LCRHallcrest

Handbook of Thermochromic Liquid Crystal Technology

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PREFACE

This booklet provides an introduction to thermo chromic liquid crystals (TLCs), how the materials work and how they are used. The major application areas are discussed and the processing and manufacturing steps necessary to produce reliable, optimized TLC products, for whatever application, are described.

A variety of chemical compounds are now used in the formulation of the thermochromic liquid crystal mixtures themselves. Most of these compounds are related and fall into one of several distinct groups of chemicals allowing a general classification of TLC mixtures to be made. Three major types can be identified according to their chemical compositions, chemical and physical properties:

(i) cholesteric
(ii) chiral nematic
(iii) combination

These three classes are described and differentiated.

The original application for TLCs, and that on which HALLCREST'S business (and the TLC industry in general) has been founded, is in the manufacture of temperature indicators. Methods of using the materials in temperature indicating applications are discussed with particular reference to microencapsulation and its importance in stabilizing and protecting the materials. Coating formulation and device manufacture are covered briefly.

More recently, the use of TLC mixtures, both unsealed and microencapsulated, in cosmetic formulations has become well- established, and the cosmetics industry now provides a significant market for the materials. Much increased interest has also been shown of late in the use of TLC products in aerospace and engineering research, as well as in non-destructive testing and thermal mapping applications in general. Finally, most recently, microencapsulated TLC mixtures have been used successfully, for the first time, in the large volume manufacture of screen printing inks, leading to a considerable new market for the materials being established.

HALLCREST has been a pioneer in almost all of the recent developments in the industry which have led to the successful commercialization of a number of new products, the implementation of new manufacturing methods and to the market for TLCs and their products growing considerably during the last few years. HALLCREST is at the forefront of TLC technology and is committed to maintaining its position as the industry leader. We, at HALLCREST, hope this booklet gives a useful insight into the interesting technology on which our business is based.

1. INTRODUCTION

1.1 Thermochromic Liquid Crystals

1.1.1 Cholesterics, Chiral Nematics and Combination Mixtures

1.1.2 Temperature-sensitive and Temperature-insensitive (Shear-sensitive) Formulations

1.1.3 Color Change Properties and Product Identification

1.2 Applications

1.3 HALLCREST Product Range and Services

1.1 THERMOCHROMIC LIQUID CRYSTALS

1.1.1 Cholesterics, Chiral Nematics and Combination Mixtures

Thermochromic liquid crystals (TLCs), as their name implies, react to changes in temperature by changing color. They have chiral (twisted) molecular structures and are optically-active mixtures of organic chemicals.

The correct name for the materials is **Cholesteric** or **Chiral Nematic** liquid crystals. The term "cholesteric" is a historical one and derives from the fact that the first chemicals to show the characteristic properties and structure of this particular type of liquid crystal were esters of cholesterol. This can be misleading, as many optically-active organic chemicals (and mixtures containing them), which are not related to cholesterol or other sterols, also show the cholesteric structure. It is important to differentiate these non-sterol materials from cholesteryl esters because, although the mechanism by which they change color is the same, they have different chemical and physical properties, and can be used in different ways to achieve different effects.

Thus, TLC mixtures can essentially be divided into 2 distinct types, according to their chemical compositions:

a) **Cholesteric**
formulations comprised entirely of cholesterol and other sterol derived chemicals

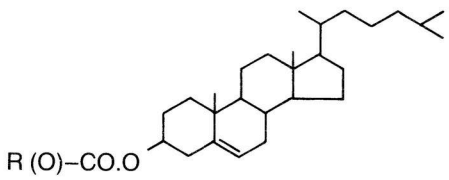
b) **Chiral Nematic**
formulations comprised entirely of non-sterol based chemicals

A third category naturally arises from the fact that cholesteric and chiral nematic chemicals can also be mixed together to give formulations which show a continuum of physical and chemical properties between those of their 100 cholesteric and 100 chiral nematic precursors:

c) **Combination**
formulations containing both cholesteric and chiral nematic components

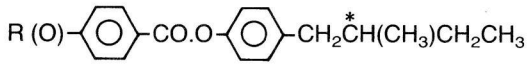
Typical constituent compounds that are available commercially have the following general chemical formulae:

a) Cholesteric



Cholesteryl esters (carbonates)

b) Chiral Nematic



(2-methylbutyl) phenyl 4-alkyl(oxy)benzoates

In the above structures R is most commonly a straight chain alkyl group.

