles. The main investigation was focused on interior textile design and technology interface. Other research has focused on combining thermochromic printed fabric with computational technology and exploring ways of heating or cooling the thermochromic printed fabric. [35]

Although thermochromic pigments incorporated in textile materials have some issues such as inadequate wash and light fastness, their high cost and limited availability, they have good commercial potential especially in the case of smart textiles. As much research is in progress in this area, it is to be hoped that the deficiencies of these materials will be overcome and they will have a significant commercial application in future.

3 EXPERIMENTAL PART

3.1 Chemicals used

For the production of thermochromic coating, organic thermochromic pigment of powder form, produced by Tianki enterprise co., LTD has been used:

Table 4: *Types of used leuco dye thermochromic pigments.*

Symbol	Activation temperature [°C]	Colour change
R38	38	Reversible red to transparent
R50	50	Reversible red to transparent
R60	60	Reversible red to transparent

Polyurethane dispersion for coating of textiles produced by TANATEX chemicals B. V.:

- **PUR OMP** – aqueous formulated aliphatic polyurethane dispersion.

Light stabilizer for coatings provided by STACHEMA CZ s.r.o.:

- **TINUVIN 292**

TINUVIN 292 is liquid hindered-amine based light stabilizers (HALS) that provides significantly extended lifetime to systems by minimizing defects such as cracking and gloss reduction. It has slightly yellow appearance. It is an almost pure mixture of the two active ingredients, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and methyl-1,2,2,6,6-pentamethyl-4-piperidyl sebacate (Figure 14).

The performance of TINUVIN 292 can be significantly improved when used in combination with a UV absorber such as recommended below. These synergistic combinations give coatings superior protection against gloss reduction, cracking, blistering, delamination and colour change.

- **TINUVIN 1130**

TINUVIN 1130 is a liquid UV absorber of the hydroxyphenyl-benzotriazole class (0). Because of its broad UV absorption (Figure 16), TINUVIN 1130 also provides efficient protection to light sensitive substrates such as wood and plastics. It appears as yellow to light amber viscous liquid.

- **Isopropanol**

Isopropanol was used for thermochromic pigment to be better dispersed in PUR OMP.

3.2 Preparation of thermochromic coating

Thermochromic dispersion for coating was prepared by mixing thermochromic pigment (TP) R38, R50 and R60 with PUR OMP, Tinuvin 292 and Tinuvin 1130 in precise concentrations given in Table 5, 6 and 7. The first part of sample´s symbol indicates thermochromic pigment that was used, second part stands for number of layers and third denotes stabilizer used.

Table 5: *One layered sample composition of textile coating with thermochromic pigment.*

Sample	R38 [%]	R50 [%]	R60 [%]	PUR OMP [%]
R38/1	4	–	–	96
R50/1	–	4	–	96
R60/1	–	–	4	96

Table 6: *Sample composition of textile coating with thermochromic pigment R50 and Tinuvin 292 HALS stabilizer.*

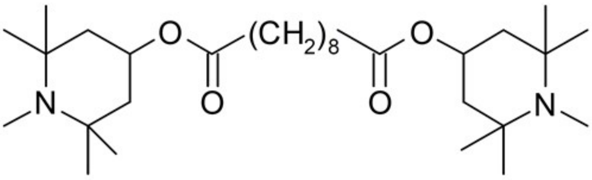
Sample	First layer		Second layer		Third layer		Forth layer	
	R50 [%]	PUR OMP [%]	Tinuvin 292 [%]	PUR OMP [%]	Tinuvin 292 [%]	PUR OMP [%]	Tinuvin 292 [%]	PUR OMP [%]
R50/2/T292	4	96	10	90	–	–	–	–
R50/3/T292	4	96	10	90	10	90	–	–
R50/4/T292	4	96	10	90	10	90	10	90

Table 7: *Sample composition of textile coating with thermochromic pigment R50 and Tinuvin 1130 UV absorber.*

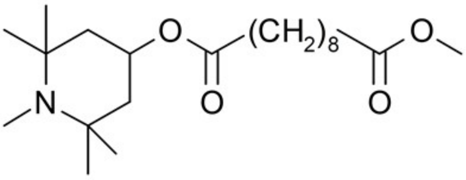
Sample	First layer		Second layer		Third layer		Forth layer		Fifth layer		Sixth layer	
	R50 [%]	PUR OMP [%]	Tinuvin 1130 [%]	PUR OMP [%]	Tinuvin 1130 [%]	PUR OMP [%]	Tinuvin 1130 [%]	PUR OMP [%]	Tinuvin 1130 [%]	PUR OMP [%]	Tinuvin 1130 [%]	PUR OMP [%]
R50/2/T1130	4	96	10	90	–	–	–	–	–	–	–	–
R50/3/T1130	4	96	10	90	10	90	–	–	–	–	–	–
R50/4/T1130	4	96	10	90	10	90	10	90	–	–	–	–
R50/5/T1130	4	96	10	90	10	90	10	90	10	90	–	–
R50/6/T1130	4	96	10	90	10	90	10	90	10	90	10	90

Note: All percentages given in Table 5, 6 and 7 are based on weight percent binder solids.

PUR OMP was cured in vacuum oven for 24 hours in laboratory temperature to find out dry solids. It was calculated that the dry solid is 51,6 %, which corresponds to safety sheet given by TANATEX chemicals B. V. Based on this result the percentage of thermochromic pigment concentration was calculated.

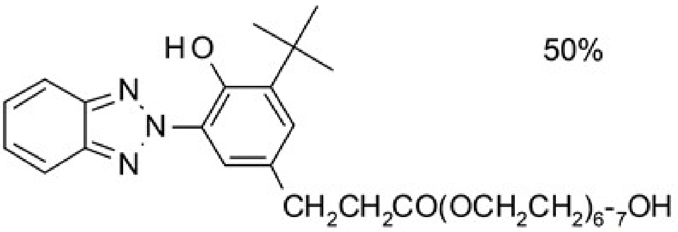


bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate

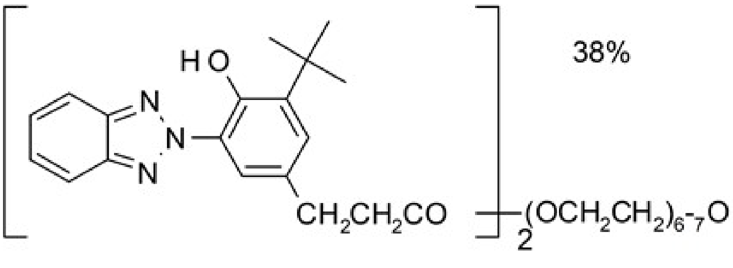


methyl-1,2,2,6,6-pentamethyl-4-piperidyl sebacate

***Figure 14**: Chemical structure of active components in TINUVIN 292.*



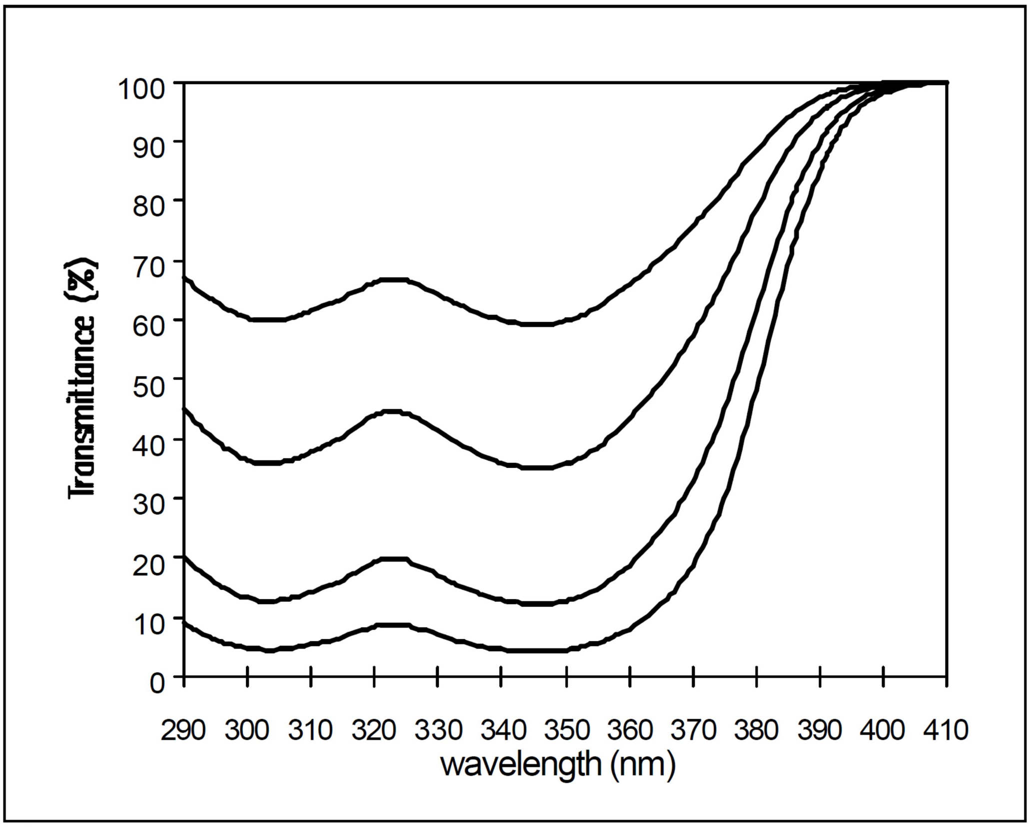
β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-tert.butylphenyl]-propionic acid poly(ethylene glycol) 300-ester



$H-(OCH_2CH_2)_{6}-_{7}OH$ 12%

Bis{b-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-tert.butylphenyl]-propionic acid}-poly(ethylene glycol) 300-ester

***Figure 15:** Chemical structure of active components in TINUVIN 1130.*



Explanation:

Top line:	0.001% TINUVIN 1130, corresponds to 0.25% in a 40 μ film
Second line:	0.002% TINUVIN 1130, corresponds to 0.50% in a 40 μ film
Third line:	0.004% TINUVIN 1130, corresponds to 1.0% in a 40 μ film
Bottom line:	0.006% TINUVIN 1130, corresponds to 1.5% in a 40 μ film

Figure 16: *Transmittance spectrum for Tinuvin 1130 dispersed in toluene.*

3.2.1 Homogenization

The dispersion of PUR OMP and thermochromic pigment used for first layer was homogenized with IKA homogenizer for 10 min at rate 2 and then UV cured for 15 min before applying floating knife technology. The dispersions used for further layers were homogenized with IKA homogenizer for 10 min.

3.2.2 Knife coating technology

One type of knife coating is blade-over-air or also called floating knife (Figure 17). The liquid coating is applied to the fabric while being run under a floating knife blade at tension. In this technology, the knife is fixed and actually touches the fabric. The depression of the knife blade and the fabric tension determines the thickness of the coating and its final weight. The blade can be angled and have different profiles to affect the coverage. This technology is usually used when applying small amount of coating material on the fabric.

Another more common technique is knife-over-roll coating (Figure 17). Unlike in the floating knife technology the blade is fixed above the roller and does not touch the substrate directly. By controlling the thickness of the gap between blade and fabric the final thickness of the coating can be determined. Although the gap can be set very accurately, the variation in substrate thickness might make the thickness of the coating non-uniform. The roller can be steel or rubber coated. [36]

In knife coating technology the main factors are blade geometry (the shape and angle), blade flexibility and the rheology of the coating fluid. All these parameters affect the amount of coating applied and the extent of penetration into the substrate. After applying the coating the material has to be dried and cured. [36]

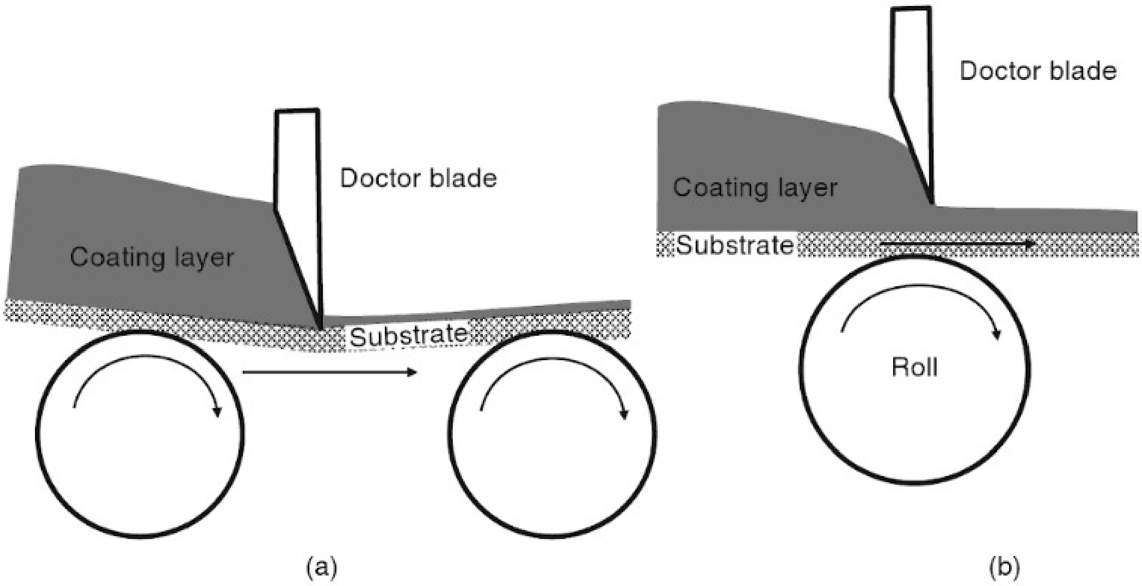


Figure 17: *Knife coating: (a) floating knife coating, (b) knife over roll coating [36].*

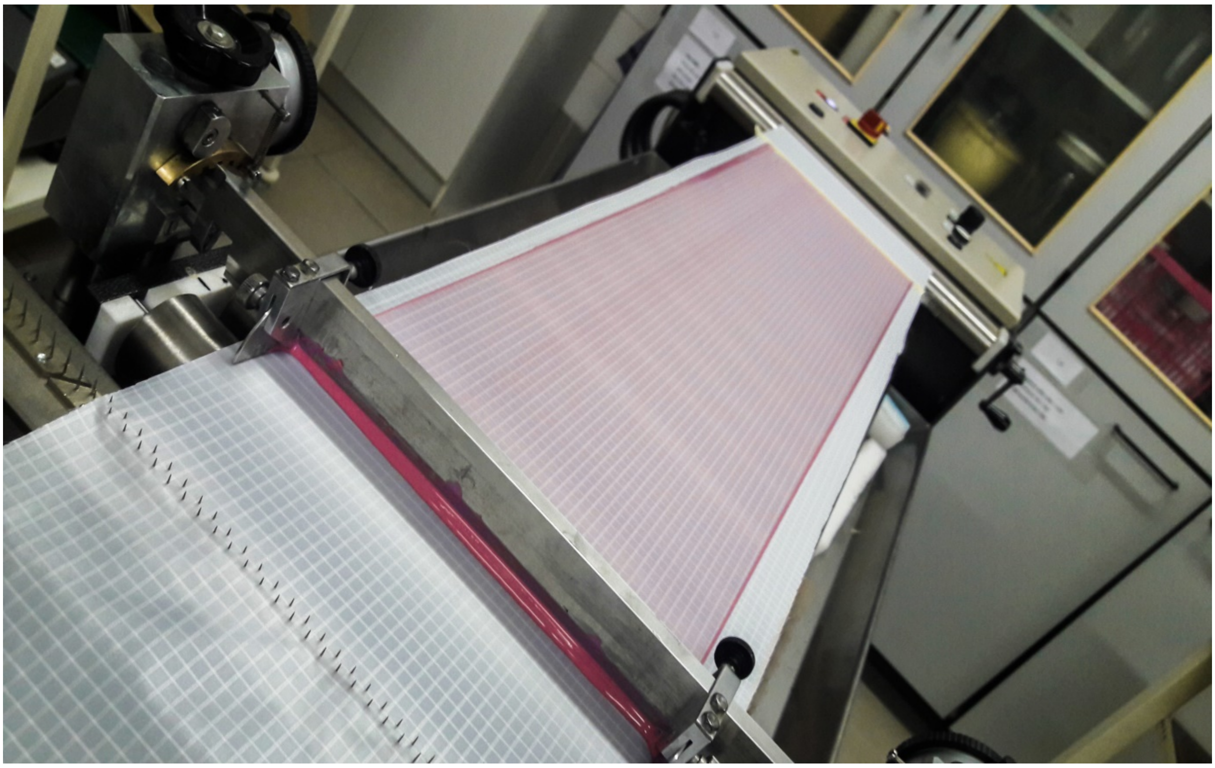


Figure 18: *A photo of application of thermochromic coating onto polyester fabric.*

In this work floating knife technology has been used for thermochromic textile coating. The coating has been applied on polyester fabric. After optimizing of the process the conditions were setup to blade pressure of 0.1 mm at the rate of 5 which corresponds to 113 cm·min^{-1}. This setup led to the best homogenized samples in terms of colour. The samples with single layer coating were cured at 150 °C for 2 min in Memmert drying oven. The samples with more layered coating were prepared as follows. The first layer was applied (Figure 18) and it was dried with Hot-air pistol Steinel HL2305LCD at 150 °C for approx. 2 min. Further layers were also applied with rate 5 and blade pressure of 0.1 mm. Every single layer was cured for 2 min at 150 °C with hot-air pistol and the final product was cured at 150 °C for 2 min in Memmert drying oven.

