Thermochromism in Commercial Products

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When a trip to the fast-food outlet leads to lunch and a toy that changes color with changing temperature, the latter offers some interesting chemistry.

Materials that undergo temperature-induced color changes are termed "thermochromic." The origins of thermochromism range from phase transitions in a compound (e.g., in an organic chromophore), to changes in ligand geometry or the number of solvent molecules in the coordination sphere (e.g., in a pure transition metal complex that derives its color from crystal field effects) (1–5), to more complex factors in multicomponent mixtures. The use of thermochromic materials in lecture demonstrations has been discussed (6–8), and thermochromic paper is available commercially (9).

To date, the most important thermochromic materials that are applied to color textiles and other commercial products involve either thermochromic liquid crystals, or organic dyes that change color depending on the molecular structure in a complex mixture (10). This paper focuses on these two sources of thermochromism and presents a brief survey of applications of thermochromism.

Thermochromic Liquid Crystals

Thermochromic liquid crystals show different colors at different temperatures because of the selective reflection of specific wavelengths of light from their structures.

In an appropriate temperature range intermediate between a low-temperature crystalline phase and a high-temperature isotropic liquid phase, these materials form cholesteric (also called chiral nematic or twisted nematic) liquid crystals. The molecules are oriented in a preferred direction, but the direction of preferred orientation varies periodically on passing through the material, as shown schematically in Figure 1. The pitch is defined as the repeat distance along the direction of periodicity; that is, different layers separated by the pitch (or an integer multiple of the pitch) have the same orientation.

Typical values of the pitch can be of the order of the wavelength of visible light (400 to 700 nm). As a result, visible light can undergo Bragg reflection from the subsequent layers, and the color of the liquid crystal will correspond to the wavelength of light for which maximum constructive interference occurs (3, 11).

In a cholesteric liquid crystal, changes in temperature result in thermal expansion, which leads to a change in layer spacing and hence pitch, and therefore the color observed will vary with temperature. Since the pitch varies continuously as the temperature changes, the color will change from black to red through orange, yellow, green, blue, violet, and again black. An illustration of the effect of thermochromism in a cholesteric liquid crystal is shown in Figure 2.

Thermochromic liquid crystals can be modified in their temperature behavior by slight changes in composition (3,11), and they have applications in devices ranging from fish-tank thermometers to "mood" rings to the detection of metabolic changes in breast cancer.

Figure 1. In a cholesteric liquid crystal, the molecules (represented by bold lines) are oriented in preferred directions that change on passing through the crystal. The pitch defines the repeat distance along the direction of periodicity.

Figure 2. The relation between temperature and wavelength of Bragg-reflected light for cholesteryl nonanoate. The pitch is the wavelength of reflected light divided by the refractive index (≈1.5) and both the refractive index and lattice spacing change with changes in temperature. Data are from ref 11.
Cholesteryl esters (see Fig. 3(a)) have been known as thermochromic liquid crystals since the 1960s, but their instability to oxygen and ultraviolet light has severely restricted their use (12). The search for improved liquid crystal display materials led to the discovery of thermochromism in cyanobiphenyls (Fig. 3(b)). These materials are now available commercially as microencapsulated liquid-crystal suspensions in water for use in water-based paints and inks (12). Liquid crystals are also used on textile materials but, because of their rather low color density, their rather high cost, and the need for a black background to maximize the color effect, their use is somewhat specialized (10). Nevertheless, thermochromic liquid crystals can have a versatile range of colors and useful color changes between -30 and 120 °C (12), often with very high temperature sensitivity.

Applications of thermochromic liquid crystals in consumer products need to take into consideration the conditions under which they will be used. For example, a thermochromic yarn that can be knitted into garments has been developed (13); it involves a thermochromic liquid crystal core surrounded by a sheath of transparent synthetic resin. The yarn is thermochromic yet resistant to degradation by heat, and it keeps its color when exposed to dry-cleaning solvents. Another process describes the use of liquid crystals for a thermochromic finish on leather products: a primer undercoat is followed by a layer of microencapsulated thermochromic liquid crystals, followed by a protective topcoat (14).

Of course, thermochromic liquid crystals are only useful when they are in the liquid crystalline phase, which is a mesophase (an intermediate phase of matter) between an isotropic liquid (high temperature) and crystalline solid (low temperature), which restricts the temperature range of their applicability.

### Organic Thermochromic Mixtures

The other major category of materials used to impart colors that change with temperature, especially used for textiles and other commercial products, involves organic dyes. A dye can be defined as a structure, usually organic, that is designed to be absorbed or adsorbed by, made to react with, or deposited within a substrate in order to impart color to that substrate (15). In the case of thermochromic organic dye mixtures, at least two chemical components are required in order to achieve colors that change with temperature.

