Color-changing inks

Color-changing inks are most often used to increase value or uniqueness in a variety of applications. The first major commercially successful color-changing ink application was the mood ring of the 1970s, but now even automobiles can change color. Applications and uses continue to expand rapidly. While there are a range of color-changing technologies, as listed in **Table 1**, the most popular and readily printable are thermochromic (changing color with temperature) and photochromic [changing color with ultraviolet (UV) light]. These inks can be reversible or irreversible, as the application dictates. However, irreversible inks are not readily available.

Microencapsulation. Many photochromics and nearly all thermochromics require microencapsulation for protection. As a result, it is beneficial to understand the basics of the process. The most common process for encapsulation is called interfacial polymerization. During the process, the internal phase (material inside the microcapsule), the external phase (wall material of the microcapsule), and water is combined under homogenization (high-speed mixing). The goal here is to make a stable emulsion of the desired particle size, usually 5 micrometers or below. By controlling all the process conditions precisely (temperature, pH, concentrations, mixing speed, etc.) the external phase will surround the internal phase droplet and crosslink. Finished microcapsuled particles under 400× enlargement are shown in **Fig. 1**.

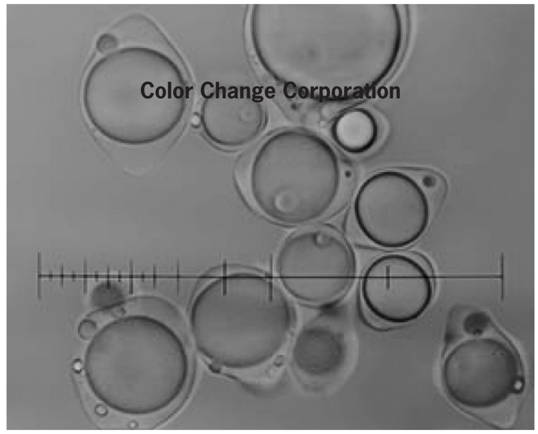


Fig. 1. Microencapsulated particles.

Thermochromics. There are two predominant reversible thermochromic classes: liquid crystals and leuco dyes.

Thermochromic liquid crystals. Thermochromic liquid crystals (TLCs) are used in the popular mood ring or aquarium thermometer strips and change color from black when cold, to red-orange-yellow-green-blue-violet, and then black upon heating, while the colors reverse upon cooling. They are very sensitive to temperature changes and can be used for medical thermometers, thermal mapping, and toys. TLCs are microencapsulated for protection, with a particle size of 5–50 μm in diameter.

TLCs can be formulated to respond from −30 to 90°C (−22 to 194°F) and require a black background to appear visibly. The full color spectrum can respond over 1°C (1.8°F) or be as wide as 25°C (45°F). This is called the bandwidth. With a narrow bandwidth, the resolution is quite high, maybe 0.2°C (1.36°F) for a 1°C wide mixture (useful for medical thermometers). The resolution drops as bandwidth is increased, so that a 25°C mixture can only resolve about a 5°C (9°F) temperature range (useful for automotive defroster testing). TLC inks are water-based, somewhat difficult to work with, and require such a thick coating that only screen printing is applicable. Special materials and environmental conditions are required to print them. TLCs are most effectively used by reverse printing them upon clear plastic and then protecting them with a black backing, so that they are applied in a strip form (**Fig. 2**). The cost for TLC ink is typically in the $100–200 per kg range in reasonable volume.

Thermochromic leuco dyes. Thermochromic leuco dyes (TLDs) change from one color when in their cool state to translucent when in their warm state. They can be made in most colors, but not white (**Table 2**). They are reversible but usually return to their colored

TABLE 2. Thermochromic leuco dye color range.

TLD colors	
Color	Pantone
Red	186C
Rose red	217C
Magenta	675C
Vermillion	1785C
Orange	172C
Yellow	393C
Yellow green	359C
Charm green	373C
Green	3435C
Sky blue	2925C
Turkish blue	320C
Blue	285C
Dark blue	287C
Violet	286C
Black	Black 3C

TABLE 1. Color-changing technologies and applications

Technology	Mode of color change	Application example
Thermochromism	Changing color with temperature	Mood ring
Photochromism	Changing color with UV light exposure	Transitions® lenses
Hydrochromism	Changing color with moisture	Water glasses that change from white to clear
Interference Pigments	Changing color by viewing angle	Specialty car paint