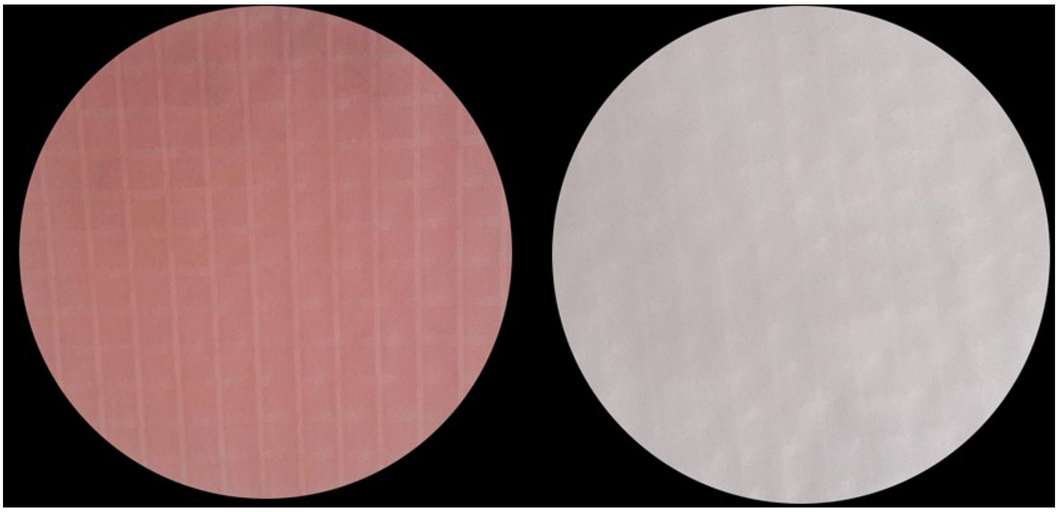


Fig. 19: *Thermochromic textile coating below (left) and above activation temperature (right).*

3.2.3 Coating mass measurement

Samples of thermochromic coating were cut with pneumatic cutting machine to the circle with 80 mm diameter. The area was therefore calculated to be $5.03 \cdot 10^{-3}$ m^2. For each sample three mass measurements were taken.

3.3 Methods used

3.3.1 Fourier transform infrared spectroscopy

Infrared radiation (IR) is a section of electromagnetic radiation with wavenumber $\tilde{\nu}$ ranging from approximately 200 to 4 000 cm^{-1}. The relation between the wavenumber, wavelength λ, frequency *f*, and angular frequency *ω* is given by the equation 3.1, where *c* denotes the light velocity in vacuum.

$$f = \frac{1}{\lambda} = \frac{\tilde{\nu}}{c} = \frac{\omega}{2\pi c} \tag{3.1}$$

Absorption of IR leads to excitation of specimen oscillation state which invokes peaks in absorbance as a function of the wavenumber. Several oscillation modes are possible: symmetrical and antisymmetrical stretching, scissoring, rocking, wagging and twisting.

IR spectra were measured with FTIR Bruker Tensor 27 with resolution of 4 cm^{-1} and 32 scans. The attenuated total reflectance (ATR) method with diamond crystal was used in the middle IR range, 4 000–400 cm^{-1}.

3.3.2 Thermogravimetric analysis

Thermogravimetric analysis (TA) uses thermobalance to measure the change in mass as a function of temperature or time. Mass changes are involved by processes such as sublimation, evaporation, decomposition, chemical reaction, adsorption or desorption.

Thermogravimetric analysis was performed with TGA TA Instruments Q 500. Samples R38, R50 and R60 having the weight 6.488 mg, 6.781 mg and 8.199 mg respectively were heated on platinum pan in nitrogen up to 700 °C with rate 10 $°C\cdot min^{-1}$. Than the purge gas was switched to compressed air and the program ended with 5 minutes isothermal step at 700 °C. The data were evaluated with program TA Instruments Universal analysis 2000.

3.3.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is an analytical method used for determining the quantity of heat that is either absorbed or released during a physical or a chemical change. The heat flow is measured as a function of temperature or time. Exothermic processes such as crystallization, curing, decomposition result in increased heat flow whereas endothermic processes such as melting, evaporation or glass transition decrease it.

Phase transition of thermochromic material R38, R50 and R60 were monitored by DSC analysis Perkin Elmer Pyris 1. The temperature range of 0 – 90 °C and the rate of temperature change of 2 $°C\cdot min^{-1}$ were set to be in match with setup applied in measurement of colour change. For evaluation, the second heating-cooling cycle was considered. The data were evaluated with program TA Instruments Universal analysis 2000. The obtained temperature data in DSC measurements refer to the temperature of the reference due to the limiting heat transfer of the sensor.

3.3.4 Optical microscopy

An optical microscope, also sometimes known as a light microscope, uses one or a series of lenses to magnify images of small samples with visible light. The lenses are placed between the sample and the viewer's eye to magnify the image so that it can be examined in greater detail. The standard optical microscope, which is still the most widely used type of microscope, has remained essentially unchanged for more than a century, since the theoretical resolution limit of about 200 nm (set by the wavelength of visible light) was attained in the 1880s.

Samples R38, R50 and R60 in dispersion with PUR OMP were analysed with Olympus BX 50 optical microscope with 50*x* magnification and with camera Olympus Camedia 5060. Photomicrograph of the samples was obtained in bright field in high quality mode. Size distribution was evaluated by image analysis with AnalySIS software. For each sample 150 measurements was taken into evaluation.

3.3.5 Colour measurement

The spectrophotometer uses a simple mechanism where a light source illuminates the sample with specific viewing geometry. The reflected or transmitted light is passed through a spectral analyser where it splits into spectral components. Light detectors and control electronics take measurements at many regular wavelengths in visible region. The spectrophotometer has the advantage over a simple colorimeter of incorporating the spectral analyser.

The colorimetric properties of the thermochromic samples were described with the CIE *L*a*b** colour space (Figure 20). CIE *L*a*b** colour space describes mathematically all perceivable colours with three dimensions. The lightness represents *L** with the darkest black at *L**=0 and the brightest at *L**=100. The red and green opponent colours are represented along the *a** axis while the yellow and blue opponent are represented along the *b** axis. *C** represents chroma or saturation. It ranges from 0 at the centre of the circle, which is completely unsaturated to 100 or more at the edge of the circle for very high chroma.

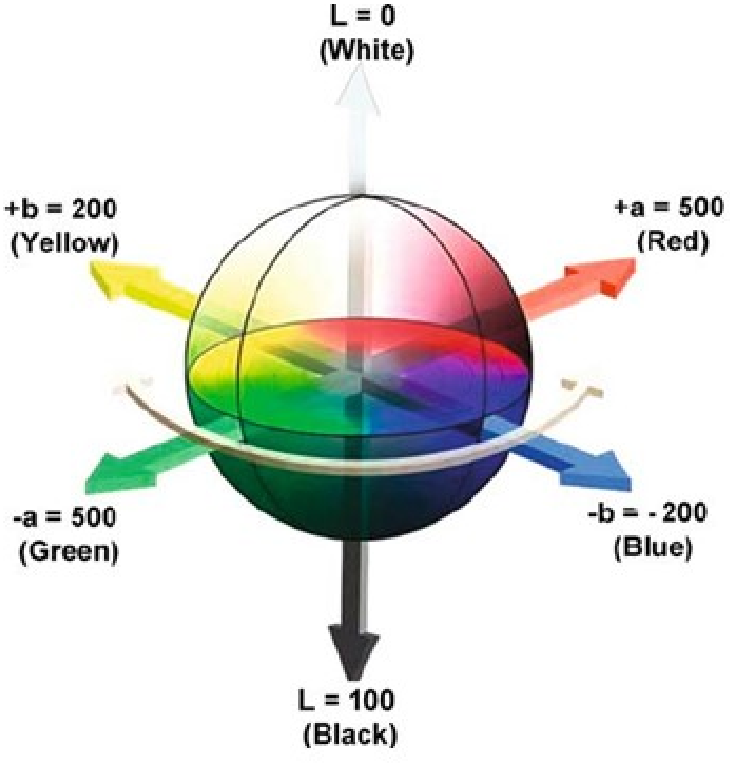


Figure 20: *Scheme of the cubical CIE Lab colour space.*

The colorimetric properties were measured with spectrophotometer Eye-One Pro at standard white base in room temperature (Figure 21). The colorimetric parameters were computed using the D50 standard illumination and the 2° standard observer. It means that sample was illuminated from all angles while reflected light is measured at 2° angle from the sample surface. The spectrum was measured from 380 to 730 nm with 10 nm step and considered parameters are *L**, *C**, *a** and *b** coordinates of CIE *L*a*b** colour space. For not temperature dependant measurement 10 values were taken into evaluation for each sample. Since the textile has specific texture the spot with same structure has been always measured to eliminate the error (Figure 21). With spectrophotometer the reflectance and $L^*a^*b^*$ axis were measured. Based on $L^*a^*b^*$ dimensions colour scale was created with Adobe Photoshop and added to reflectance spectrum for better visualization. Cumulative colour difference (ΔE) was calculated from $L^*a^*b^*$ values as it is described in equation 3.2.

$$\Delta E = \sum_{i=1}^{T} \sqrt{[\mathrm{L}^*(i) - \mathrm{L}^*(i-1)]^2 + [\mathrm{a}^*(i) - \mathrm{a}^*(i-1)]^2 + [\mathrm{b}^*(i) - b^*(i-1)]^2} \tag{3.2}$$

Since the colour difference is well known and used method for evaluating colour, the scale for evaluating degree of colour change has been created (Table 8).

Table 8: *Scale for evaluating degree of colour change*

ΔE	0.2–1.0	1.0–2.0	2.0–4.0	4.0–8.0	more then 8.0
Difference	imperceptible	perceivable	not disturbing	slightly disturbing	disturbing

The temperature dependant measurement was taken with controlled heat mechanism. A hot stage with decimal place controlled temperature was used. The printed thermochromic sample was gradually heated to a specific temperature, which was then maintained for a couple of minutes at the required level before taking measurements with spectrophotometer. The samples were heated from lowest to highest temperature. The measurement have been taken in 1 °C intervals 10 °C above a below transition temperature. Larger temperature difference has been allowed elsewhere (up to 5 °C). The colorimetric properties were measured with USB-650 Red Tide Spectrometer. The colorimetric parameters were computed using the D50 standard illumination from 45° angle and reflected light was measured also at 45° angle from the sample surface. Since the hot plate was not designed for cooling, it was not able to maintain specific temperature for long time. Thus, the cooling measurement is not as precise as the heating one.

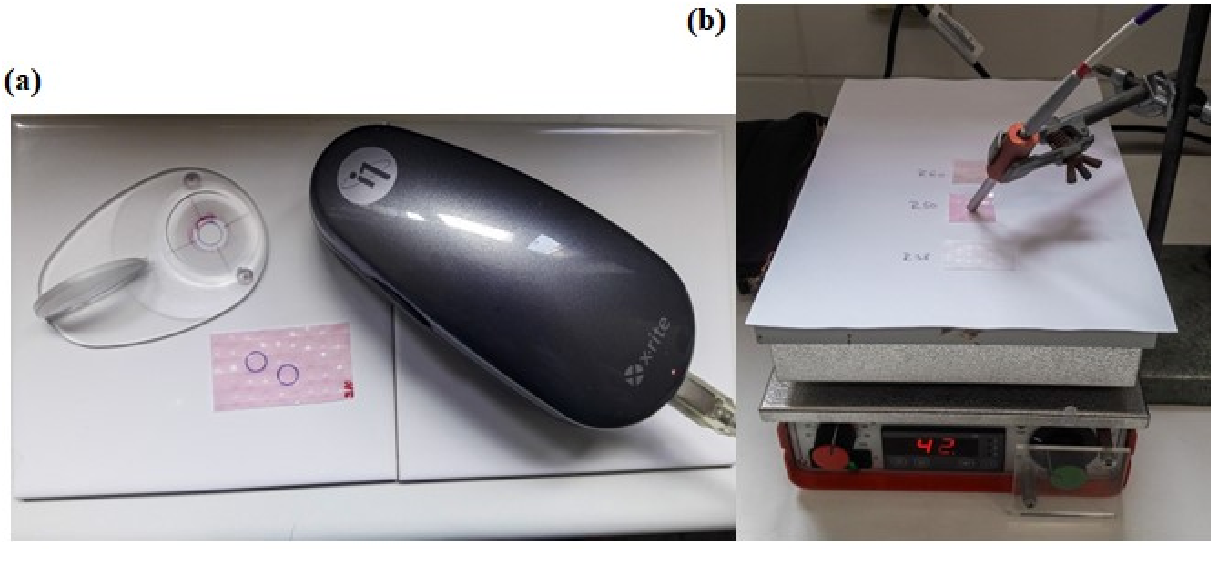


Figure 21: *Colorimetric measurement with Eye-One Pro spectrophotometer (a) and temperature dependant measurement (b).*

3.3.6 Accelerated aging

Accelerated aging is testing that uses aggravated conditions of heat, humidity, oxygen, sunlight, etc. to speed up the normal aging processes of items. It is used to help determine the long-term effects of expected levels of stress within a shorter time, usually in a laboratory by controlled standard test methods. The usually monitored values are lightfastness, colourfastness and photostability.

The measurement was taken with the Q-SUN xenon chamber which reproduces the damage caused by sunlight. It has a single xenon arc lamp that provides the best match to the full spectrum of sunlight. The irradiance was set to 0.35 $W \cdot m^{-2}$ at 340 nm. Due to the chiller the temperature in chamber was hold on 35 °C, which is below their activation temperature. The samples were exposed to light for 1, 2, 4, 8, 16 and 24 hours and the corresponding colour measurements were taken with the spectrophotometer.

Figure 22: *A photo of accelerated aging test in Q-SUN xenon chamber.*

4 RESULTS AND DISCUSSION

Three types of thermochromic leuco day based pigment of powder form have been chosen for further investigation. Reversible thermochromic pigments R38, R50 and R60 with transition temperatures 38, 50 and 60 °C respectively. Colour change for all pigments is from red (below transition temperature) to transparent (above transition temperature). Pigments have been characterized by FTIR, TGA, DSC methods and optical microscopy and then used for thermochromic textile coating. Textile coating was then characterized in terms of light and thermal stability and attempts for stabilizing the pigment have been made. Results and discussion are given below.

4.1 Microcapsule shell characterization

Thermochromic textile coating is a mixture of thermochromic pigments and a polymer binder while the phases are separate and have no influence on each other. For this to be true thermochromic pigment powder has to be microencapsulated when used on textiles and therefor FTIR ATR analysis was carried out.

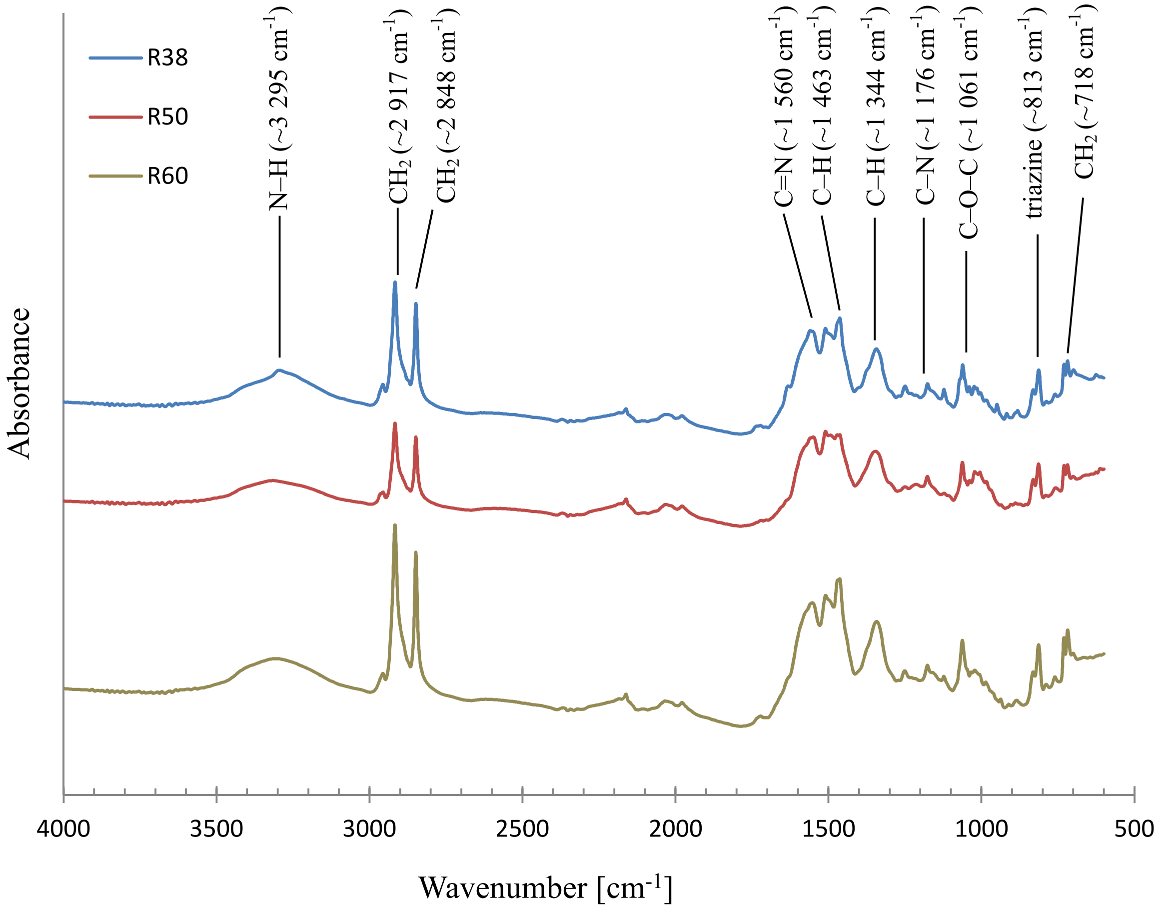


Figure 23: *FTIR spectra of R38, R50 and R60 thermochromic pigment.*

Figure 23 shows the FTIR spectra of R38, R50 and R60 thermochromic pigment, which are for all three samples almost identical. The spectra for sample R38 show absorbance at 3 295 cm^{-1} corresponding to the stretching vibrations of primary amine. The absorption at 2 917 cm^{-1} and 2 848 cm^{-1} is due the CH_2 stretching vibration, which gave a strong evidence for methylene bridge formation. C=N ring vibration is observed at 1 560 cm^{-1}. The peak at 1 463 cm^{-1} and 1 344 cm^{-1} corresponds to the methylene C–H bending vibrations. Absorbance at 1 176 cm^{-1} is attributed to aliphatic C–N vibration. The peak at 1 061 cm^{-1} corresponds to the stretching vibration of ether group. Bending vibration of triazine ring was found at 810 cm^{-1} [43]. Specific absorption bands of the FTIR absorption spectra confirmed that thermochromic pigments are microencapsulated and microcapsules are composed of the melamine resin as a shell [42]. IR spectral data of the thermochromic pigment are compiled in Table 9. Measured data were compared with the FTIR tabulated values given in reference 39 and 40.

