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Thermochromics: A Temperature Sensitive Smart Material

Manisha Dey and Yeasin Sikdar*
Department of Chemistry, The Bhawanipur Education Society College, Kolkata 700020, West Bengal

Abstract

The capacity of a substance to change color in response to temperature changes is known as thermochromism. Recently, thermochromic materials have gained a lot of attention because of their rich and controlled physicochemical characteristics. In this short review we have discussed the origin and application of different types of thermochromic material from pure organic compound to pure inorganic compound.

Keywords: Thermochromism, Colour change, Transition temperature

1. Introduction

Why do we use Sun-Glass? What is the Science behind the 'Mood Ring'? These two examples of accessories come in the genre of chromic material. Chromic materials are those that change color in different ways due to variations in a substance's electron density (π or d electron) brought on by outside influences. Most of the time, there is controllable and reversible color change. Chromic phenomena are termed using the suffix chromism preceded by a prefix that describes the stimulus causing the color shift, depending on the type of external stimulus. Like thermochromism is associated to external stimuli heat, photochromism is associated with light, ionochromism occurs due to exchange of ions, electrochromism is related with electric potential as stimuli, solvatochromism deals with solvents, vapochromism is influenced by vapours and in mechanochromism mechanical actions works as external stimuli. Table 1 provides a comprehensive list of chromic event and the responsible stimuli. [1–4]

Table 1: Stimulus associated with classification of Chromic material

Stimulus	Chromic phenomenon
Heat	Thermochromism
Light	Photochromism
Electric Current	Electrochromism
Solvent	Solvatochromism
Vapour	Vapochromism
Mechanical action	Mechanochromism
Magnetic Field	Magnetochromism
Pressure	Piezochromism

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* Correspondent Author: email: yeasin.sikdar@thebges.edu.in (Y. Sikdar)

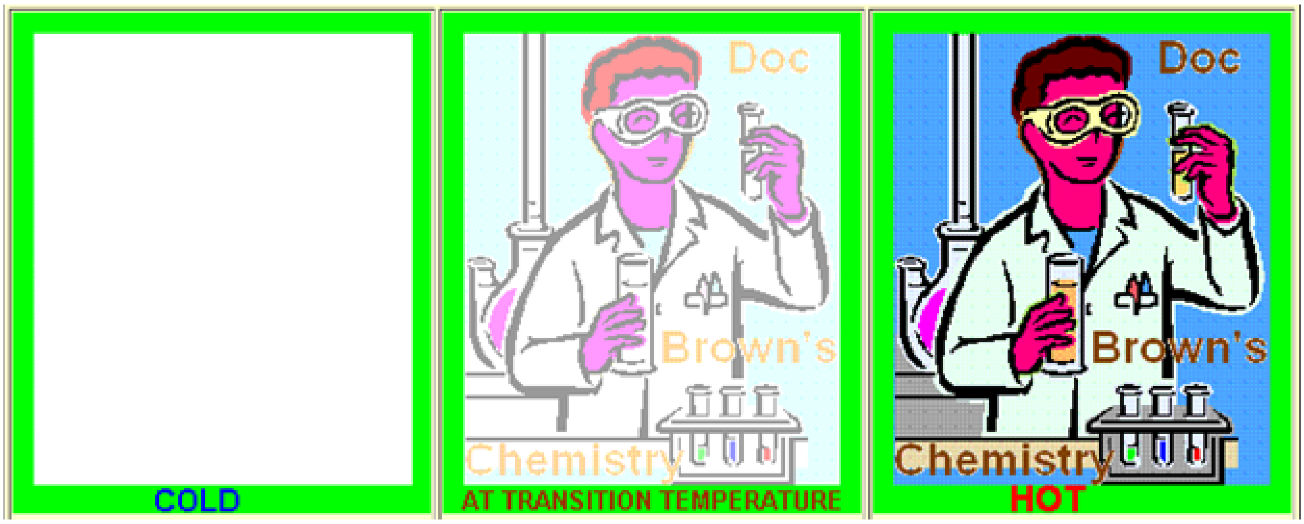

Figure 1: Application of thin layer thermochromic pigment paint in a preprinted coffee mug. At room temperature (COLD), the picture does not appear; but pouring a hot drink into it, at a specific transition point, such as 35 ^{0}C, the plain layer thermochromic pigment starts to turn transparent. The image in its entirety eventually appears (middle photo). The fully colored image appears heated (right picture). Retrieved from ref 4