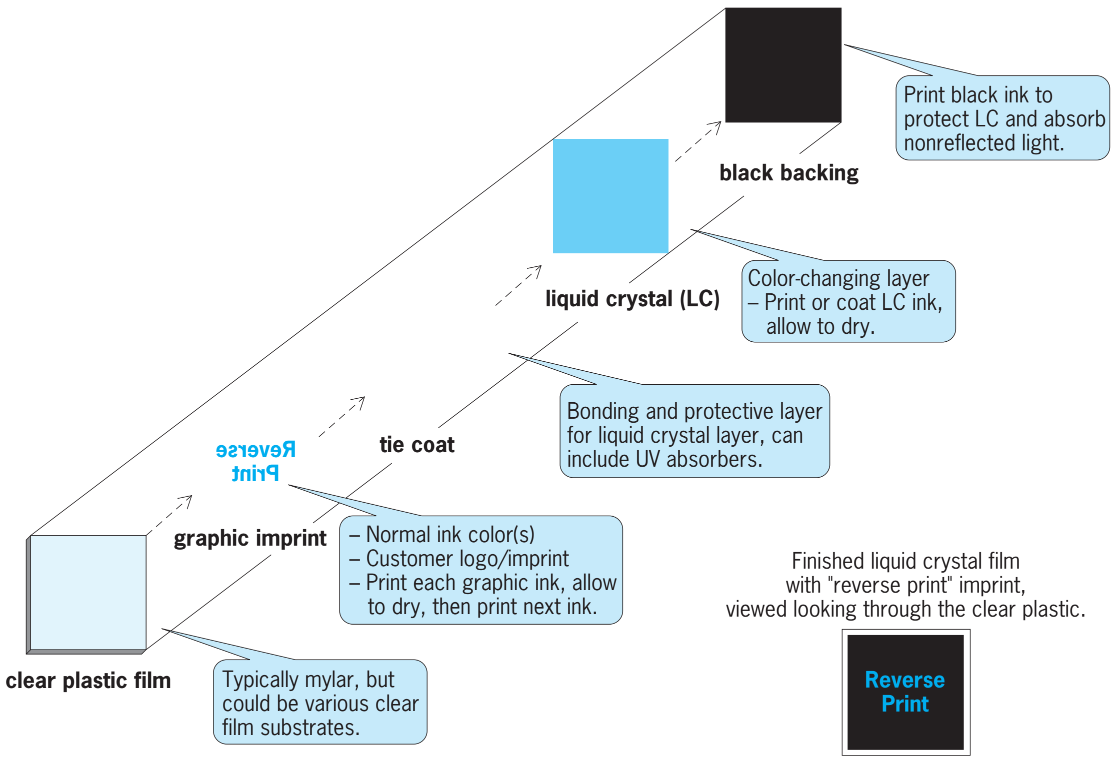


Fig. 2. Reverse printing process.

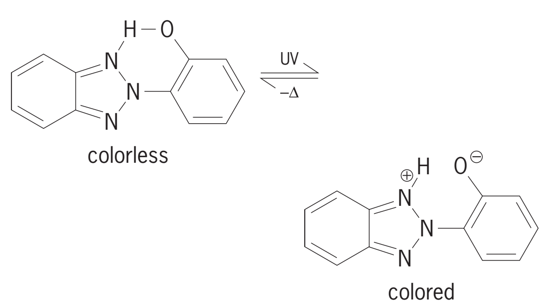
(cool) state a few degrees Celsius below the temperature that made them clear while heating. They are used in a wide range of products, from the hot or cool indicating food and beverage labels, to coffee mugs, toys, and security applications such as check anticopy protection (**Fig. 3**). TLDs are microencapsulated and have an average diameter of 2–5 μm.

TLDs can be formulated to change color from −15 to 60°C (5–140°C). The transition from colored to clear occurs over a 3–10°C (5.4–18°F) range. Consequently, the materials are not suitable for most sensitive thermometer-type applications but work well for general temperature indication such as cold, warm, or hot. TLDs are dyes and not pigments, so they must be printed over a lighter background, and the background color will influence the TLD color if it is any color other than white. For example, a black TLD printed over a red background would appear to change from black to red upon heating (the black TLD revealing the red underneath as it went translucent). A blue TLD printed over a yellow background would appear blue or green depending upon how thickly the blue TLD was printed, and then yellow when warm. TLDs are quite robust and can be used in a wide range of inks (solvent, water-based, UV cured, epoxy, etc.) and printed using most processes (screen, flexographic, offset, gravure, etc.). Costs for inks range from $75 for large-volume screen-printing inks to $500 per kg for offset inks.

(a) (b)

Fig. 3. Beverage label printed with a thermochromic leuco dye in their (*a*) colorless and (*b*) colored states.

Photochromics. Photochromics (PCs) are relatively new (1990s) compared to thermochromics (1970s), and the underlying technology continues to change rapidly. Most photochromics change from colorless to clear upon exposure to UV light, and then fade back to colorless upon removal from the UV source, as shown in the chemical formula below.



The normal wavelength of excitation is around 360 nanometers. And while sunlight works the best, a fluorescent black light, which emits near-UV

Fig. 4. Application of a photochromic ink in which customers would expose the container to sunlight to see if the ink changed color, revealing if they were a "winner."

(320–400 nm) light, will usually work. There is a full spectrum of photochromic colors available.

The most famous use of PCs is in Transition® photochromic lenses for glasses, but a popular ink application was the Dairy Queen Blizzard® promotion as shown in **Fig. 4**.

Different PC dyes have different kinetics, meaning some will color and fade quickly, while others will color and then fade slowly. The raw PC dyes tend to be quite expensive, ranging from $3 per gram to over $200 per gram. However, they are often used in low concentrations (0.2–1% by weight). Typical inks are expensive, ranging from $100 to over $500 per kg.

Very few PC dyes are water-soluble, so for waterborne applications microencapsulation is required. For many nonaqueous inks, microencapsulation is often preferable because it protects the PC dyes.

The same unique nature that allows PC dyes to change color makes them inherently unstable. Lifetimes for the photochromic dyes can be as short as 1 hour outside without stabilizers. With a stabilization package, lifetimes of about 1 month of outdoor exposure are possible. Because the PCs are dyes, they are most effective on white or very light backgrounds.

For background information *see* DYE; EMULSION POLYMERIZATION; INK; PRINTING; ULTRAVIOLET RADIATION in the McGraw-Hill Encyclopedia of Science & Technology.

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Bibliography. P. Bamfield, *Chromic Phenomena: Technological Applications Of Colour Chemistry*, 2001; R. Muthyala, *Chemistry and Applications of Leuco Dyes*, 1997.