Table 9: *IR spectral data of R38, R50 and R60 thermochromic pigment.*

Group	**Vibration**	**Wavenumber [cm^{-1}]**		
		R38	**R50**	**R60**
N–H (primary amine)	bending	3 295	3 312	3 307
CH_2 group (methylene bridge)	asymmetric stretching	2 917	2 917	2 917
CH_2 group (methylene bridge)	symmetric stretching	2 848	2 848	2 848
C=N (ring vibration)	stretching	1 560	1 557	1 552
C–H (methylene)	bending	1 463	1 463	1 463
C–H (methylene)	bending	1 344	1 345	1 343
C–N (aliphatic)	stretching	1 176	1 176	1 176
C–O–C (ether group)	stretching	1 061	1 062	1 062
N–C=N (triazine cycle)	asymmetric stretching	813	813	813
CH_2 group	asymmetric stretching	718	718	718

4.2 Thermal stability

Thermochromic pigments are reported as being heat sensitive and therefore it was anticipated that they may lose colour strength or be destroyed at high temperatures. Thermochromic pigments R38, R50 and R60 were characterized by thermogravimetric analysis for detection of temperature and weight change of decomposition reactions. Conclusions regarding thermal stability, which depends on thermal stability of the melamine resin shell have been stated.

To check the thermal stability of leuco dye base thermochromic pigments against time exposure samples R38/1, R50/1 and R60/1 were exposed to 150 °C for certain amount of time and then characterized with Eye-One Pro spectrophotometer. Cumulative colour difference (ΔE) was used as comparative value.

4.2.1 Stability towards heat

Thermochromic pigments were characterized by thermogravimetric analysis for detection of thermal stability, which depends on thermal stability of their melamine resin shell.

The results for thermochromic pigment R38 can be seen at TGA thermogram as shown in Figure 27. We can define four temperature ranges where the weight losses appeared, from 0 to 200, 200 to 340, 340 to 380 and 380 to 700 °C. In the first region from 0 to 200 °C the weight loss is related to the thermal curing process of melamine resin. Also we can state, that the sample consists of relatively high amount of low molecular substances. Corresponding 3.1 % weight loss is due to the evaporation of water during the condensation process. Water elimination can occur due to the selfcondensation of methylol groups, leading to ether bridge formation or during the condensation reaction between melamine and the methylol group, which leads to the methylene bridge as per the curing reaction shown in Figure 24.

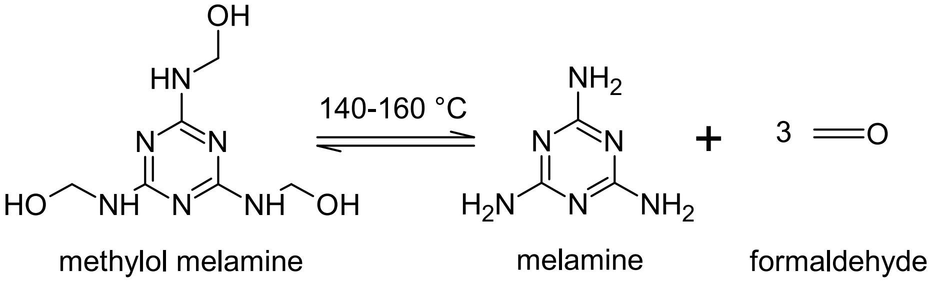


Figure 24: Decomposition of methylol melamine.

Above 200 °C significant loss of weight occurs and sample is no longer stable. Temperature range 200–340 °C corresponds to the elimination of formaldehyde from the ether bridge, forming methylene bridge as shown in Figure 25. The weight loss is 29.2 %.

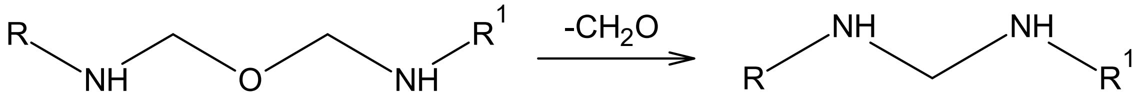


***Figure 25**: Scheme of elimination of formaldehyde from the ether bridge, forming methylene bridge.*

Third, weight loss of 53.8 % observed in the temperature range 350–390 °C is attributed to the breakdown of methylene bridges. Possible reaction mechanism of the methylene bridge breakage is shown in Figure 26.

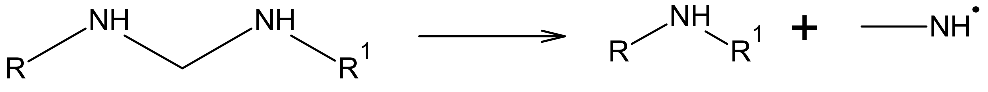


***Figure 26:** Breakage mechanism of methylene bridge.*

Weight loss beyond 390 °C is attributed to the thermal degradation of the triazine ring, and it is assumed that melamine resin progressively deaminates to form HCN.

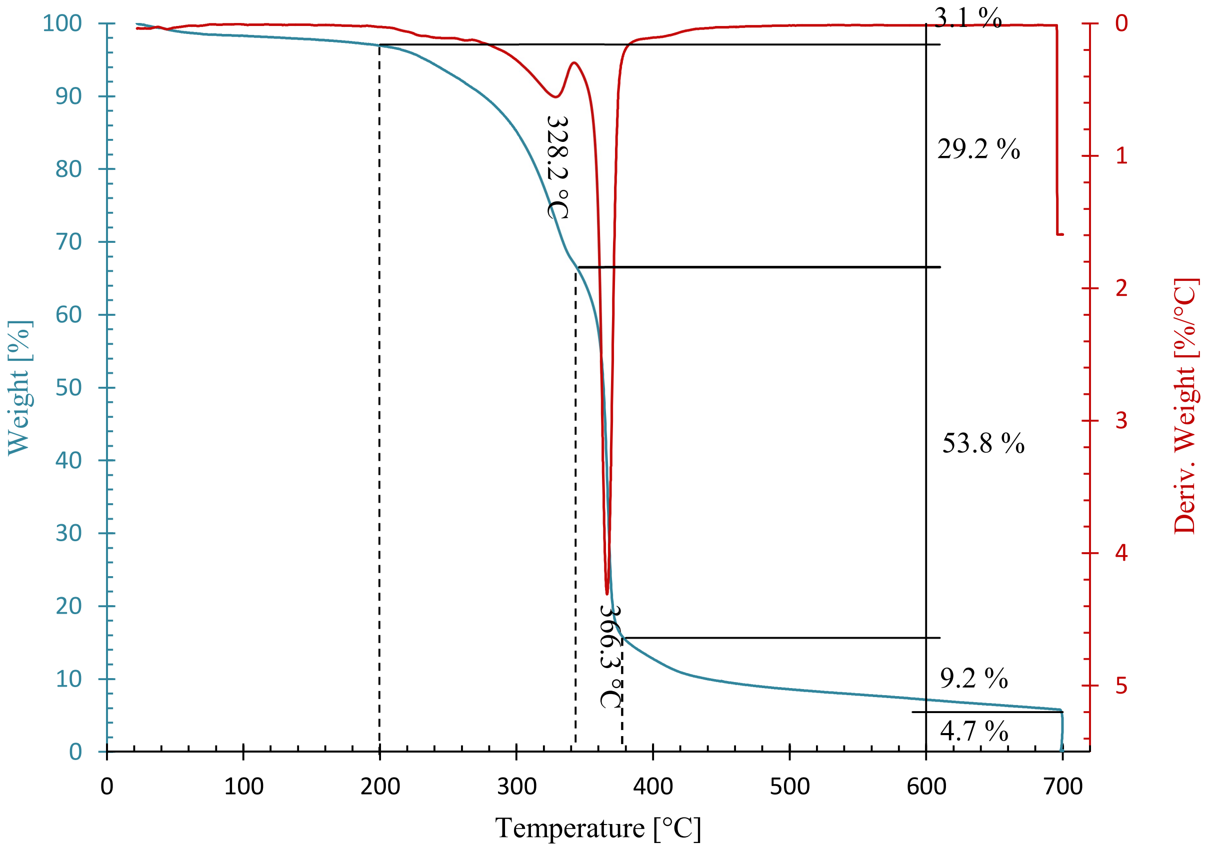


Figure 27: *TGA thermogram of thermochromic pigment R38.*

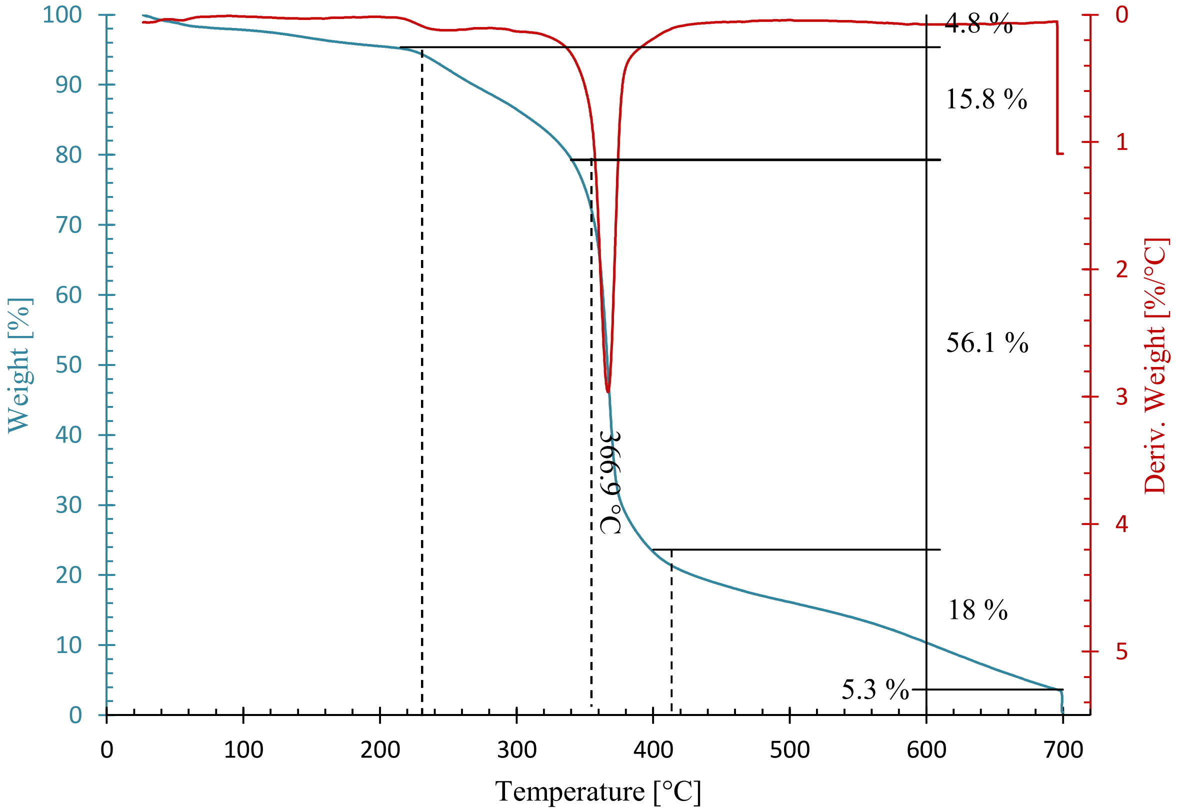


Figure 28: *TGA thermogram of thermochromic pigment R50.*

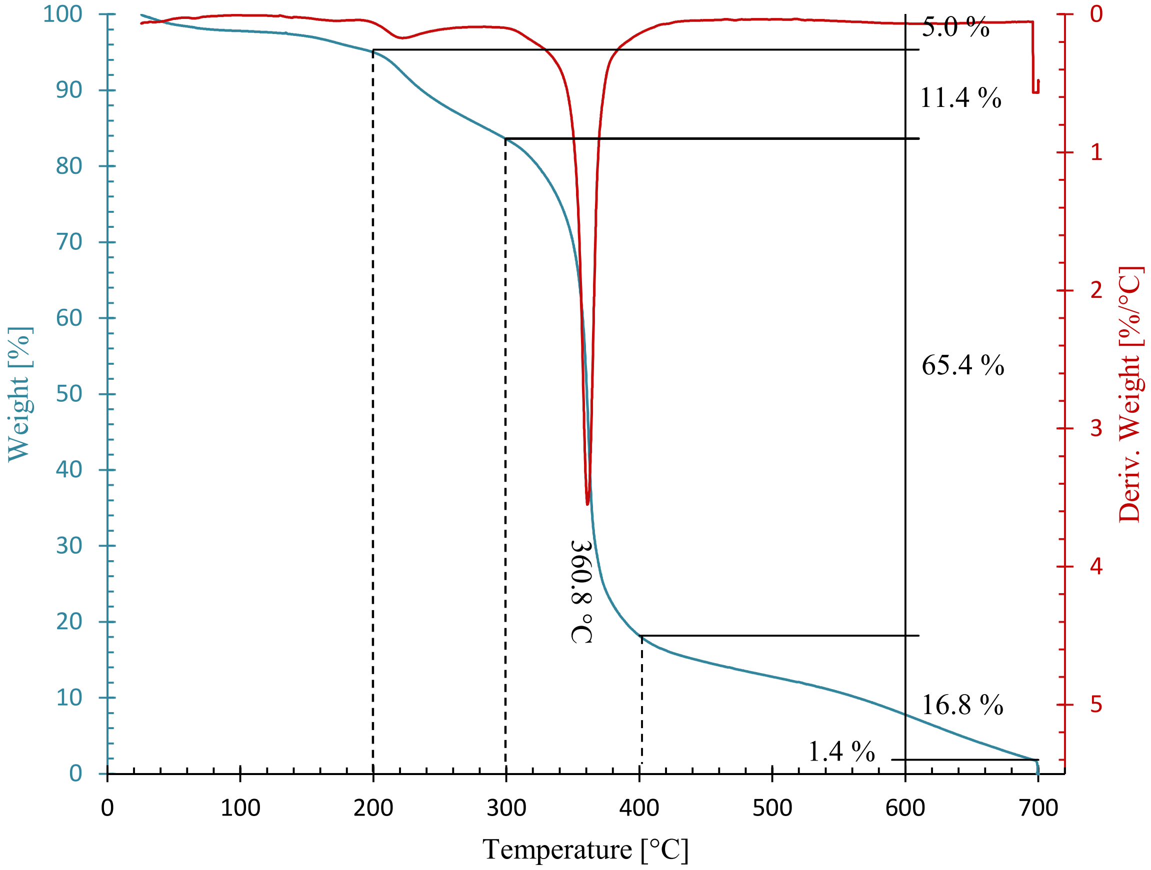


Figure 29: *TGA thermogram of thermochromic pigment R60.*

Although samples R50 and R60 undergo same thermal degradation processes as sample R38, sample R38 shows noticeable peak at 328 °C which indicates additional component. Another significant peak at deriv. weight curve which is similar for all samples occurs at ~365 °C. Around this temperature the samples loose most of their weight.

In contrast to sample R38, sample R50 is stable up to 215 °C. We can define four temperature ranges where the weight losses appears, from 0 to 215, 215 to 344, 344 to 404 and 404 to 700 °C. The corresponding weight losses can be seen in Figure 28. Sample R60 is stable up to 200 °C and the temperature ranges are 0 to 200, 200 to 302 and 302 to 400. Thermograph with corresponding values can be seen in Figure 29.

Although it has been stated that TP R38, R50 and R60 are stable up to 200, 215 and 200 °C respectively, there is weight loss even below this temperature. This weight loss is related to the thermal curing process of melamine resin and to relatively high amount of low molecular substances. For this reason samples should be exposed to such high temperatures only while processing, if necessary and for short time period. Otherwise the shell will be faulted and the reversible colour change will not be longer possible.

TGA curves have been compared to the ones in literature [43]. All results given in this section corresponds to conclusions given in this article concerning curing studies of melamine resin.

4.2.2 Thermal stability towards time exposure

Thermochromic colours are reported as being heat sensitive. Therefore, it was anticipated that they may lose colour strength, or even be destroyed at high temperatures. To establish the thermal stability towards time exposure of leuco dye based thermochromic pigments, three thermochromic coatings R38/1, R50/1 and R60/1 were cured at 150 °C and for different time periods. The temperature was chosen because of the binder PUR OMP, which needs to be cured at 150 °C. All samples were measured by the spectrophotometer according to the optimised calibration conditions as discussed in section 3.3.5. Since possible colour loss was anticipated at high temperatures, cumulative colour difference which is directly related to the visually assessed strength of the colour, rather than the hue, were chosen for evaluation. As comparative values for cumulative colour difference were chosen samples R38/1, R50/1 and R60/1, which were cured for 2 minutes. Colour difference values were calculated as stated in equation 3.2. The curing conditions used are shown in Table 10.