#### The Components

**The Dye**

These are usually leuco dyes ("white dyes") to indicate that, in some conditions, they are colorless. They are most commonly spirolactones such as fluorans or crystal violet lactone, spiropyran or fulgides (10); see Figures 4 and 5 for structures. Strictly speaking, these dyes are not thermochromic but rather change color with a change in pH, as shown by the change in structure of crystal violet lactone on protonation in Figure 5. In solution, the colored protonated form predominates at a pH more acidic than about 4; when the solution is made more alkaline, the compound becomes colorless (10). The position of this equilibrium can be shifted with temperature when other components are present. This dye component determines the color of the final product in its colored state. (If additional dyes are present, the overall color will be the combination of colors from all the dyes.)
The Color Developer

A second component is used as a color developer. In patents these materials are often referred to as “electron acceptors” but they are more accurately described as proton donors that can affect the equilibrium, as shown in Figure 5 (10). Typical color developers are bisphenol A, octyl p-hydroxybenzoate, methyl p-hydroxybenzoate (16), 1,2,3-triazoles, and 4-hydroxycoumarin derivatives (10) (see Fig. 6), all weak acids. The last two examples have the advantage over phenols that they exhibit increased color fastness. Some phenol derivatives tend to fade with exposure to light (10); however, a large number of phenols in the molecular weight range of 200 to 800 Da are suitable (16). Weak acids impart the reversible color change to the mixture, but stronger acids lead to an irreversible color change. This component imparts the reversible color change to the thermochromic material and is responsible for the color intensity of the final product.

The Solvent

A third component is generally a polar solvent such as an alcohol (M, 150–500), ester (M, 150–1000), ketone (M, 150–500), or ether (M, 150–1000). Examples include lauryl alcohol (1-dodecanol), cetly alcohol (1-hexadecanol), and butyl stearate (CH₃(CH₂)₆COO(CH₂)₃CH₃). Alcohols and esters are preferred because of their low volatility and wide range of applications (16). The melting point of this third component controls the temperature at which the color change will take place.

Two-Component Mixtures

A recent investigation of thermochromism in a fluoran dye mixed with octadecylphosphonic acid (17), typifies thermochromic dyes used in heat-sensitive FAX paper (10). This study showed that the colorless dye is stable in the solid ink matrix and, when the host matrix (i.e., octadecylphosphonic acid) melts, the dye reacts with the acid, resulting in the ring-open colored tautomer. The study showed that the colored protonated form of the dye is favored above the melting point of the acid (which acts as both a proton donor and a solvent), and the colored state could be quenched at lower temperatures by rapid cooling. However, slower cooling resulted in loss of color. Through the use of X-ray diffraction, the authors have shown that the colorless state has the same structure as octadecylphosphonic acid (indicating that crystallization of the developer/solvent no longer allowed the dye to be protonated), whereas the colored state is a lamellar structure, different from pure octadecylphosphonic acid, in which the protonated dye molecules are incorporated optimally in a 7:1 mole ratio with respect to octadecylphosphonic acid (17). This study gives some indication of the importance of molecular packing in thermochromism in complex organic mixtures.

Three-Component Mixtures

Microencapsulated three-component thermochromic organic mixtures—that is, those with a leuco dye, a weak acid and a solvent—are commonly used in consumer applications (10). The temperature at which they change color can range from ~100 to 200 °C, using 0.1–100 parts of color developer and solvent per part of dye (16). Uses include thermochromic coloring agents for toys and other plastic materials, for printing inks, for writing instruments (inks and crayons), for paints, and for foils (16).

It is somewhat surprising that three-component mixtures are colored at low temperature (below the melting point of the solvent component) and colorless at higher temperature. The thermochromic process is not simply a matter of increased acid–base chemistry allowed in the melt, because in that case, an increase in temperature would be expected to lead to a colored material (the protonated form of the dye). A similar reaction of a stronger acid with a leuco dye leads to the irreversible formation of color on application of pen pressure to a carbonless copy paper (18).

Although hundreds of combinations of dye-developer–solvent are known for three-component thermochromic dye mixtures (see ref 10 for a review of patents and ref 16 for an example patent), the mechanism of their operation is not yet known definitively (10). Possible explanations for the stability of the protonated form in the solid state at low temperature include phase separation of one or more of the components on solidification, more favorable packing considerations for the colored (protonated) species on solidification, or changes in dielectric properties of the solvent on solidification (10). Further microscopic studies of the three-component mixtures could elucidate the mechanism of their thermochromism and lead to new thermochromic materials.

More Complex Mixtures

The principles under which the thermochromic Hypercolor T-shirts, popular in the early 1990s, worked (19) are rather similar to those described so far. In the Hypercolor case, the microencapsulated mixture included a leuco dye (crystal violet lactone), a weak acid (1,2,3-benzotriazole), a solvent (lauryl alcohol), and a salt such as myristylammonium oleate (CH₃(CH₂)₇CH(CH₃)₂COOH)₃N(CH₂)₁₃CH₃. These salts tend to dissociate into the free amine and carboxylic acids at high temperature. At low temperatures, the leuco dye and the weak acid allow for a colored complex, as described for the three-component mixtures described above. At higher temperatures, the leuco dye and the weak acid allow for a colored complex in dielectric properties of the solvent on solidification (10). Further microscopic studies of the three-component mixtures could elucidate the mechanism of their thermochromism and lead to new thermochromic materials.