Chromic phenomena can be seen in materials with diverse origins, including organic molecules, conjugated conducting polymers, dyes and pigments, and inorganic oxides. Chromic Materials like these have a lot of uses. While some of the applications are still in the development stage, others have reached a technological level and are commercially commercialized. Industrial temperature indicators [5,6,] photo-chromic windows [7], smart windows (a device that combines solar cell and electrochromic windows), electrochromic displays [8], molecular switches, memories [9,10], and so on are examples of realistic applications of chromic materials that have been effective. High end technology like ophthalmics [11], thermometry [12], electronics and biomedicine [13] also uses different chromic phenomena based on application.

In this short review we will emphasize on the most versatile chromic phenomenon, Thermochromism. Different mechanisms of thermochromism will be discussed along with their potential applications.

2. Basic property of thermochromic material

The basic characteristic of thermochromic materials is their ability to change color, either irreversibly or reversibly, in response to changes in temperature or heat (as a stimulus) (Figure 1). The primary requirement for thermochromism is thought to be a reversible color change. Irreversible thermochromism is frequently discussed, nevertheless, because there are important uses for thermochromic materials when an irreversible change is necessary. For an easier approach we generally identify reversible thermochromism as simply “thermochromism” and wherever irreversible reaction takes place we specify it as “irreversible thermochromism”.

3. Choice of materials for Thermochromic behaviour

3.1 Organic material

According to the view of Organic Chemistry, thermochromism is frequently observed in substances due to structural and chemical modifications i.e. resonance, extended conjugation, tautomeric equilibrium, stereoisomerism between two crystal structures, formation of free radicals, ring opening reactions which is influenced by temperature changes.[14-16] The molecule's delocalized π-electronic structure is altered by these structural and chemical alterations, resulting in the striking color shifts.[17] In the following, we represent a short description of different organic materials that have this unique property of thermochromicity.

Crowded ethenes: These are a class of organic compounds with a double bond separating the two polycyclic aromatic rings (Figure 2). For example: bianthrone and dixanthylene. At room temperature, two cyclic rings stayout of plane for steric crowding and show their individual properties. However, at elevated temperature, the central double bond becomes weak and electron density of the π-bond gets delocalized over two cyclic rings to acquire a planar arrangement. The entire molecule experiences π-bonding conjugation due to the increased coplanarity, which lowers the absorption energy and ultimately causes the color shift. [18]

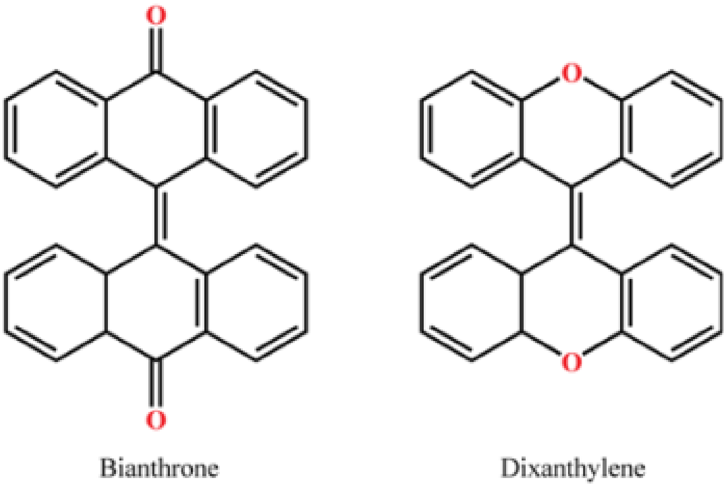

Figure 2: Structures of some crowded ethenes

Schiff Bases: In general, *enol-imine* form and *keto-enamine* form of a Schiff Base co-exist in equilibrium. An elevated temperature promotes the intramolecular tautomerisation reaction to occur. Due to the electronic rearrangement, the keto-enamine form has a longer π-bonding structure than the parent enol-imine, which lowers the energy of the π-electrons' electronic transitions and alters the compound's color. (Figure 3) [19,20]