***Table 10:** Curing time periods for evaluation thermal stability at 150 °C.*

Sample	TP concentration [%]	Time period [min]					
R38/1	4	2	4	6	8	10	12
R50/1	4	2	4	6	8	10	12
R60/1	4	2	4	6	8	10	12

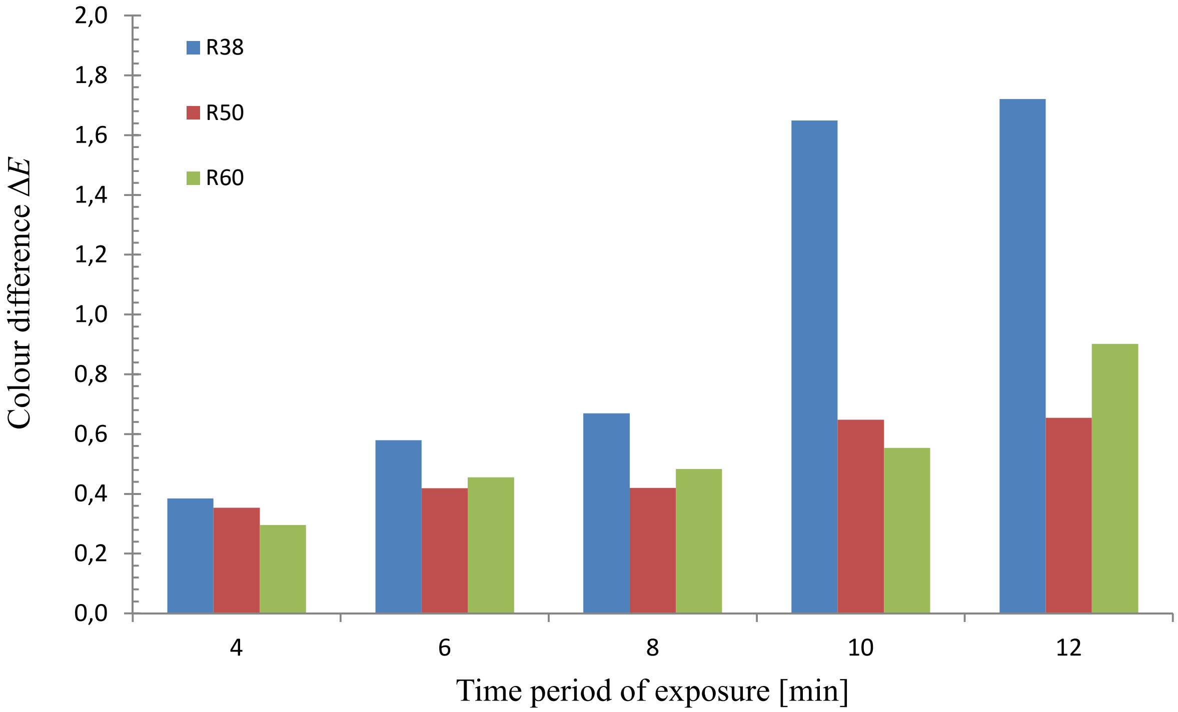


***Figure 30:** Colour difference illustrating thermal colour stability of thermochromic coating at various exposure times at curing temperature 150 °C.*

Although from Figure 30 can be seen gradual and regular decrease in colour strength with time, this colour change is not very significant for most of the samples. The colour difference between 0 and 1 is weak and almost unrecognizable for human eye. This means that even though samples R50 and R60 show decrease in colour strength, the difference is very small and undistinguishable. This cannot be stated for sample R38. As can be seen in Figure 30, sample R38 has the lowest thermal stability towards time exposure compared with other samples and its colour strength decrease with exposure time most significantly. The change in colour is already recognizable for human eye after 10 minutes exposure at 150 °C. The colour difference for samples exposed to heat for 10 and 12 minutes is for thermochromic coating with pigment R38 twice as big as for the coatings with pigments R50 and R60.

Generally, the thermochromic prints are sensitive towards high temperatures and exposure time. However, for samples R50/1 and R60/1 the exposure time has less impact on colour strength compared with sample R38/1. This conclusion corresponds with the one from thermogravimetric analysis where have been stated that already below 200 °C a weight loss occurs. This weight loss has impact on colour stability and that why it is suggested that the curing time should be kept as low as possible.

4.3 Colour formation principle

Colour formation principle, that was already described theoretically in section 2.2.1, is explained further by differential scanning calorimetry. Due to this analysis phase transition temperatures have been detected and competitive reactions between dye-developer and solvent-developer have been clarified. Moreover, the dynamic colour change has been measured with temperature dependant spectrophotometric test and compared to the phase transition temperatures detected from DSC.

4.3.1 Phase transitions of thermochromic pigment

Thermochromic material R38, R50 and R60 were analysed by differential scanning calorimetry to find out the relationship between colour and structural changes. For evaluation, the second heating-cooling cycle was considered.

For thermograph of R38 pigment see Figure 31. Long chain alcohols, predominantly used as solvents, show several phase transitions. On cooling, firstly the liquid-solid transition takes place to form α-phase also called as rotator phase. By further cooling the solid-solid transition occurs and crystalline β-form or δ-form structure of the solvent is formed. As expected, there is only a single peak on heating. This peak represents the overlapping solid-solid and solid-liquid transitions. A broad peak of melting point can be seen, i.e. the peaks corresponding to the solid-solid and solid-liquid transitions are less overlapped. This can be caused for example by addition of bisphenol A as a developer, according to the literature [41]. The melting point (T_{S-L}) of solvent is 37,25 °C, the liquid-solid transition (T_{L-S}) occurs at 30,81 °C and solid-solid transition (T_{S-S}) take place at 21,44 °C. As a solvent could have been used tetradecanol, that is aliphatic alcohol with melting point at 38.0 °C [44].

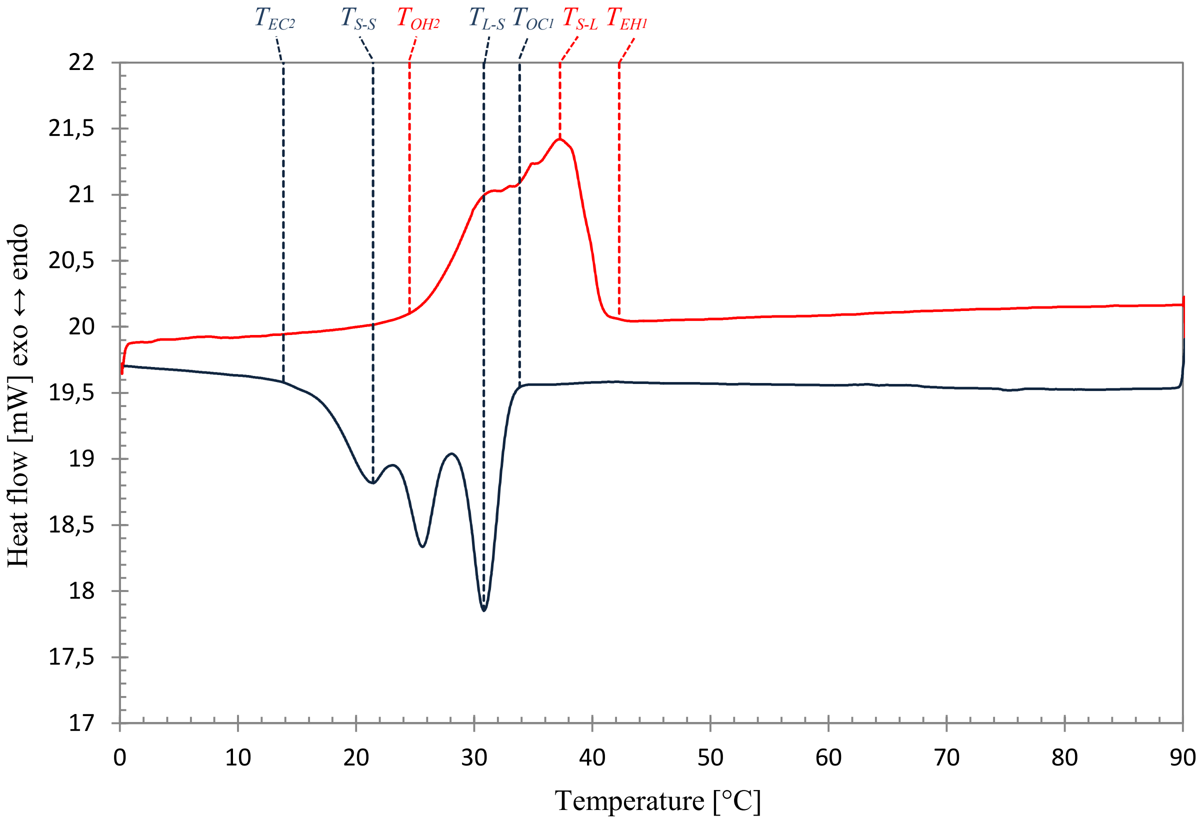


Figure 31: *DSC thermograph of sample R38 with specific temperatures that characterize colour formation.*

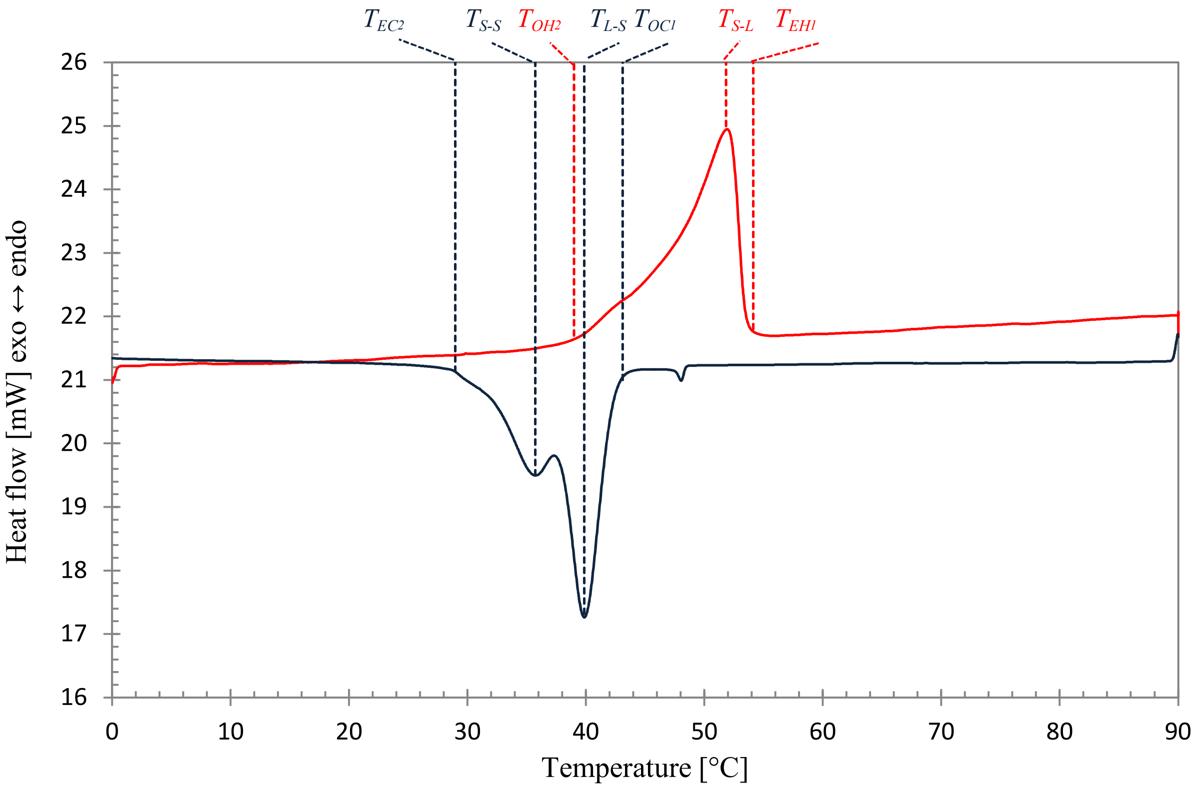


Figure 32: *DSC thermograph of sample R50 with specific temperatures that characterize colour formation.*

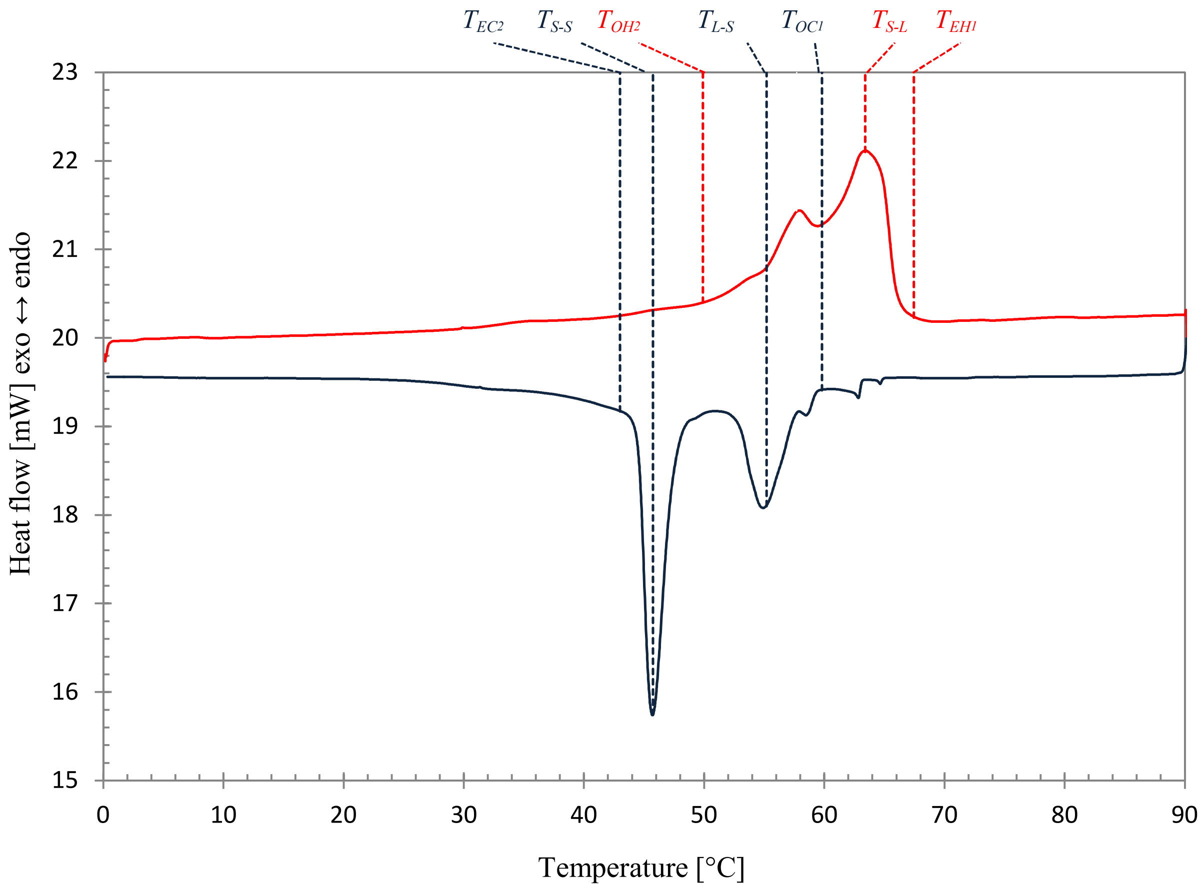


Figure 33: *DSC thermograph of sample R60 with specific temperatures that characterize colour formation.*

Table 11: *Temperatures characterizing the phase change transitions and dynamic colour change.*

	Characteristic temperature	**Symbol**	**R38**	**R50**	**R60**
Heating	onset temperature	T_{OH2} [°C]	24.52	39	49.9
	initial achromatic	T_{IH} [°C]	28.2	38.7	55.5
	solid-liquid transition	T_{S-L} [°C]	37.25	51.84	63.4
	endset temperature	T_{EH1} [°C]	42.28	54.14	67.46
	final achromatic	T_{FH} [°C]	40.4	54.9	68
Cooling	initial chromatic	T_{IC} [°C]	37	51.1	64.3
	onset temperature	T_{OC1} [°C]	33.84	43.1	59.82
	liquid-solid transition	T_{L-S} [°C]	30.81	39.87	55.2
	final chromatic	T_{FC} [°C]	25.5	43	50,8
	solid-solid transition	T_{S-S} [°C]	21.44	35.73	45.74
	endset temperature	T_{EC2} [°C]	13.85	28.97	43

For thermograph of R50 thermochromic pigment see Figure 32. As well as for sample R38 we can distinguish formation of α-phase on cooling and by further cooling formation of crystalline β-form or δ-form structure of the solvent. There is only a single distinct peak on heating. The liquid-solid and solid-solid transitions of even alcohols are clearly separated in DSC spectrum on cooling, whereas on heating they are overlapped. However, the results do not show evidence of the complex formation of solvent and developer. As a solvent could have been possibly used hexadecanol, which is aliphatic alcohol with melting point at 49.3 °C or 2,2,5,5-tetramethylhexanol, which has melting point at 52.5 °C [44].