Microencapsulation

Neither thermochromic liquid crystals nor thermochromic organic dye mixtures can be applied directly for use in coloration; both require microencapsulation. Microencapsulation is defined as the coating of small solid particles, liquid droplets, or gas bubbles with a thin film or coating or in dielectric properties of the solvent on solidification (10). For the three-component organic mixtures, particle sizes are <50 μm (16). Microencapsulation allows the additional advantage of combinations of several thermochromic dyes, resulting in several narrow color ranges, and very sharp color changes, as well as protection of the coloring agent in the environment (16).

The microencapsulation process most often used for containment of thermochromic materials is known as the type A process, in which microencapsulation occurs exclusively in a tubular reactor or a liquid-filled stirred tank (20).
processes involve spray deposition of coatings on liquid or solid materials that are dispersed in a gas phase or vacuum [20]. The processes used to microencapsulate thermochromic materials include complex coacervation and interfacial polymerization techniques [10], as described below.

Complex coacervation microencapsulation occurs in aqueous media and is used to encapsulate water-immiscible liquids or solids. In the coacervation of gelatin with gum arabic, the water-insoluble core material (the thermochromic mixture in this case) is dispersed at the required drop size in warm gelatin, and then gum arabic and water are added and the pH is adjusted to form a liquid complex coacervate of gelatin, gum arabic, and water. The system is cooled and glutaraldehyde is added to cross-link the shell of the capsule. This process is used to encapsulate some thermochromic materials dyes and to prepare the materials used for carbonless copy paper, the largest market for microencapsulation at present [10, 20].

Microcapsules also can be produced by polymerization reactions that take place at interfaces. An example of an interfacial polymerization technique used to encapsulate thermochromic materials involves the interaction between formaldehyde and either urea or melamine. The reactants meet at a phase boundary and rapid polycondensation results in polymer formation [10, 20].

Both complex coacervation and interfacial polymerization methods are used to microencapsulate thermochromic materials; the final choice depends on the application and on such factors as particle size, wall thickness, impermeability, thermal stability, and compatibility with and adhesion to the surrounding in the end use.

Other Applications of Thermochromism

Thermochromic toys are eye-catching, but thermochromatic materials can have other applications. In some cases, understanding of thermochromism allows the color change to be induced by other physical or chemical processes, to suit a particular application.

For example, polydiacetylene (∼C≡C≡C≡C≡C)n, also known as PDA, and its derivatives have been studied extensively for the past decade owing to their interesting nonlinear optical properties and thermochromic transitions [21]. Of related importance is the thermochromism of Langmuir–Blodgett films of polydiacetylene modified with N-acetylneuraminic acid (a sialic acid); the films exist in a blue form or a red form, depending on the temperature. This same chemistry is being used for biosensors: when the sialic acid–modified polydiacetylene film is exposed to influenza virus, the virus binds to the film and changes the color from blue to red, an immediately detectable optical event [22].

Thermochromic compounds have become increasingly important in recent years in the study and production of “smart coatings”, that is, coatings that respond to their environment. As in any thermochromic material, there is a change in color with a change in temperature. Incorporated into a window system, a thermochromic material could be used to control the flux of solar energy by changing the transmission of visible light in response to the heating effect of sunlight. Thin films of materials such as Fe₃O₄, FeS₂, NbO₂, NiS, Ti₂O₃, and VO₂ could be used to control the infrared emittance and the solar transmittance of a glaze, owing to their change at a threshold temperature from a semiconducting state to a metallic state (also known as the Mott transition temperature) [23].

Another type of smart coating involves gels that control insulation by a change in optical properties with temperature, although there is no change in color [24]. The gel consists of water, a polyether with ethylene oxide groups, carboxyvinyl copolymers, and an antifreezing agent. Below the switching temperature, the polyether molecules are nearly indistinguishable from the gelled water–glycol mixture, and the material is transparent. Above the critical temperature, the polyether molecules expel water and aggregate, forming micron-sized particles that strongly scatter visible light and make the material opaque. Major advantages are that the transition temperature can be moved by modification of the composition of the gel, and the gel can easily be placed in narrow spaces or crevices such as the space within a double-paned window.

Concluding Remarks

Applications of thermochromism can range from the whimsical—toys that change color with temperature—to potentially life-saving, such as road signs that change color at the onset of freezing conditions. Although purposeful thermochromism has many applications, thermochromism can also lead to undesirable features such as changes in color of a slide film upon projection [25] or changes in optical properties of colorimetry standards [26]. Understanding the basis of thermochromism will increase knowledge of the relationships between structure and properties of materials, inspiring new generations of thermochromic and related materials.

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Literature Cited

9. Thermostim paper is available from Educational Innovations, Inc., 151 River Road, Cos Cob, CT 60870; tel. 203/629-6049.