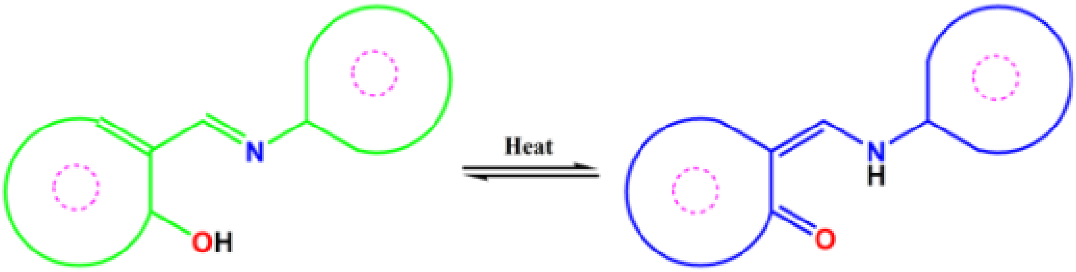

Figure 3: Schiff base fall under a category of compounds which exhibit the keto-enol equilibrium responsible for thermochromism. The cyclic part denotes different aromatic system.

Spiro compounds: These types of compounds fall under another important category which show thermochromicity. It includes triarylmethane dyes (TAM dyes), fluorandyes, spiropyrans, spironaphthalenes, and spirooxazines.[21-26] Their thermochromic behavior results from the transformation of the sp3 spiro carbon center into a sp2 carbon center. Upon conversion to the sp2 carbon center, the molecule's π-bonding electron density can undergo extended conjugation and resonance, resulting in electronic transitions that fall within the visible region of the electronic spectrum, thereby producing visible color (Figure 4).

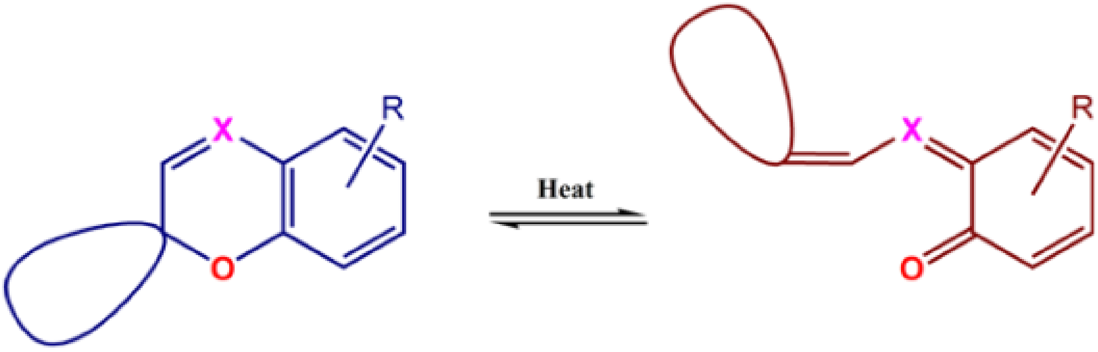

Figure 4: Tautomeric ring-opening equilibrium of a spiro compound between its merocyanine (MC) and spiropyran (SP) forms. When X = CH, spiropyrans; X = N: spirooxazines

Acid-sensitized dyes like fluorans, crystal violet lactones, and spiro pyrans go through ring opening rearrangements to produce color. These compounds are extensively used as colorant in textile industry. [27-29]

3.2 Inorganic material

In this section, we will now focus on inorganic mechanistic pathways for thermochromism of different compounds. Generally, such color change happens due to the variations in geometry of ligand, crystalline phase, and number of solvent molecules within the coordination sphere. But the reasons behind it changes from one compound to another.