In comparison to samples R38 and R50, in the thermograph of sample R60 (Figure 33) the liquid-solid and solid-solid transitions on cooling can be resolved more clearly. On heating the peaks corresponding to the solid-solid and solid-liquid transitions are less overlapped and might be detected. As a solvent could have been possibly used nonadecanol, which is aliphatic alcohol with melting point at 63.3 °C or octadecanol, which has melting point at 59.5 °C or eicosanol with melting point at 64.9 °C [44].

From the DSC measurements we can conclude that the phase transitions of solvent have essential impact on colour formation. Phase change transition temperatures for all samples are shown in Table 11.

4.3.2 Dynamic colour change

For evaluation of transition temperature further measurements have been made with the adjustment stated in section 3.3.5. Samples R38/1, R50/1 and R60/1 were investigated. Thermochromic coatings were heated with controlled mechanism to obtain L^*, a^* and b^* coordinates of CIE $L^*a^*b^*$ colour space. Since all thermochromic pigments are red coloured at low temperature and non-coloured at elevated temperature, the a^* coordinates has been chosen for evaluating transition temperatures. While measuring, all temperatures were kept well below the highest temperatures recommended as acceptable by producer (200 °C). The temperature dependant colour test was measured applying small temperature gradient on samples with relaxed colour. The measurement have been taken in 1 °C intervals 10 °C above a below activation temperature. Larger temperature difference has been allowed elsewhere (up to 5 °C).

The leuco dye-based thermochromic coating´s colour depends on temperature and on thermal history. This effect is known as hysteresis. The temperature of decolourization is generally not equal to the temperature of colourization. The shape of colour hysteresis can be characterized by four temperatures. The decolourization effect that occurs while heating can be described by two temperatures, initial achromatic (T_{IH}) and final achromatic (T_{FH}). The first initial temperature denotes where the corresponding competing reaction between developer and solvent starts whereas this reaction prevails at second final temperature. The colourization effect that occurs while cooling can be also described with two temperatures, initial chromatic (T_{IC}) and final chromatic (T_{FC}). Therefore these four temperatures characterise the chemical reaction producing colour change in thermochromic leuco dye pigments. Activation temperature is the only temperature given by the producer and describes dynamic colour change. This temperature supposed to be higher than T_{FC} and lower than T_{FH}. Thus, the activation temperature gives us no particular information about the whole thermochromic process.

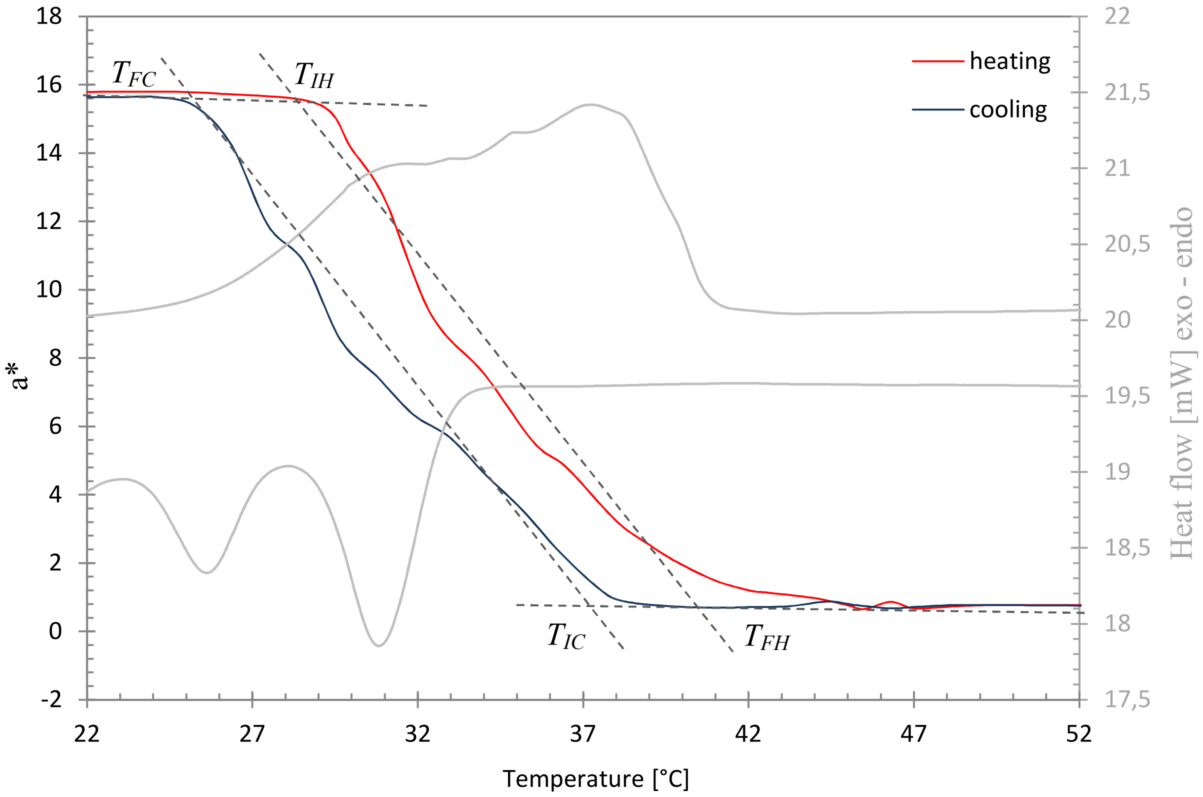


***Figure 34:** a*(T) graph showing dynamic colour change with corresponding temperatures for sample R38/1.*

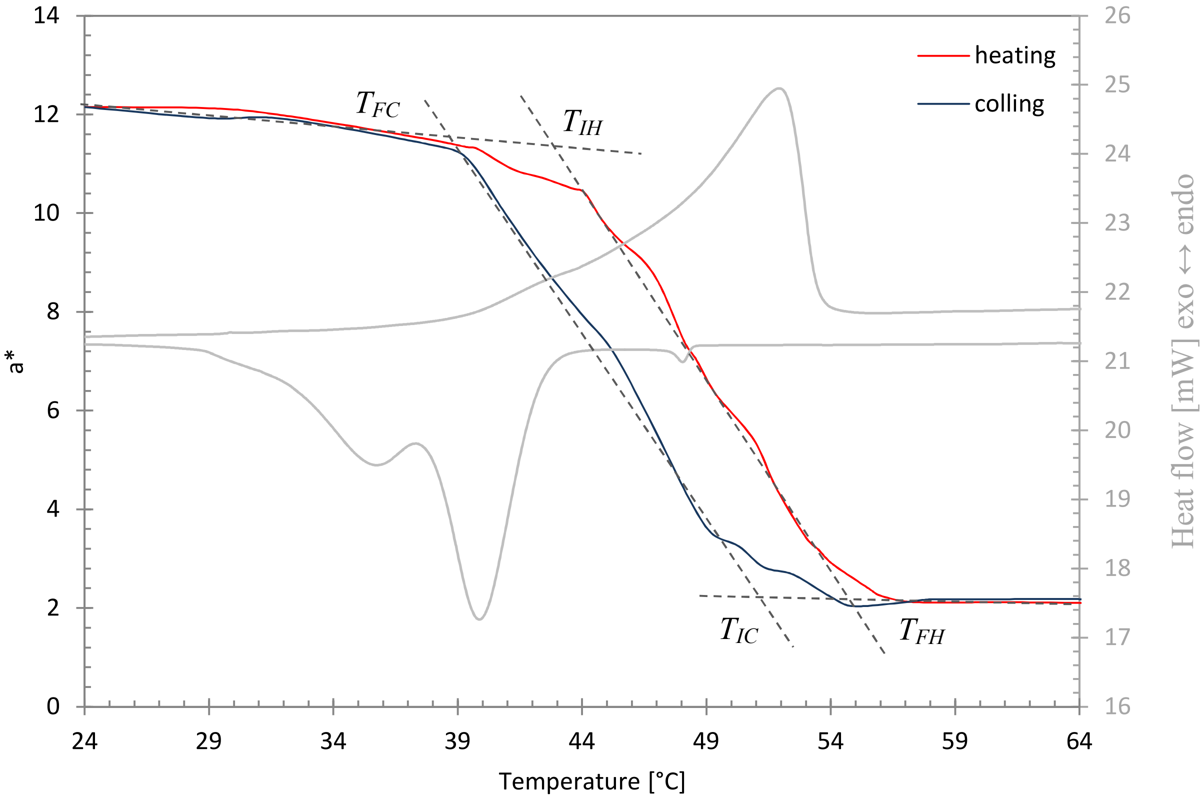


***Figure 35:** a*(T) graph showing dynamic colour change with corresponding temperatures for sample R50/1.*

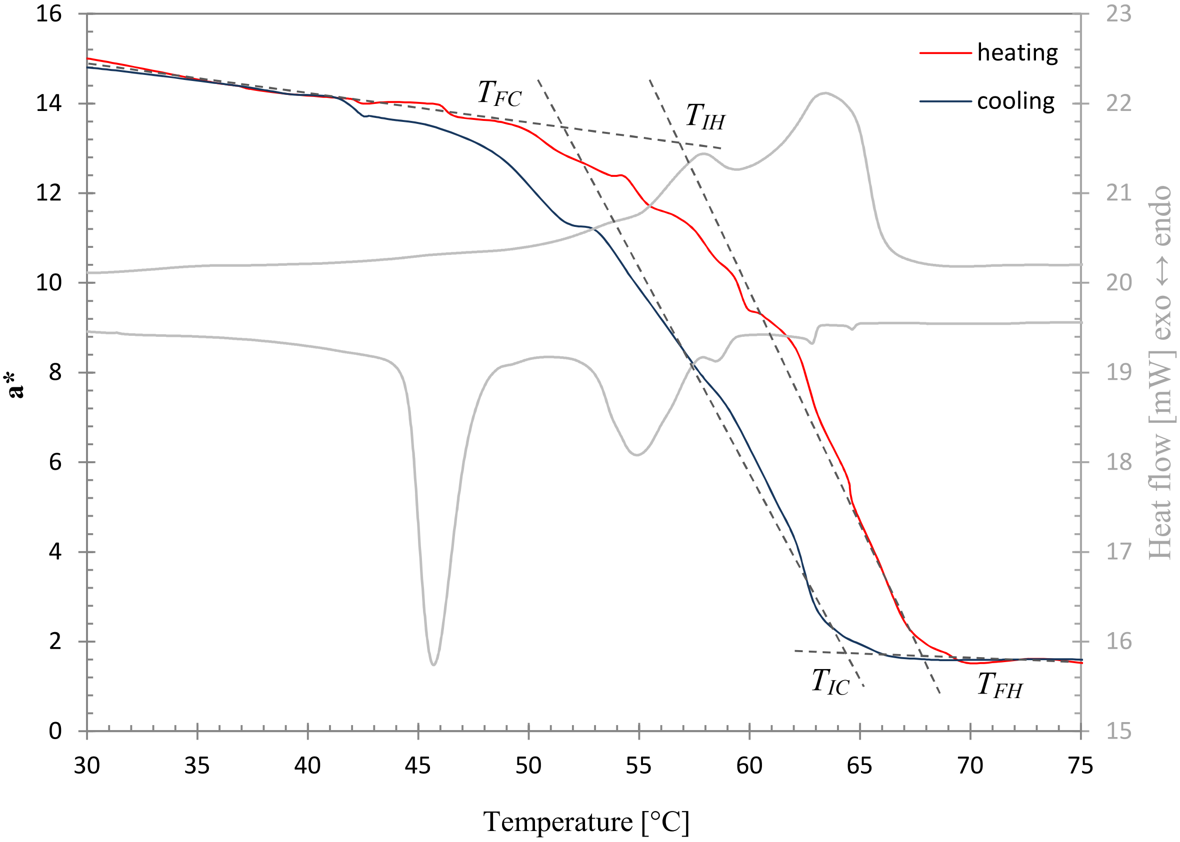


Figure 36: *a*(T) graph showing dynamic colour change with corresponding temperatures for sample R60/1.*

It has been already stated in section 2.2.1 that two metastable long-lived complexes are formed in thermochromic leuco dye system as a result of competitive reactions between dye-developer and solvent-developer. Below transition temperature dye-developer interactions prevail and coloured state is formed. Above transition temperature the solvent melts and solvent-developer interactions win and form colourless state. Regardless of thermal history of the sample, coloured complexes prevail at temperatures below final chromatic temperature while cooling (T_{FC}) and colourless complexes above final achromatic temperature while heating (T_{FH}). Between these two temperatures the system undergoes changes which dependant on thermal history. Between T_{IH} and T_{FH} the decolourization occurs and between T_{IC} and T_{FC} the system regains colour again.

These four temperatures were determined for samples R38/1, R50/1 and R60/1 from two-dimensional graph $a^*(T)$ showing colour hysteresis (Figure 34, 35 and 36). The curves obtained differ in temperature where the loop starts and finishes and in its steepness and area. The activation temperature specified by producer, 38, 50 and 60 °C for pigments R38, R50 and R60 respectively, does not correspond to any of the four obtained temperatures that characterize dynamic colour change. But the activation temperatures for all samples lay between T_{FC} and T_{FH}. The temperatures characterising dynamic colour change were compared to the phase change temperatures obtained from DCS curves. For better visualization the DSC curves have been added to graphs. For heating curves, it has been observed that, the temperature at which decolourization ends (T_{FH}) is closely related to endset temperature

(T_{EHI}). Initial achromatic temperature (T_{IH}) is slightly higher than the onset temperature. This means that there has to be certain amount of melted solvent for the decolourization to start. For cooling curves, the initial temperature is higher than all phase change exothermic temperatures. Thus, the colourization begins before the α-phase of co-solvent is formed. The final chromatic temperature is higher than solid-solid transition and therefore can be concluded that the colourization ends after crystalline β-form or δ-form structure of the solvent is formed.

Also the temperature difference between final chromatic and final achromatic temperate has been calculated. The results are 14.9, 8.9 and 17.2 °C for samples R38/1, R50/1 and R60/1 respectively. These values characterize the temperature range where the colourization/decolourization occurs. From these results we can conclude that the most rapid colour switching properties have sample R50/1 and the slowest sample R60/1.

All dynamic colour change temperatures can be seen in Table 11 together with the phase change temperatures.

4.4 Characterization of polyurethane dispersion

Leuco dye thermochromic pigments are designed to change colour with temperature, normally becoming colourless from coloured. Together with this special characteristic, they also degrade when subjected to high temperatures and curing times as has been already proved in section 4.2. For this reason binders which are fixed at high temperature may not be suitable. Therefore, for the thermochromic textile coating PUR OMP with curing temperature 150 °C and good fastness properties was selected as a binder. The PUR OMP is one-component heat-crosslinkable aliphatic isocyanate used for textile coating.

FTIR analysis was performed on binder PUR OMP. Because PUR OMP is an aqueous dispersion, the sample had been first dried in vacuum to avoid absorption peaks caused by water molecules. Also FTIR analysis of cured binder at 150 °C for two minutes was done. FTIR spectra can be seen in Figure 37 and spectral data in Table 12.

For sample dried in vacuum the FTIR spectrum shows a broad peak at 3 349 cm^{-1}, which is assigned to the stretching vibration of NH. Characteristic band of the carbonyl group was obtained in the 1 718 cm^{-1} region. The spectrum also exhibits other characteristic bands of polyurethane at 1 539 and 1 258 cm^{-1} due to the N–H bending vibration and (O=)C–O–C/C–O stretching vibration, respectively. The two bands observed in 2 933 and 2 859 cm^{-1} were attributed to symmetric and asymmetric stretching of the CH bond with carbonyl. The absorption at 1 455 cm^{-1} results from the CH_2 bending vibration in the backbone chain. Also there is no sharp absorption peak between 2 285 and 2 250 cm^{-1} which would be attributed to isocyanate group. This indicates that the PUR OMP is blocked.

In the cured polyurethane sample the infrared shows the same spectral peaks as for dried one, but with the higher intensity at 1716 and 1260 cm^{-1} which belong to ester and urethane stretching vibration respectively. The absorption spectra of cured PUR OMP shows no NCO groups because the polyurhethane reaction is complete and no isocyanate group is left.

All results obtained from FTIR spectra corresponds with the information given by the producer, that the PUR OMP is composed of hexamethylene diisocyanate (HDI), 3,5-dimethyl pyrazole and 1,6-hexanediol, where 3,5-dimethyl pyrazole is used as blocking agent.

