The fourth state
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The Fourth State

Liquid crystals present the greatest oxymoron in cosmetic science

By Steve Herman

*"There are more things in heaven and earth, Horatio,
Than are dreamt of in your philosophy."*[1]

Hamlet was surely thinking of his father's ghost when he spoke those lines to Horatio. His premise could be applied with equal validity to the states of matter, and particularly to that grandest oxymoron in cosmetic science, liquid crystals.

Everyone is familiar with three states of matter: with increasing temperature, a substance usually changes from solid to liquid to gas. Exceptions occur, such as sublimation, where a solid is transformed directly into the gaseous state. In addition to temperature, pressure is a factor in changes of state: we tend, naturally enough, to evaluate most transitions at atmospheric pressure.

In 1888, Friedrich Reinitzer encountered a cholesteric material which appeared to have two melting points. The Austrian botanist observed that at 145.5°C the substance became a cloudy liquid, and at 178.5°C it became a clear liquid. This substance, which we now know to be cholesteryl benzoate, also exhibited a blue color at the point where the cooling clear liquid turns cloudy, and blue-violet as the cloudy liquid crystalizes.

One might fairly claim that Reinitzer didn't exactly observe two melting points. Nonetheless, his claim that the transition from a cloudy liquid to a clear liquid indicated a significant change of state was an inspired conceptual leap. The discovery triggered the investigation of a unique and significant new state of matter. A contemporary of Reinitzer, Otto Lehmann, referred to this state as *Fliessende Krystalle* (flowing crystals) or *Flussige Krystalle* (fluid crystals). Today they are described as liquid crystals (LC).

Two basic classes of LC's are lyotropic and thermotropic. The properties of lyotropic LC's depend on solvents and concentration. The liquid mush that develops under a wet soap bar is an example. Amphiphilic molecules in solution tend to form these structures.

Lyotropic LC's are crucial for life itself at the cellular level. Cells need enough rigidity for spatial integrity, but selective permeability is also essential for the transport of materials in and out of the cells. Lipid bilayers, which are LC in nature, provide those qualities. These lipid structures are also important in the biochemistry of skin, and thus have a significant effect on the application of skin treatment products.

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Thermotropic LC's are temperature dependent. There are two main varieties, nematic and smectic. Cholesteric LC's are nematic with the additional feature of optical activity. The LC state is more ordered than liquids and less ordered than solids. Smectic LC's are more ordered than nematic, as

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***Greek kosmEtikos, skilled in adornment or decorating.**

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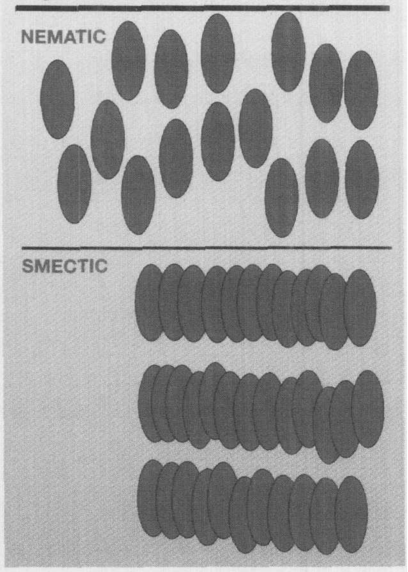
shown in Figure 1. The nematic molecules are loosely aligned in the same direction, while the smectic are also ordered as planes.

FIGURE 1
Two levels of liquid crystal order



LC's come in many varieties. Selecting from them, examples can be found which change properties with small variations of electromagnetic radiation, mechanical stress or chemical environment. In 1971 it was found that certain LCs could turn from clear to black with the application of a minute electrical current, a feature soon applied to numerous consumer goods such as watches and calculators.

The first high profile use of LC's for visual as well as functional use in cosmetics was Estée Lauder's Eyezone. The patent[2] describes it as "a composition comprising vitamin A or a vitamin A containing material, a cholesteric liquid crystal and a translucent or transparent polyacrylic gel carrier..." Simply put, a water-based gel with a pretty LC swirled through it containing an oil-soluble active.

An attractive temperature-insensitive LC appropriate for cosmetic applications can be made by heating and mixing the following materials[3]:

cholesteryl oleyl carbonate (OCC)	**50**
cholesteryl nonanoate (CN)	**25**
cholesteryl chloride (CCL)	**25**
	100

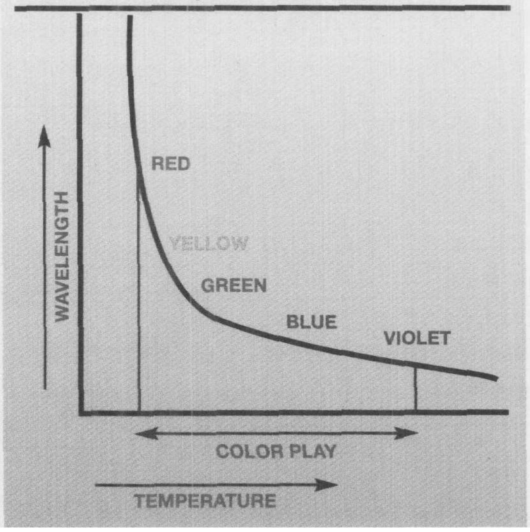
Temperature sensitive LCs can be characterized by "color play." It is necessary to specify either the red start or mid-green temperature plus the bandwidth. R34C1W represents a red start at 34°C and a 1°C bandwidth, G98F2W has a mid-green temperature of 98°F and a 2°F bandwidth. Figure 2 illustrates a typical color evolution.

Friberg and his colleagues introduced LCs, which they termed "mesomorphous phases," into emulsion theory in 1969[4].

Their premise was that a system consisting only of micelles in a continuous phase cannot explain the stability of emulsions. The LC structures in the continuous phase, primarily formed by amphiphiles or fatty acids and alcohols, provide essential stabilization.

More recently, emulsions based on LC structures rather than conventional micelles

FIGURE 2
LC color-temperature response



have been promoted for cosmetic applications. Some examples of LC emulsion bases are Arlatone 2121 from Uniqema, ProLipid™ 131 from ISP, and BIOBASE™ from Tri-K.

From a chance discovery by an obscure researcher a century ago, liquid crystals have been found to be important for a myriad of consumer applications, for emulsion theory and other aspects of cosmetic science—and for life itself. ■

References

Collings, Peter J., Liquid Crystals: Nature's Delicate Phase of Matter, *Princeton University Press, 1990.*

Interested readers are directed to a primary source of much of the material in this column:

Parsley, Michael, The Hallcrest Handbook of Thermochromatic Liquid Crystal Technology, *Hallcrest Products, 1991.*

1. *Shakespeare,* Hamlet, *I.5.166-167.*
2. *Cioca, Gheorghe et al., US4999348, March 12, 1991.*
3. *Parsley, Michael, private correspondence, Oct. 6, 1994.*
4. *Friberg, Stig et al., Mesomorphous Phases, A Factor of Importance for the Properties of Emulsions, J. Colloid and Interfactial Sci., Vol. 20, No. 1, January 1969.*