Different thermochromic materials and their applications are as follows:

In solid state, copper chloride hexahydrate is blue in colour but on heating above temperature 60^{0}C, its color changes to green. The chemistry underlying the observed thermochromism phenomena is the loss of water from crystallization molecules during heating, which causes the octahedral structure of the hexahydrate complex of copper salt to change to a tetrahedral chloro complex (Figure 5). At room temperature, copper is present at the centre of the octahedral complex: hexaaquacopper(II) complex,

$$Cu^{2+} + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+}$$

And on heating, dehydration of coordinated water molecule takes place from coordination sphere and conversion to tetrachlorocuprate(II) complex occurs.

$$[Cu(H_2O)_6]^{2+} + 4Cl^{-} \leftrightharpoons [CuCl_4]^{2-} + 6H_2O$$

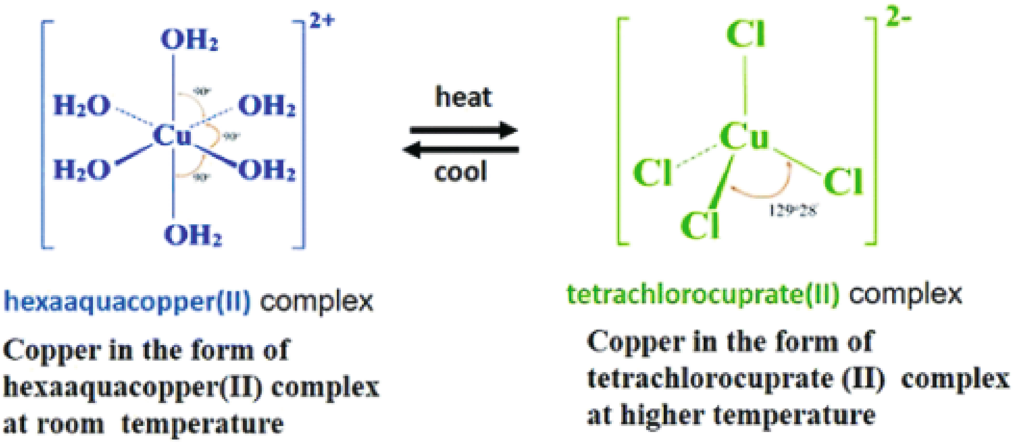

Figure 5: Structural change on heating $[Cu(H_2O)_6]^{2+}$

Polyethylene dioxythiophene–polystyrene sulphonate (PEDOT:PSS) polymer is utilized in an organic–inorganic composite system to create a reversible thermochromism–based temperature sensor. [30]

One of the most promising "smart and intelligent materials" is vanadium dioxide (VO_2), which has a thermochromic mechanism that makes it temperature-sensitive. Depending on the temperature, vanadium dioxide exists in two stable polymorphs: rutile (VO_2 (R)) and monoclinic (VO_2 (M)). (Figure 6). These two types experience a sharp and reversible first order metal-to-insulator transition (MIT) at around 68°C as temperature rises. There is a significant alteration in its near-infrared optical characteristics along with the structural transition from monoclinic VO_2 (M) form (low temperature) to rutile VO_2 form (R) (high temperature) (Figure 7). The monoclinic VO_2 form acts like a semiconductor in the low-temperature zone, absorbing or transmitting a significant quantity of solar radiation. When the temperature of the reaction rises over the transition point (T_C), VO_2 exhibits metallic characteristics and reflects radiation in the near-infrared (NIR) spectrum. Almost half of the heat energy transported by solar radiation is found in the infrared area. The material reflects infrared light over T_c. Its transparency below T_c, however, is essential for its use as a thin-film coating for "intelligent" architectural glass. [31]