Table 12: *IR spectral data of PUR OMP.*

Group	**Vibration**	**PUR OMP [cm^{-1}]**	
		Dried in vacuum	**Cured at 150 °C**
N–H	stretching	3 349	3 348
CH_2 group	asymmetric stretching	2 933	2 935
CH_2 group	symmetric stretching	2 859	2 860
C=O (ester)	stretching	1 718	1 716
–NH–COOC– (carbamate)	deformation	1 539	1 527
CH_2 group	deformation	1 464	1 465
(O=)C–O–C/C–O (urethane)	stretching	1 258	1 260
C–O–C	asymmetric stretching	1 122/1 071	1 121/1 071
CH_2 group	bending	742	741

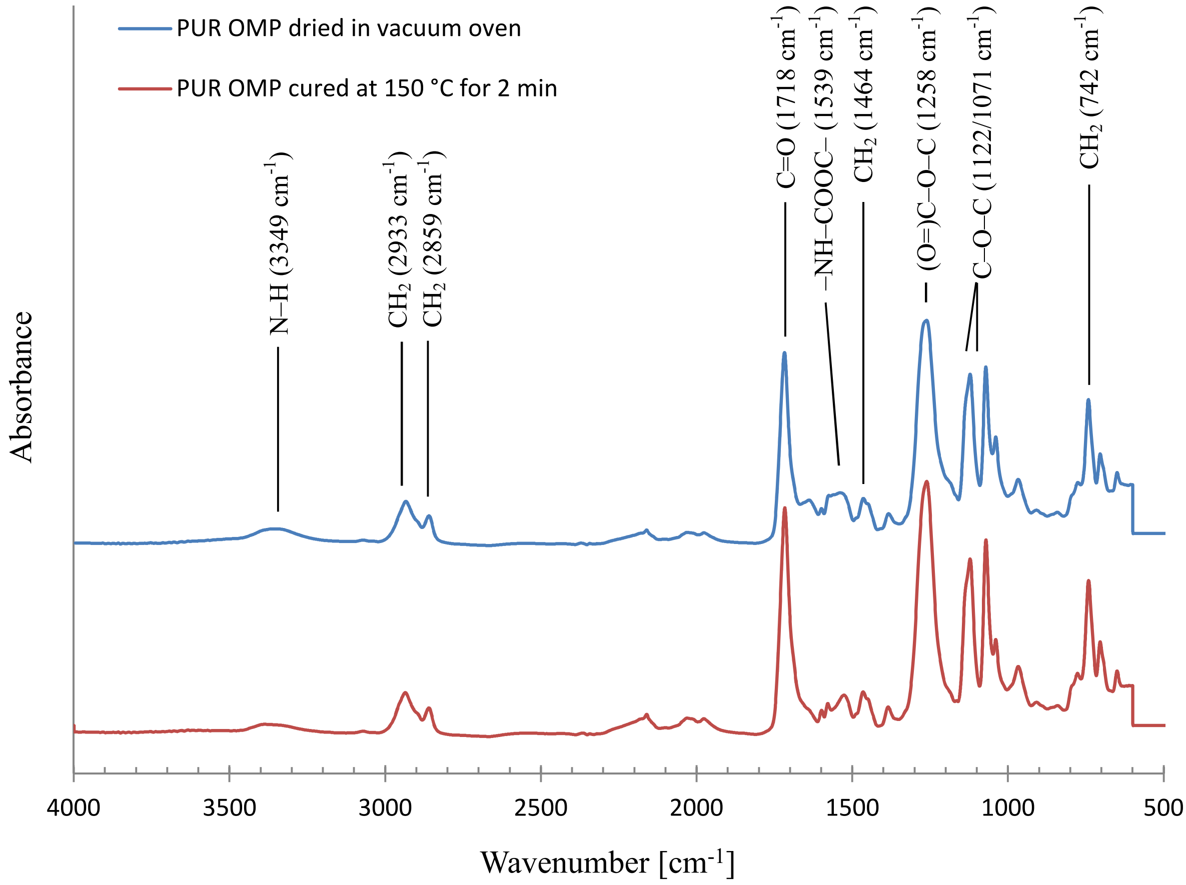


Figure 37: *FTIR spectra of dried and cured PUR OMP.*

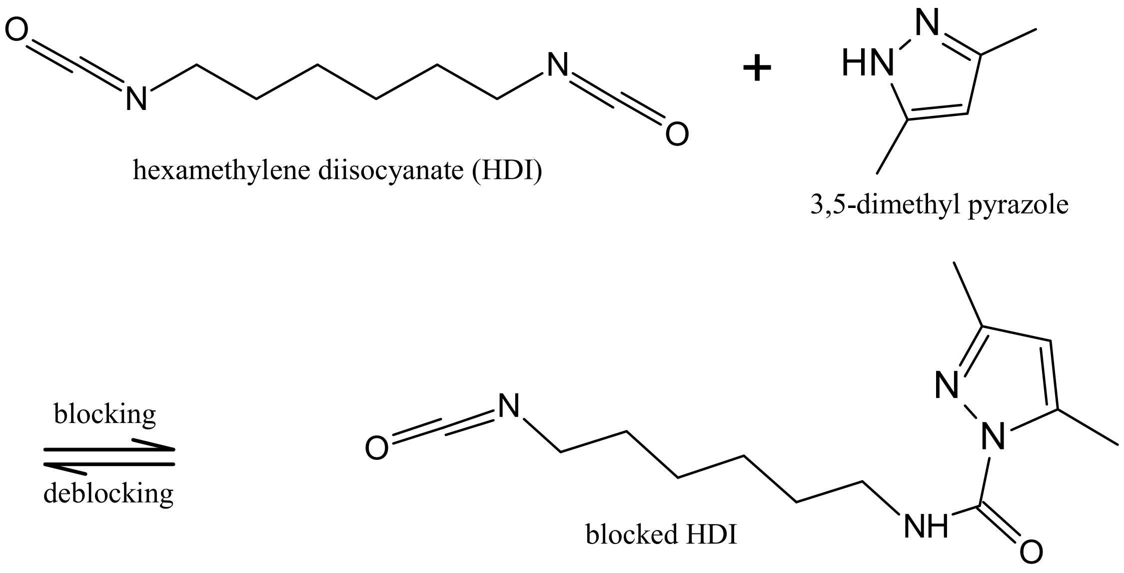


Figure 38: *Reaction forming active hydrogen blocked haxamethylene diisocyanate with blocking agent 3,5-dimethyl pyrazole.*

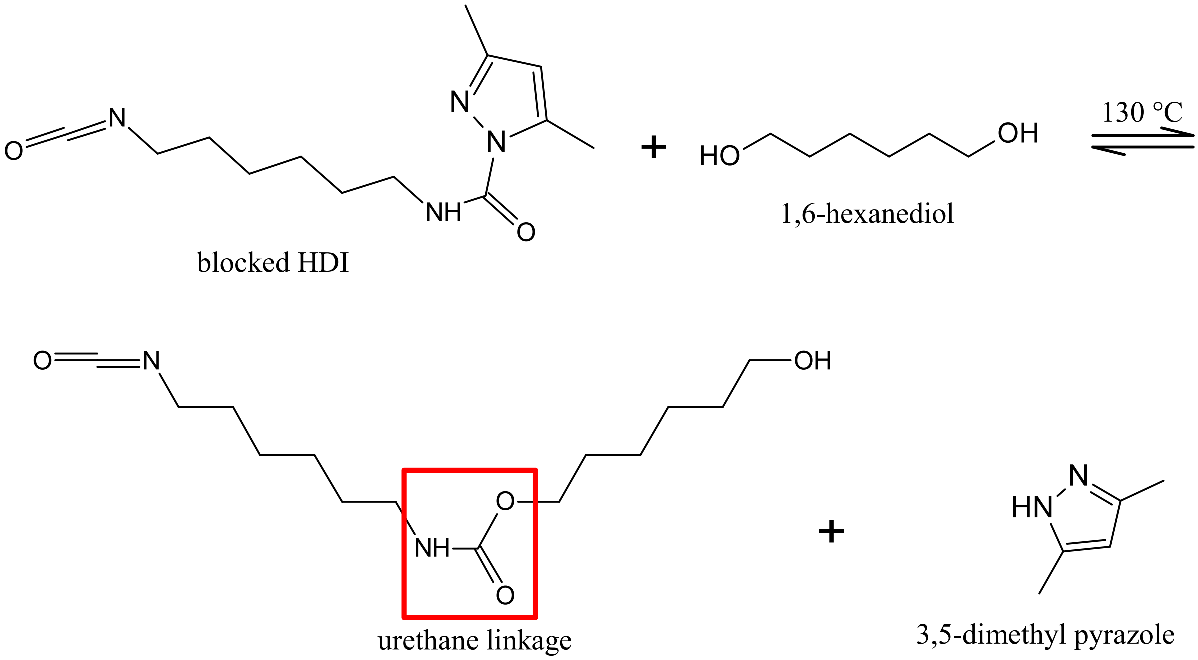


Figure 39: *Urethane linkage formation reaction by releasing blocking group and reacting with the hydroxyl functional polyol.*

The polyurethane reaction without blocking agent can be very rapid, even at room temperature, so the liquid mixture becomes solid very quickly. Shipping and storage of liquid urethanes requires preventing the urethane linkage reaction from occurring. This can be done by the reaction between isocyanate and blocking agent (Figure 38). The blocking group can be eliminated at elevated temperatures, yielding the reactive isocyanate and initiating the cross-linking reaction (Figure 39). The curing temperature depends on blocking agent.

Even though for the 3,5-dimethyl pyrazole is the curing temperature 130 °C, the producer recommend 150 °C. This is probably to speed up the elimination of blocking agent and make the process more efficient.

4.5 Thermochromic pigment particle size distribution

Optical microscopy was taken to optimize the process of incorporation of thermochromic pigment into the polymer binder. The samples showed the best results when they were homogenized for 10 min with IKA Homogenizer and then UV cured for 15 min. Samples prepared like this showed very few agglomerates of thermochromic pigment. As you can see in Figure 40 the particle geometry has been proved to be round for all three thermochromic pigments. Their size distribution was evaluated by image analysis and the results are shown Figure 41. The transparent melamine resin shell was recognized for all samples and the diameter of the particles was measured with it.

Dispersion with TP R38, R50 and R60 showed size distribution with maximum around 7, 6 and 7 µm respectively. Some agglomerates were spotted for all samples and their size was in average around 12 µm. The melamine formaldehyde shell has been calculated to be 1.4 µm in average.

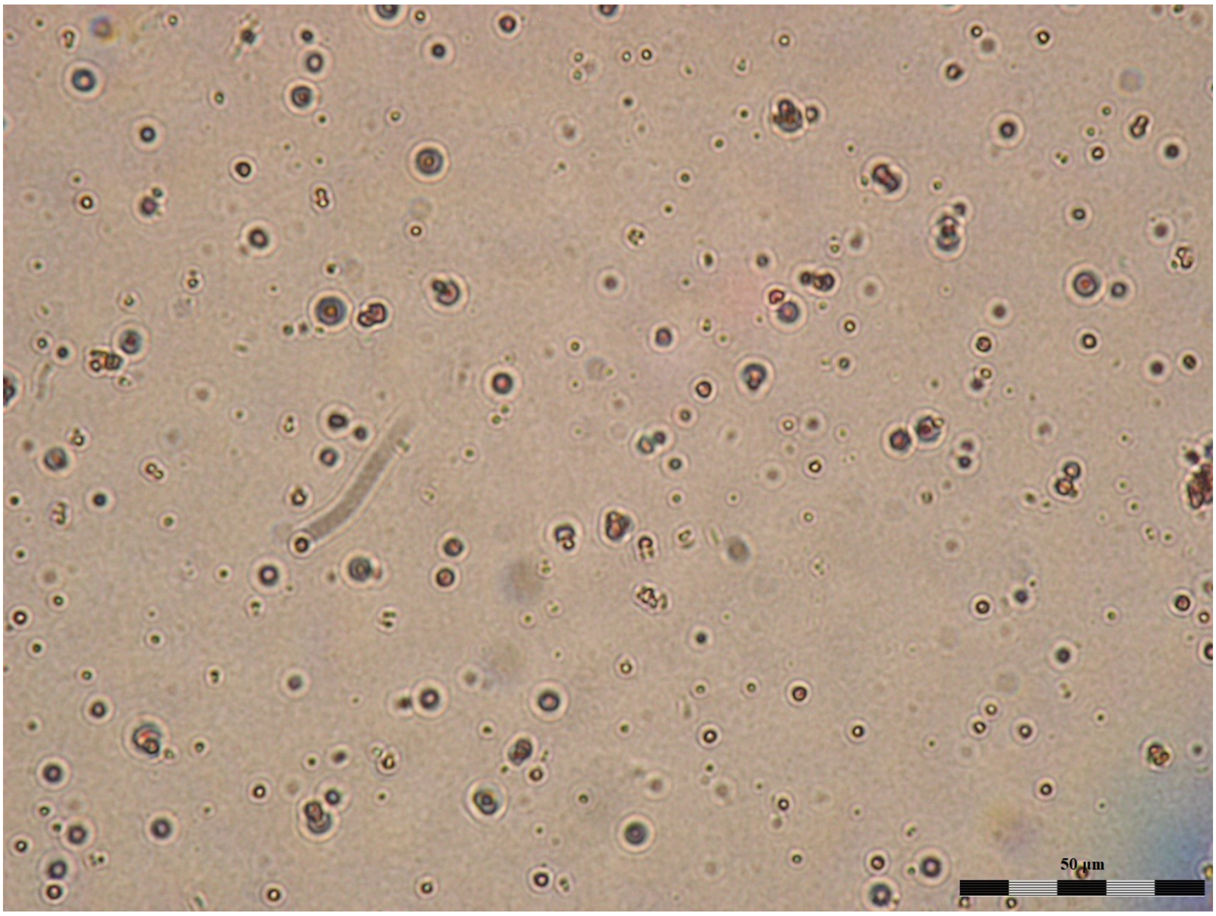


***Figure 40:** Photomicrograph of the R38 sample obtained in the bright field with magnification 50x.*

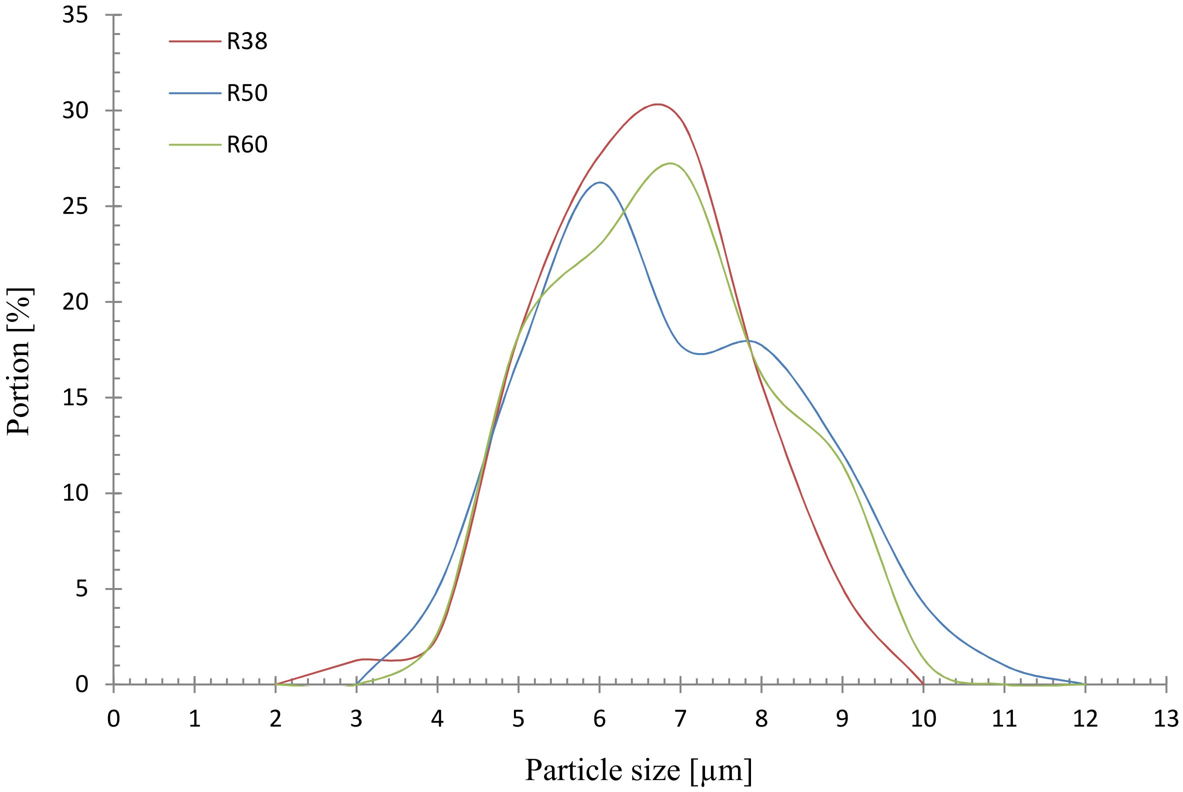


Figure 41: *Particle size distribution of R38/R50/R60 after dispergation in PUR OMP.*

4.6 Thermochromic coating characterization

With the floating knife technology thermochromic textile coating has been prepared. The coating has been prepared in three different concentrations, 2, 4 and 8 wt% of the pigment based on weight percent binder solids. For further colour fastness analysis the thermochromic coating with 4 wt% of TP has been chosen because of better colour strength than 2 wt% sample and better pigment dispergation than 8 wt% sample. Since the floating knife technology applies small amount of coating material on the fabric, the pigment which was red in a powder form turned to be pink in a coating. For stronger red colour the percentage of pigment would have to be increased. Considering the high price of the thermochromic pigment in comparison to the other used materials, the increasing of the pigment amount would rapidly increase the the price of the final product. The sample with 4 wt% of TP shows already well visible colour change and good homogenization.

4.6.1 Colour fastness

The spectral reflectance and colour coordinates were measured for each sample given in Table 5. The accelerated ageing measurement was taken in coloured state due to the chiller that held temperature in the chamber on 35 °C, which is below activation temperature given by the producer for all samples. Reflectance and CIE L^*a^*b values for every sample before the exposure and after 1, 2, 4, 8, 16 and 24 hour exposure were obtained and the colour difference ΔE was calculated (Table 13). The spectral reflectance of the samples was measured at a range of 380–730 nm with 10 nm step which includes visible part of solar spectrum. The reflectance spectra can be seen in Figure 42, 43 and 44.