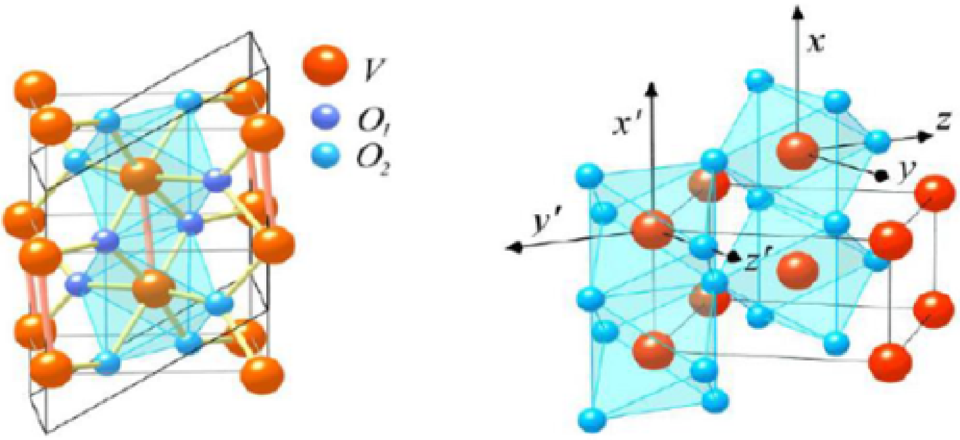

Figure 6: Crystal structures of Vanadium dioxide (VO_2)in Monoclinic (left) and Rutile (right) form observed in lower and higher temperature. Retrieved from ref 32

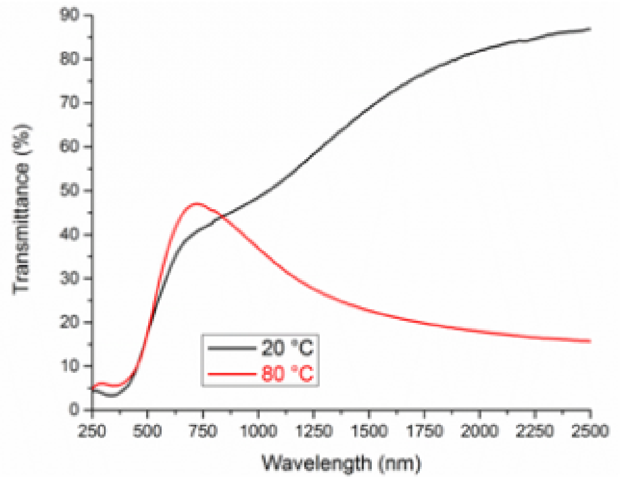

Figure 7: Representative VO_2 thermochromic performance below and above T_c

Due to this novel characteristic, VO_2 becomes a promising base material for a coating of windows in equatorial region to reduce the inner temperature of the house. [32]

Order-disorder phase changes is another mechanism of thermochromism. Cu_2HgI_4 is a thermochromatic chemical. When the temperature changes, it reversibly changes color. This compound is brilliant red at low temperatures and dark brown at high ones. The Cu^+ and Hg^{2+} ions are stacked in distinct, alternating layers between layers of I^-ions in the low-temperature form (Figure 8). The I^- ions remain in the same places in the high-temperature version, but all of the tetrahedral holes in the iodide array are now randomly occupied by metal ions. The transition from one crystal structure to another occurs abruptly about 70ºC. The Metal-Metal charge transfer appears to be the most likely reason for the evolution of colour. The d-d transition and Metal→Lig and transition is ruled out due to d^{10} configuration of Hg^{2+} and π-acceptor property of chloride respectively. [33-34]

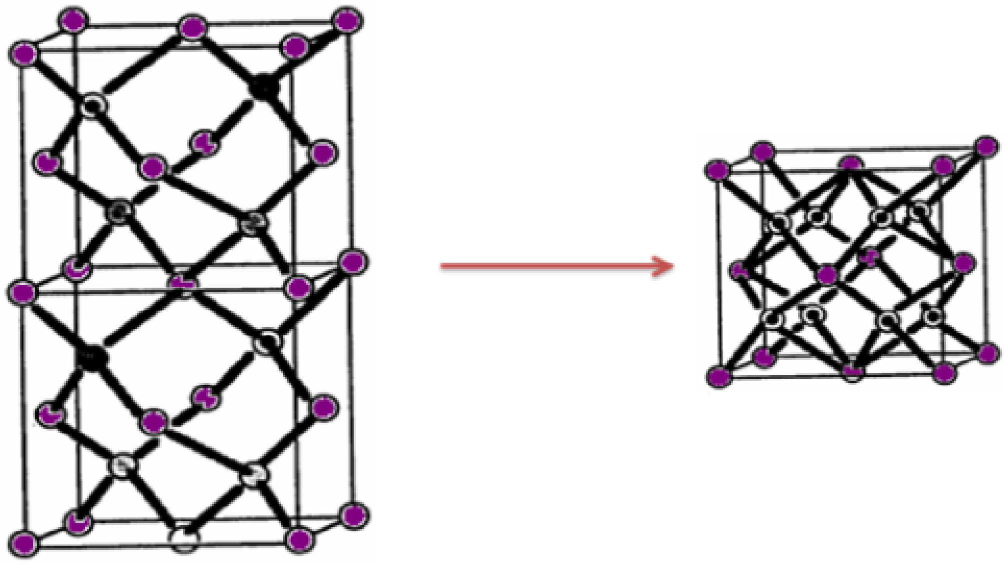

Figure 8: The structure of ordered low temperature (left) and randomly distributed high temperature (right) form of Cu_2HgI_4.Violet ball= I^-,Violet ball=I^-, filled black ball= Hg^{2+}, scattered black ball = Cu^+

Cr-doped Al_2O_3, usually known as ruby, are another class of inorganic materials that depicts thermochromism. The theory of crystal fields in transition metal complexes provides an explanation for the color shift observed in Cr-doped Al_2O_3. The electronic transitions between the splitted d-orbitals caused by octahedral field of the ligands are the source of color in these transition metal complexes. The splitting of the d-orbitals of Cr^{3+}, which results in the electronic transitions $^4A_{2g} \rightarrow {}^4T_{1g}$ (410–461 nm) and $^4A_{2g} \rightarrow {}^4T_{2g}$ (561–600 nm), is the source of the pink color of the Cr-doped Al_2O_3. Squeezing a Cr^{3+} into the too-small octahedral cage of O^{2-} ions results in doping of the Cr^{3+} in the Al_2O_3 crystal lattice at low temperatures. At elevated temperatures, the chemical bonds in this compound expand due to enhanced molecular vibration, and the Cr^{3+} ions instead of being squeezed become more relaxed and regain its proper green color as of pure Cr_2O_3. The change of ligand field strength in lieu of changes of Cr─O distance at high temperature is thus the origin of such kind of thermochromism. [35-36]

Some nickel based coordination complexes like dichlorobis (triphenylphosphine) nickel(II) and $[R_xNH_{4-x}]^2NiCl_4$, (where R = alkyl or aryl group) shows thermochromism for structural isomerism. A shift in coordination numbers from an octahedral (CN = 6) to a tetrahedral (CN = 4) geometry accounts for the thermochromism seen in the later complexes. (Figure 9) For stereochemical as well as experimental considerations, it is possible to rule out the notion that the thermochromism involves a five-coordinate nickel(II) complex. In case of former complex different colour in temperature is due to the equilibrium between square planar and tetrahedral geometry. [37,38]

$$\underset{\substack{\text{Brown-yellow}\\ \text{Octahedral}}}{(\{R_xNH_{4-x}]_2NiCl_4)_x} \xrightarrow{\text{heat}} \underset{\substack{\text{Blue}\\ \text{Tetrahedral}}}{2(R_xNH_{4-x})^+ + NiCl_4^{2-}}$$