Table 13: *L*, a*, b* and colour difference values for samples R38/1, R50/1 and R60/1.*

Sample	**R38/1**				**R50/1**				**R60/1**			
Exposure time	***L****	***a****	***b****	**Δ*E***	***L****	***a****	***b****	**Δ*E***	***L****	***a****	***b****	**Δ*E***
no exposure	85.82	16.77	-4.53	0.00	88.05	14.12	-4.70	0.00	87.30	16.10	-4.27	0.00
1 hour	86.79	16.37	-3.07	1.79	88.57	13.02	-3.90	1.45	87.41	15.25	-3.09	1.46
2 hours	86.61	15.93	-1.69	3.06	88.86	12.29	-3.81	2.19	87.81	14.93	-2.59	2.11
4 hours	89.44	10.80	-0.84	7.90	89.18	11.17	-3.52	3.37	88.74	12.63	-1.96	4.41
8 hours	91.16	7.01	-0.64	11.79	90.49	8.47	-3.57	6.25	90.32	9.19	-0.80	8.30
16 hours	93.10	1.94	-0.12	17.10	92.59	3.73	-2.34	11.58	92.23	4.48	0.20	13.39
24 hours	93.35	1.71	-1.74	17.06	93.20	2.31	-1.36	13.30	93.12	2.77	-0.73	14.97

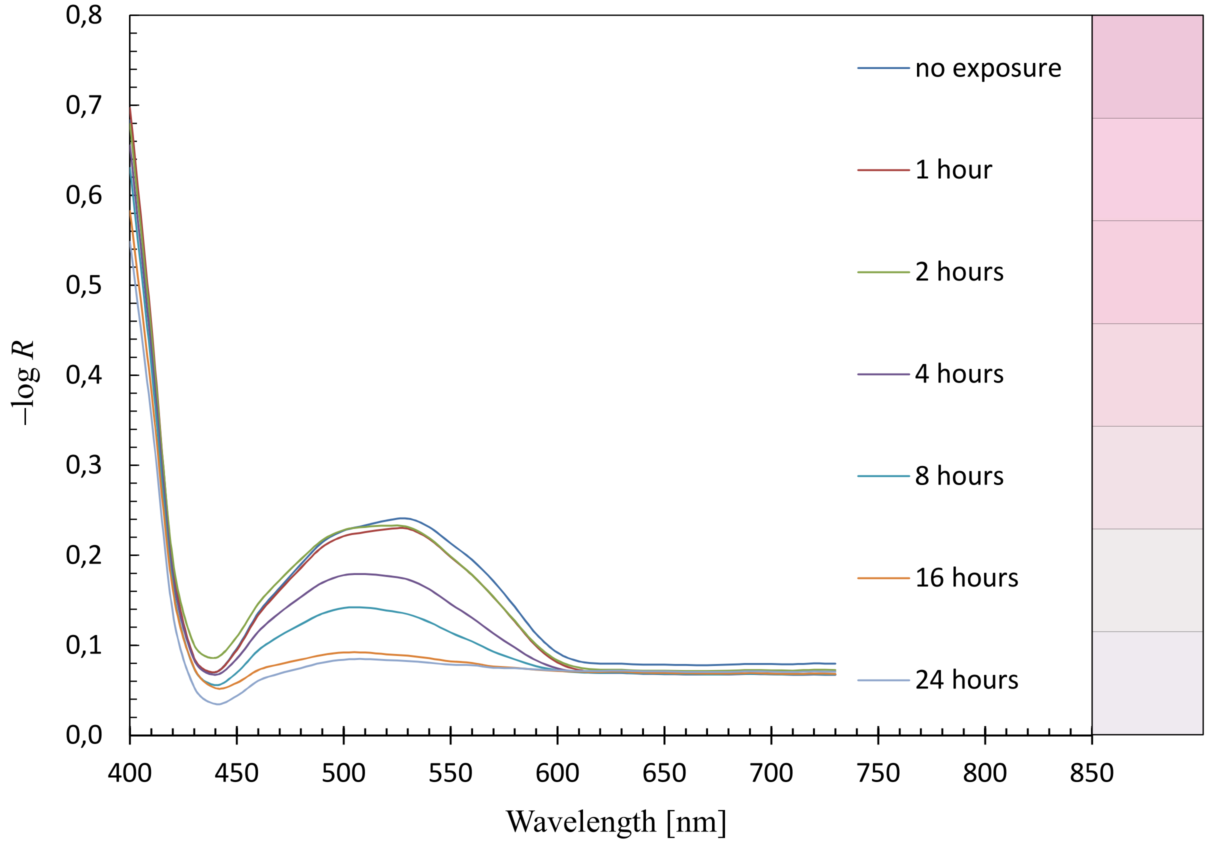


Figure 42: *Reflectance spectrum of sample R38/1 before and after accelerated ageing with colour scale based on L*a*b* coordinates.*

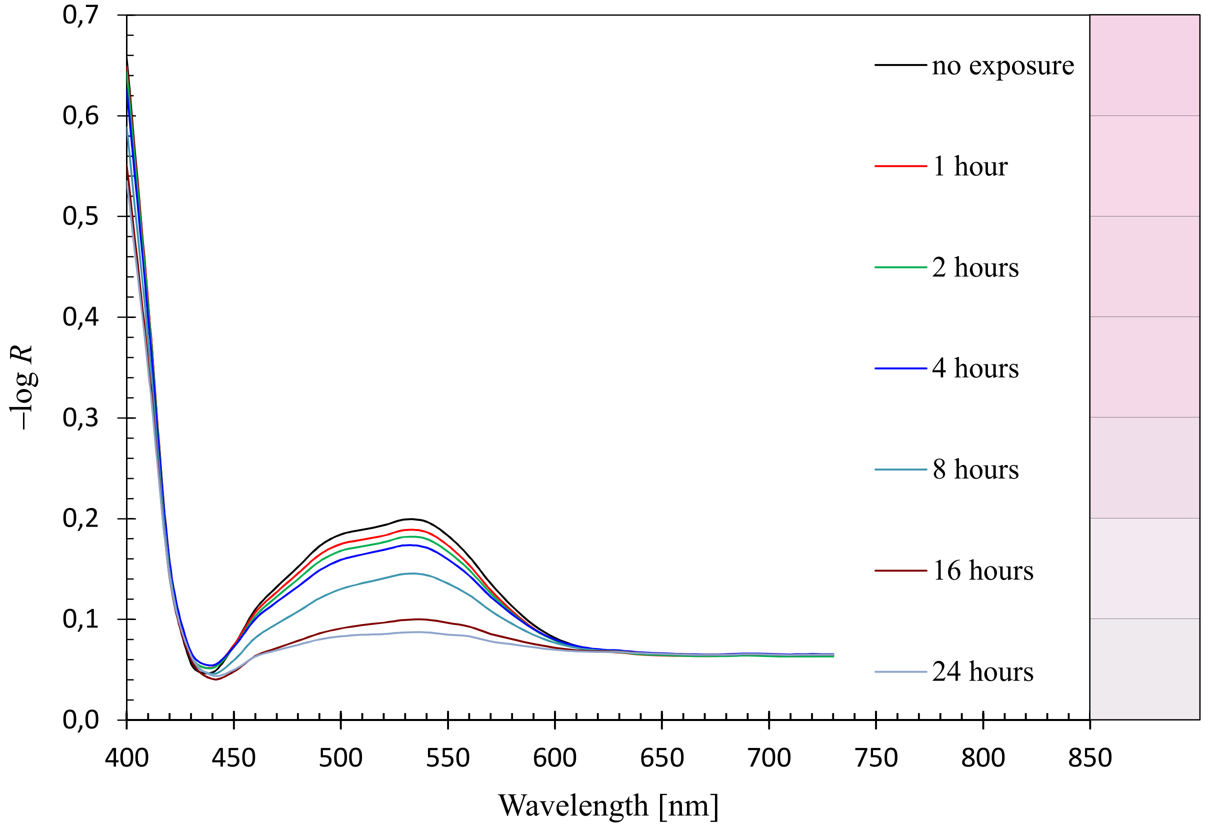


Figure 43: *Reflectance spectrum of sample R50/1 before and after accelerated ageing with colour scale based on L*a*b* coordinates.*

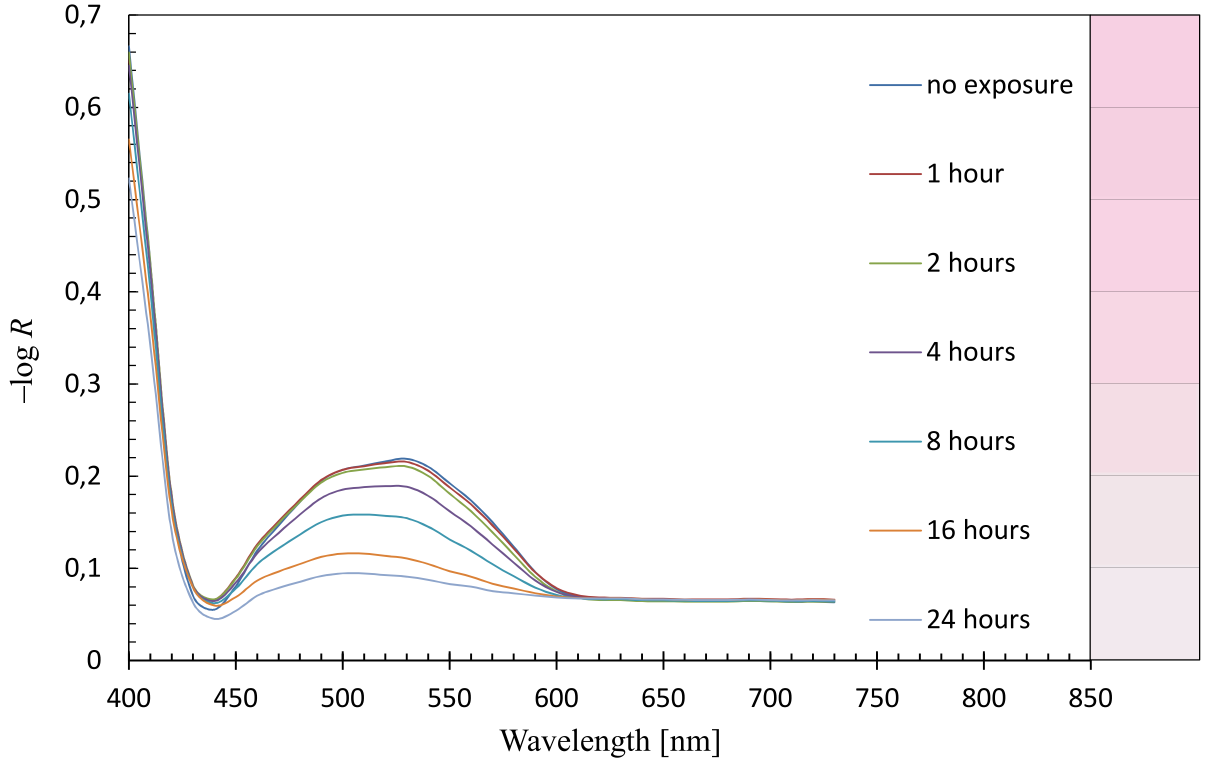


Figure 44: *Reflectance spectrum of sample R60/1 before and after accelerated ageing with colour scale based on L*a*b* coordinates.*

While exposing the samples to aggravated sunlight conditions the colour fades with time from pink to white as can be seen from colour scale added to all reflectance spectrums. This confirms the L^* and b^* values, which increase with time exposure, while the a^* values, that are attributed to red when $a^*>0$, decrease. From the colour difference ΔE values we can state, that the colour fastness of all samples is very low. Already after one hour there is perceivable colour change for all samples and after eight hours of exposure is the colour change already disturbing. Scale for evaluating the degree of colour change is given Table 8. Of all three samples the best fastness properties showed sample R50/1 with colour difference 13.3 after 24 hours exposure. Sample R60/1 has colour difference 14.97 after 24 hours exposure. Sample with the worst colour fastness proved to be R38/1 with colour difference 17.06 after 24 hours exposure.

4.6.2 Colour fastness enhancement

As was proved in previous section, thermochromic pigments have very low colour stability when exposed to sunlight. Therefor selected stabilizers were used to improve their lightfastness. In this research investigation was carried out to determine whether producer of such thermochromic coating can improve colour fastness at the application stage. For this purpose, two light stabilizers from different classes, hindered amine light stabilizer (HALS) and UV absorber (UVA), were selected. Both stabilizers, Tinuvin 292 (HALS) and Tinuvin 1130 (UVA), have been chosen because they are in liquid form and can be easily incorporated into water borne systems such as PUR OMP coating material.

Tinuvin 292 is liquid hindered amine light stabilizer especially developed for coatings. It is an almost pure mixture of the two active ingredients given in Figure 14. It is this combination that keeps the product liquid, unlike the pure diester which tends to solidify, even at room temperature. The efficiency of Tinuvin 292 should provide extended life time to coatings by minimizing paint defects such as cracking and loss of gloss. Tinuvin 1130 is a liquid UV absorber of the hydroxyphenylbenzotriazole class (Figure 15) specifically developed for coatings. Because of its broad UV absorption (Figure 16), Tinuvin 1130 also provides efficient protection to light sensitive substrates.

For this study red thermochromic pigment with activation temperature 50 °C (R50) has been chosen because it showed best colour fastness as the results proved in section 4.6.1. The lightfastness enhancers were incorporated separately into second and further layers over the first coating layer with thermochromic pigment. The concentration of lightfastness enhancers used was 4 % by weight as recommended by the producer. Since this addition showed no improvement for Tinuvin 292 neither for Tinuvin 1130, the amount of lightfastness enhancer was increased up to 10 % by weight. This unusually large amount of stabilizer was added to find out if these materials have any effect on colour fastness of thermochromic leuco dye pigments.

The samples given in Table 6 and 7 were prepared as described in section 3.2.2 and exposed to light in Q-SUN xenon chamber for 1, 2, 4, 8, 16 and 24 hours. All samples with addition of stabilizer Tinuvin 292 and Tinuvin 1130 were compared with original sample R50/1. Colour measurements were taken on the spectrophotometer with the calibration conditions discussed in section 3.3.5. The colour difference values of samples at different exposure times were calculated (Table 14) and plotted against time (Figure 46 and 47).

Table 14: *Cumulative colour difference (ΔE) values for samples with thermochromic pigment R50 exposed to accelerated ageing.*

	1 hour	**2 hours**	**4 hours**	**8 hours**	**16 hours**	**24 hours**
R50/1	1.45	2.19	3.37	6.25	11.58	13.30
R50/2/T292	1.02	2.17	3.35	6.60	12.02	13.57
R50/3/T292	1.24	1.93	3.54	6.27	11.34	13.25
R50/4/T292	1.02	2.03	3.23	5.72	11.60	13.29
R50/2/T1130	0.93	0.99	2.31	4.64	9.99	12.03
R50/3/T1130	0.83	1.16	2.21	4.50	6.63	9.16
R50/4/T1130	0.91	1.03	2.29	4.09	6.68	10.94
R50/5/T1130	0.50	0.77	1.89	5.06	8.86	11.44
R50/6/T1130	0.51	1.31	1.98	4.40	8.17	10.53

The Tinuvin 292 (HALS) showed no improvement in colour fastness with 4 % nor with 10 % loading by weight. Also adding second and third layer which increased the amount of light stabilizer over area of thermochromic coating led to no improvement as can be seen in Figure 46. The inability of Tinuvin 292 to stabilize TP origins in the way HALS stabilizer works. HALS protect the chromophore by interacting with the colorant or intermediate species produced during chromophore degradation. Since the thermochromic pigment R50 as well as the R38 and R60 is microencapsulated as was proved in section 4.1, HALS can only come into contact with the walls of microcapsules. Therefor is unable to interact with the colour formers and stop the degradation process. This statement is likely to be true for most of HALS type of stabilizers, not just the Tinuvin 292.

Also Tinuvin 1130 (UV absorber) has been examined for his colour fastness abilities. With concentration 10 % by weight binder solid, there has been an improvement already in the first coating layer with UVA. In contrast to HALS, the UV absorber protects the chromophore by absorbing UV light. Thus, the HALS needs direct access to colorant or intermediate species produced during chromophore degradation, while the UV absorber can perform its function to absorb UV light even when located outside the microcapsules. By reducing the level of damaging UV light which reaches the colour formers and other components, the UV absorber is able to protect the pigment and its thermochromic properties.

Since Tinuvin 1130 proved to be useful when stabilizing the thermochromic pigment, further investigations have been made. UV absorbers undergo the Beer–Lambert law (equation 4.1), where $A(\lambda)$ is absorbance (also called extinction) at wavelength λ, c is concentration of the absorbing substance, I is width of the layer and ε is molar absorptivity.

$$-\log T = A; A = \varepsilon \cdot c \cdot I \qquad (4.1)$$

Based on this knowledge, the colour fastness should increase either with increasing concentration or layer width. Since concentration has been already increased, the next step is to increase the layer width. Samples with 1 (R50/2/T1130), 2 (R50/3/T1130), 3 (R50/4/T1130), 4 (R50/5/T1130) and 5 (R50/6/T1130) layers over the original thermochromic layer have been prepared. Although the same set up was used when applying layers with floating knife technology, the amount of applied material does not have to be same for all layers. Therefor the mass of samples have been recorded as written in section 0, the density of coating has been calculated (Table 15) and plotted against number of layers (Figure 45). From the graph can be seen that with the floating knife technology we are able to apply larger amount of coating for the first and second layer than for the following once. The amount of coating is same for first and second layer and the dependence of coating density on number of layers is linear. This is caused by the fact that liquid used for coating is applied not only on the surface of the fabric but also into the fabric between fibres. From third to sixth layer there also exists linear dependence of coating density on number of layers. The amount of applied coating materiel is lower because the material is added only on the surface of previous coating.

Table 15: *Values for coating density with regards to number of layers.*

Number of layers	1	2	3	4	5	6
Coating density [g·m^{-2}]	7.80 ± 0.27	16.80 ± 0.41	20.90 ± 0.23	24.32 ± 0.58	27.94 ± 0.31	30.12 ± 0.48

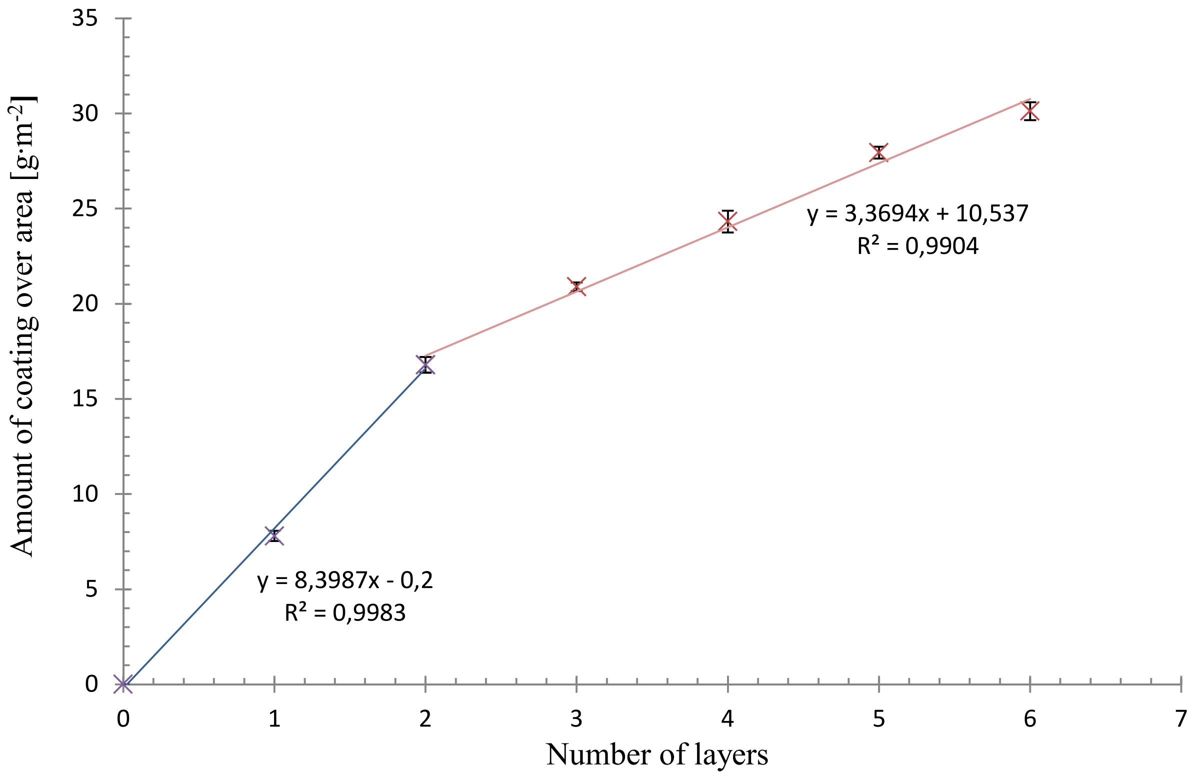


Figure 45: *Graph showing the dependence of amount of coating over area on number of layers.*

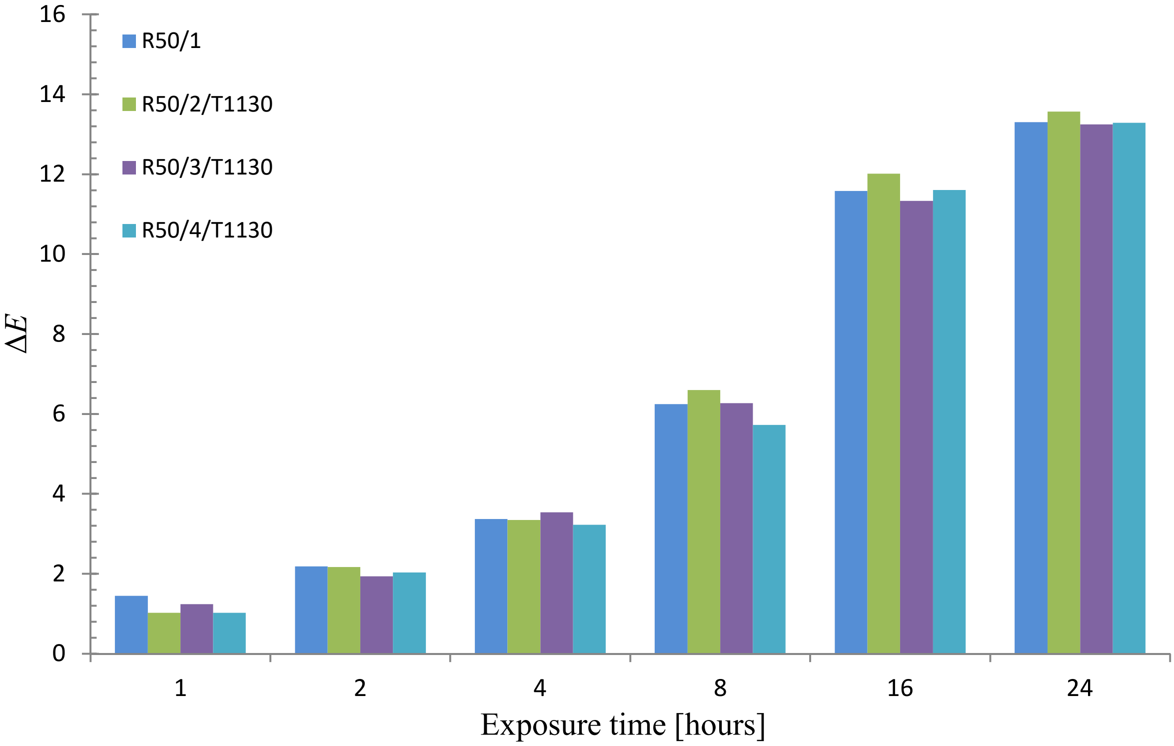


Figure 46: *Colour difference values of thermochromic coating with TINUVIN 292 (HALS) stabilization.*

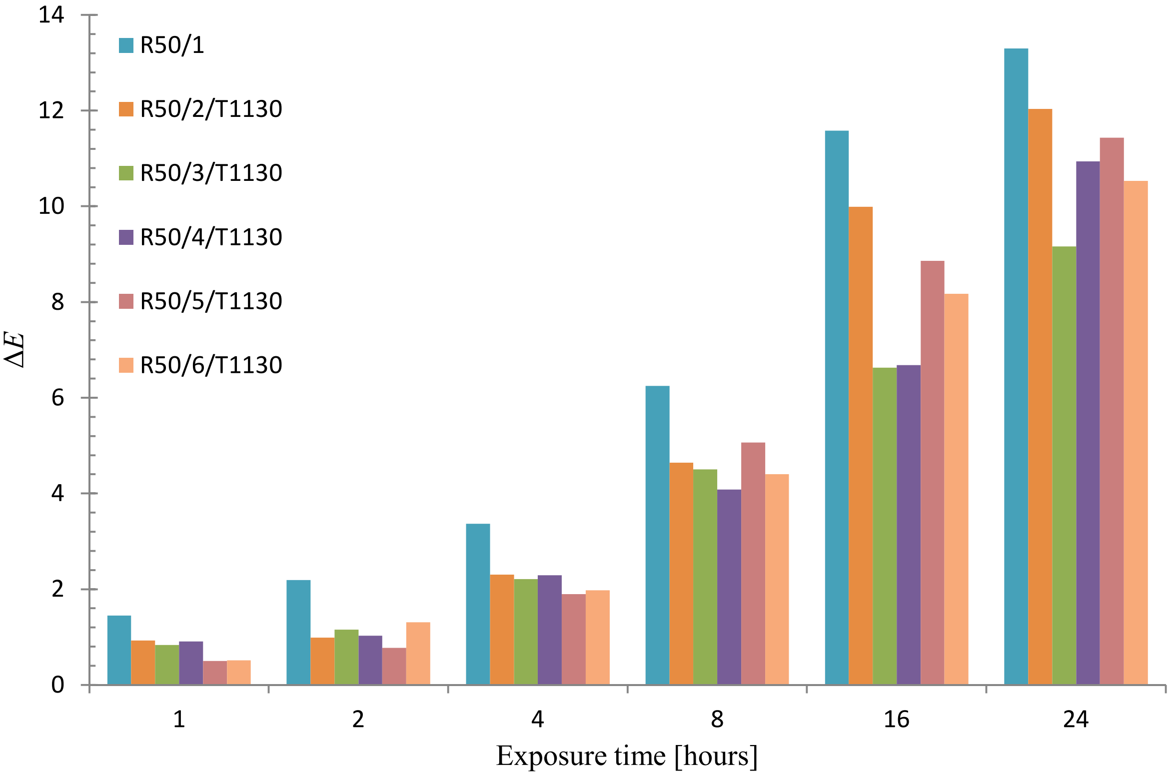


Figure 47: *Colour difference values of thermochromic coating with TINUVIN 1130 (UV absorber) stabilization.*

Thus, there was expected enhancement of colour fastness for all samples with the UV absorber, Tinuvin 1130. Based on mass measurements, this enhancement should have been rapid for sample R50/2/T1130 and then linearly increase for samples R50/3/T1130 R50/4/T1130, R50/5/T1130 and R50/6/T1130. From Figure 47 is obvious that this assumption was not confirmed. The colour fastness was enhanced for all samples with Tinuvin 1130 to compare with the sample R50/1 without UV absorber. However, up to four hours exposure the enhancement is almost the same for all samples even though we expected that the enhancement will increase with number of layers. This is probably caused by the fact that samples with more layers had to be cured at 150 °C for longer time (each layer is cured for 2 min). As has been proved in section 4.2, thermochromic pigment has low heat stability and even at 150 °C there is already weight loss. Even though this weight loss is not as significant as the one above 200 °C, it still has negative impact on stability of the whole thermochromic system. Thus, the more layers we apply, the longer is the pigment exposed to elevated temperature and the more weight is loss which has negative effect on colour fastness. Overall the best colour fastness properties showed sample R50/3/T1130 and its reflectance spectra with colour scale can be seen in Figure 48.

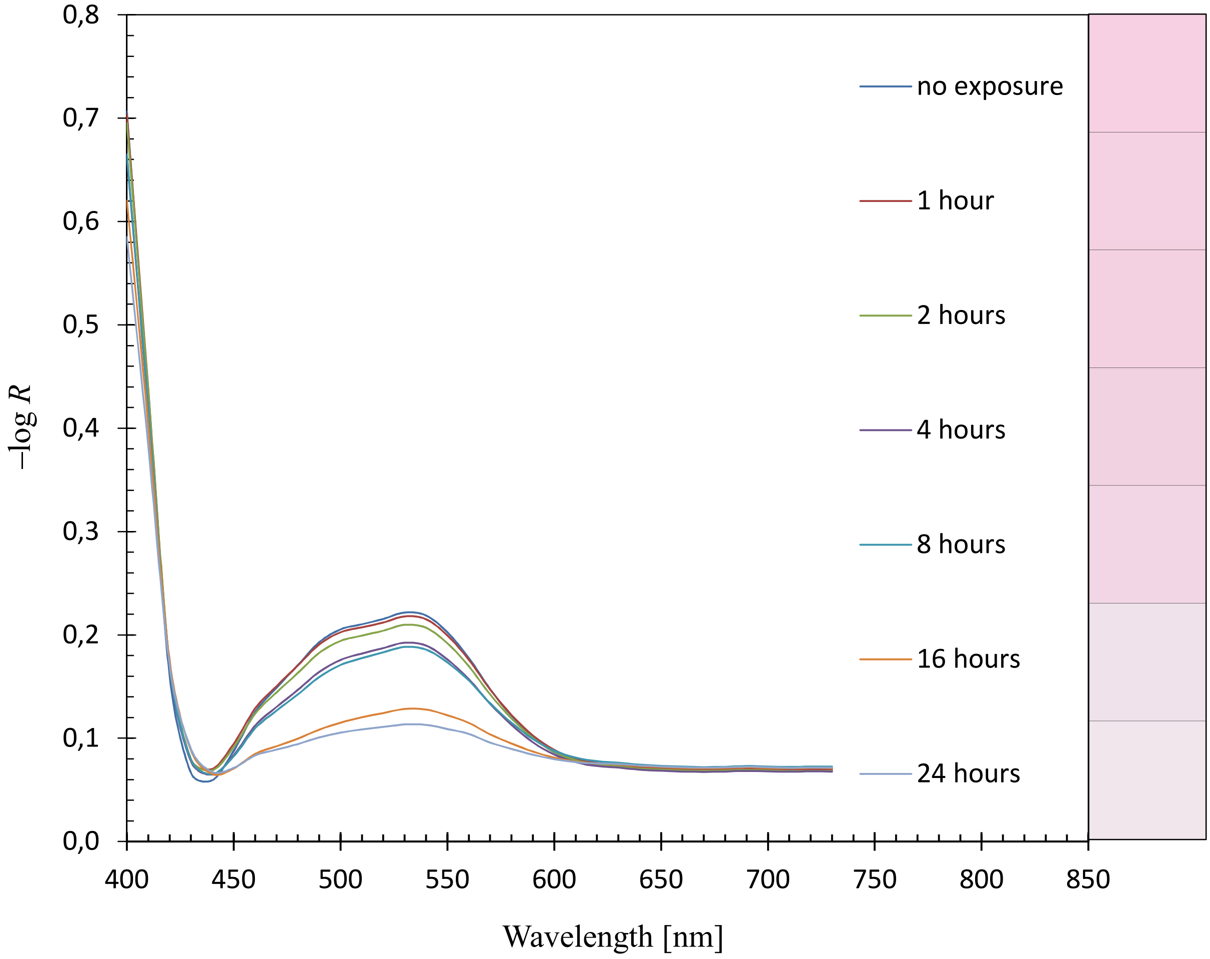


Figure 48: *Reflectance spectrum of sample R50/3/T1130 before and after accelerated ageing with colour scale based on L*a*b* coordinates.*

Hence, it is concluded that the UV absorber is a useful lightfastness enhancer for improving the performance of textile prints based on microencapsulated leuco dye based thermochromic pigments, but the enhancement is not sufficient enough for the textiles to be used outdoor. For the outdoor usage the stabilizers should be incorporated by the pigment manufacturer prior to microencapsulation. This would most likely minimise colour loss due to light exposure by direct interaction with the colour former and other components of thermochromic pigments.

4.6.3 Repeatability of thermochromic effect

Samples R38/1, R50/1 and R60/1 have been repetitively exposed to temperature 10 °C above their activation temperature. The samples were exposed 25, 50, 100, 150 and 200 times and then their reflectance a CIE L^*a^*b values were measured.

Even after 200 times repetition of thermochromic effect there was colour difference below 0.3, which is considered as imperceptible colour change. Thus, when the coating is not exposed to elevated conditions in terms of heat and sunlight, the repeatability of thermochromic effect is sufficient.

5 CONCLUSION

The primary aim of this study was to understand colour formation principle and prepare thermochromic textile coating. For this purpose three types of thermochromic leuco dye based pigments with reversible colour change from red (below transition temperature) to transparent (above transition temperature) were chosen. The pigments differed in transition temperature which was 38 (R38), 50 (R50) and 60 °C (R60). The thermochromic textile coating was prepared with floating knife technology and after optimizing of the process the conditions were setup to blade pressure of 0.1 mm at the rate of 5 which corresponds to 113 $cm{\cdot}min^{-1}$.

The powder pigments were characterized with FTIR analysis and it was proven that all pigments are microencapsulated and the microencapsulation is formed of melamine resine. Based on this fact, the pigments could have been further mixed with polymer binder used for textile coating, while knowing that the phases are separate and have no influence on each other.

Also the thermal stability of the pigments was investigated. TGA measurement proved that the pigments may be considered as stable up to 200 °C for samples R38 and R60 and up to 215 °C for R50. However, there is a weight loss even below this temperature, which is related to the thermal curing process of melamine resin and to relatively high amount of low molecular substances. It was found out that the colour loss also depends on the exposure time. Therefore, it is proposed that the processing temperature of thermochromic prints should be kept as low as possible.

With DSC analysis the colour formation principle was examined. Due to this analysis, the phase transition temperatures have been detected and competitive reactions between dye-developer and solvent-developer have been clarified. Moreover, the dynamic colour change has been measured with temperature dependant spectrophotometric test and compared to the phase transition temperatures detected from DSC.

The pigments were successfully incorporated into one-component heat-crosslinkable aliphatic isocyanate and their particle size was measured. Dispersion with thermochromic pigments showed size distribution with maximum around 7 μm. The optical microscopy proved that the pigments are well dispersed in binder, which led to very well colour homogenized thermochromic coating.

Furthermore the colour fastness of thermochromic textile coating was investigated with accelerated aging. From the colour difference values we can state, that the colour fastness of all pigments is very low when exposed to sunlight. Therefor the attempts for colour enhancement have been made. UV absorbers were found to be useful with colour fastness enhancement, whereas HALS showed no improvement. This is probably due to the different mechanisms of protection. The UV absorbers absorb harmful UV radiation while the HALS protect by reacting with the chromophore or intermediate species produced during UV degradation. In the case of microencapsulated thermochromic pigments, HALS cannot react with colour former due to inaccessibility, while UV absorbers may protect the colour former by absorbing UV radiation. Although the UV absorbers showed improvement in colours fastness, it is still not sufficient enough for the products to be used outdoor.

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7 LIST OF ABBREVIATIONS

TP	thermochromic pigment
CVL	crystal violet lactone
HDI	hexamethylene diisocyanate
DSC	differential scanning calorimetry
TGA	thermogravimetric analysis
FTIR	fourier transform infrared spectroscopy
POM	polarized optical oicroscopy
HALS	hindered amine light stabilizer
UVA	UV absorber