Figure 9: Change in geometry induced thermochromism in quaternary nickel complex

4. Conclusion

Altogether we can conclude that thermochromism is a colour changing phenomena due to temperature changes. Thermochromism is frequently observed due to structural and chemical modifications. At molecular level, the colour change happens due to the change in ligand geometry, crystalline phase, number of solvent molecules in the coordination sphere. The loss of water from crystallization molecules during heating causes the hexahydrate complex of copper salt to change into a tetrahedral chloro complex, which is the origin of the thermochromism phenomena in the solid form of copper chloride hexahydrate. This reasoning went into creating a temperature sensor with a reversible thermochromism based on the Polyethylene Dioxythiophene–Polystyrene Sulphonate (PEDOT:PSS) polymer. Depending on the temperature, vanadium dioxide coexists in two polymorphs: the rutile form and the monoclinic form. The material's ability to reflect infrared light above T_c and remain transparent below T_c is essential for its use as a thin-film coating for windows that are part of "intelligent" architectural glazing. Thermochromatic Cu_2HgI_4 results from Metal-Metal charge transfer. Cr-doped Al_2O_3 is another class of inorganic material that depicts thermochromism. The color change of the Cr-doped Al_2O_3 (Ruby gemstone) can be explained from the basis of electronic transition arises from the crystal field theory of transition metal complexes.

References

[1] Day, Jesse H. “Thermochromism.” Chemical Reviews 63.1 (1963): 65-80.

[2] Day, Jesse H. "Thermochromism of inorganic compounds." *Chemical Reviews* 68.6 (1968): 649-657.

[3] Christie, R. M. "Chromic materials for technical textile applications." *Advances in the dyeing and finishing of technical textiles*. Woodhead Publishing, 2013. 3-36.

[4] Sivaramakrishnan, C. N. "The use of surfactants in the finishing of technical textiles." *Advances in the dyeing and finishing of technical textiles*. Woodhead Publishing, 2013. 199-235.

[5] Pechini, Maggio P. "Washington, DC: US patent and trademark office." *US patent* 3 (1967): 697.

[6] White, Mary Anne, and Monique LeBlanc. "Thermochromism in commercial products." *Journal of chemical education* 76.9 (1999): 1201.

[7] Wang, Xuanjie, and Shankar Narayan. "Thermochromic materials for smart windows: a state-of-art review." *Frontiers in Energy Research* 9 (2021): 800382.

[8] Malti, Abdellah, et al. "Freestanding electrochromic paper." *Journal of Materials Chemistry C* 4.41 (2016): 9680-9686.

[9] Andreasson, Joakim, and Uwe Pischel. "Storage and Processing of Information Using Molecules: The All-Photonic Approach with Simple and Multi-Photochromic Switches." *Israel Journal of Chemistry* 53.5 (2013): 236-246.

[10] Tian, He, and Songjie Yang. "Recent progresses on diarylethene based photochromic switches." *Chemical Society Reviews* 33.2 (2004): 85-97.

[11] Xiao, Wenjing, et al. “Ophthalmic devices comprising photochromic materials with reactive substituents.” U.S. Patent No. 9,052,438.9 Jun. (2015). https://patents.google.com/patent/US9052438B2/en

[12] Seeboth, Arno, and Detlef Lötzsch, eds. Thermochromic and thermotropic materials.CRC Press, (2013). https://doi.org/10.1201/b16299

[13] Chen, Huadong, et al. "Photonic crystal materials and their application in biomedicine." *Drug Delivery* 24.1 (2017): 775-780.

[14] Tanaka, Masashi, et al. "Thermochromism of the Crystals of 2, 3-Bis (phenylthio)-1, 4-naphthoquinone." *Bulletin of the Chemical Society of Japan* 70.2 (1997): 329-337.

[15] Sugawara, Tadashi, and Isao Takasu. "Tautomerism in the solid state." *Advances in Physical Organic Chemistry*. Vol. 32. Academic Press, 1999. 219-265.

[16] Fujiwara, Toshikatsu, Jun Harada, and Keiichiro Ogawa. "Solid-state thermochromism studied by variable-temperature diffuse reflectance spectroscopy. A new perspective on the chromism of salicylideneanilines." *The Journal of Physical Chemistry B* 108.13 (2004): 4035-4038.

[17] McQuarrie, Donald A. *Quantum chemistry*. University Science Books, 2008.

[18] Biedermann, Paul Ulrich. "Overcrowded bistricyclic aromatic enes." *(No Title)* (2004).

[19] Vitry, J. "Photochromie et thermochromie." *Chim. et Indus.–Genie Chim* 102 (1969): 1333-1349.

[20] Robert, François, et al. "Trans-keto* form detection in non photochromic N-salicylidene aminomethylpyridines." *CrystEngComm* 14.13 (2012): 4396-4406.’

[21] Jarikov, Viktor V., and Douglas C. Neckers. "Photochemistry and photophysics of triarylmethane dye leuconitriles." *The Journal of Organic Chemistry* 66.3 (2001): 659-671.

[22] Azizian, Farid, et al. "Intrinsically thermochromic fluorans." *Chemical Communications* 48.5 (2012): 750-752.

[23] Dickinson, Robert, and Isidor Morris Heilbron. "CCXVIII.—Styrylpyrylium salts. Part IX. Colour phenomena associated with benzonaphtha-and dinaphtha-spiro pyrans." *Journal of the Chemical Society (Resumed)* (1927): 1699-1705.

[24] di Nunzio, Maria Rosaria, et al. "Photochromism and Thermochromism of some Spirooxazines and Naphthopyrans in the Solid State and in Polymeric Film." *The Journal of Physical Chemistry C* 114.13 (2010): 6123-6131.

[25] Berkovic, Garry, Valeri Krongauz, and Victor Weiss. "Spiropyrans and spirooxazines for memories and switches." *Chemical reviews* 100.5 (2000): 1741-1754.

[26] Kinashi, Kenji, et al. "Reversible multi-coloring reaction of spironaphtooxazine controlled by long-chain molecule." *Journal of Photochemistry and Photobiology A: Chemistry* 213.2-3 (2010): 189-193.

[27] Ito, Kengo, et al. "Thermal recording media using clay-fluoran dye intercalation as a stable colour former." *Dyes and pigments* 34.4 (1997): 297-306.

[28] Kulčar, Rahela, et al. "Dynamic colorimetric properties of mixed thermochromic printing inks." *Coloration technology* 127.6 (2011): 411-417.

[29] Friškovec, Mojca, Rahela Kulčar, and Marta Klanjšek Gunde. "Light fastness and high-temperature stability of thermochromic printing inks." *Coloration technology* 129.3 (2013): 214-222.

[30] Mehta, Sunita, et al. "Fabrication of a reversible thermochromism based temperature sensor using an organic–inorganic composite system." *RSC advances* 10.36 (2020): 21270-21276.

[31] Kiria, Pragna, Geoff Hyett, and Russell Binions. "Solid state thermochromic materials." *Advanced materials letters* 1.2 (2010): 86-105.

[32] Nag, Joyeeta, et al. "Ultrafast compact silicon-based ring resonator modulators using metal-insulator switching of vanadium dioxide." *Physics and Simulation of Optoelectronic Devices XVIII*. Vol. 7597. SPIE, 2010.

[33] Kittaka, Shigeharu, et al. "Interlayer Water Molecules in the Vanadium Pentoxide Hydrate, V2O5 n H2O. 6. Rigidity of Crystal Structure against Water Adsorption and Anisotropy of Electrical Conductivity." *Langmuir* 12.4 (1996): 1078-1083.

[34] Aldrich, Emily P., et al. "Crystal structure of the thermochromic bis (diethylammonium) tetrachloridocuprate (II) complex." *Structure Reports* 72.1 (2016): 40-43.

[35] Nguyen, Duy Khiem, Heesoo Lee, and In-Tae Kim. "Synthesis and thermochromic properties of Cr-doped Al2O3 for a reversible thermochromic sensor." *Materials* 10.5 (2017): 476.

[36] Orgel, L. E. "Ion compression and the colour of ruby." *Nature* 179.4574 (1957): 1348-1348.

[37] Ferraro, John R., and Anne T. Sherren. "Some new thermochromic complexes of nickel (II) of the type [RxNH4-x] 2NiCl4." *Inorganic Chemistry* 17.9 (1978): 2498-2502.

[38] Greenwood, Norman Neill, and Alan Earnshaw. *Chemistry of the Elements*. Elsevier, 2012.