TLC formulations in general and combination mixtures in particular, may contain some components which, individually, exhibit nematic and/or smectic liquid crystalline properties rather than cholesteric; chemicals which do not exhibit liquid crystalline properties at all individually can also be used at low percentages. TLC mixture formulation is discussed in more detail in section 3.6 later in this booklet.

Combination mixtures are becoming increasingly important as they extend the application possibilities and working ranges of TLC formulations by combining the respective advantages of both groups of component chemicals.

TLCs have been categorized above by their chemical compositions. However, it should be noted that, according to generally accepted (theoretical and historical) nomenclature, all TLC mixtures are **Cholesteric Liquid Crystals**, whether sterol-derived, non-sterol derived or a mixture of the two.

The terminology differentiating cholesterics from chiral nematics (and combination mixtures) outlined above has been adopted recently to avoid some of the confusion that might easily otherwise arise when discussing the physical and chemical properties of different formulations. This is particularly important when considering the relative advantages and disadvantages of using one type or another in a particular application.

A number of good sources currently exist worldwide for cholesteric and chiral nematic raw materials.

TLCs (cholesteric liquid crystals), as described above, fall into the general classification of liquid crystals as one of the three major classes of **Thermotropic** liquid crystals (those produced by the action of heat) as opposed to **Lyotropic** liquid crystals (which result from the action of solvents). The two other classes of thermotropic liquid crystals are smectics and nematics. Full details of the general classification of liquid crystal materials and how TLCs fit into it are given in section 3.3 later in this booklet.

1.1.2 Temperature-sensitive and Temperature-insensitive (Shear-sensitive) Formulations

TLCs show colors by selectively reflecting incident white light. Conventional temperature-sensitive mixtures, in thin films, reflect bright, almost pure colors, turning from colorless (black, against a black background) to red at a given temperature and, as the temperature is increased, pass through the other colors of the visible spectrum in sequence (orange, yellow, green, blue, violet) before turning colorless (black) again at a higher temperature still. The color changes are reversible and on cooling the color change sequence is reversed. A typical wavelength (color) / temperature response is shown in figure 1.

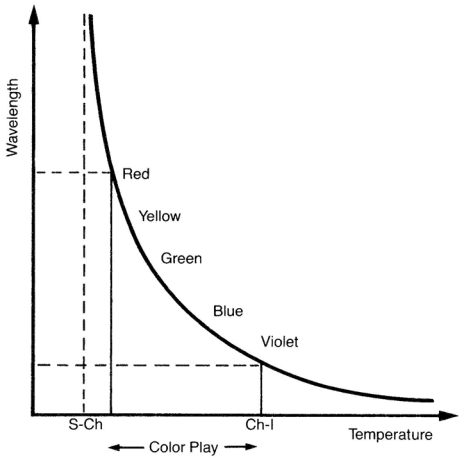


Figure 1: Typical reflected wavelength (color)/temperature response of a temperature-sensitive TLC mixture

Temperature-insensitive (sometimes called shear-sensitive or clearing point) formulations can also be made. These mixtures reflect just a single color below a given transition temperature (called the clearing point) and change to colorless (black) above it. Both reversible and hysteretic (memory) formulations can be made. Some of the important considerations that need to be borne in mind in the formulation of both temperature-sensitive and temperature-insensitive mixtures are discussed in section 3.6 later in this booklet.

All TLC mixtures should be viewed against non-reflecting backgrounds (ideally black–totally absorbing) for best visualization of the colors.

The color change effects described above are thin-film effects. In bulk, the materials also reflect light but the predominant observed effect is one of iridescence, caused by interference and diffraction of the reflected and scattered light. Unsealed TLC mixtures, in bulk, thus have the characteristic appearance of liquid mother-of-pearl tinted with either red, orange, yellow, green, blue or violet depending on the wavelength of maximum reflection at the temperature in question.

1.1.3 Color Change Properties

Temperature-sensitive TLC mixtures and products made from them all have characteristic red start or mid-green temperatures and color play bandwidths. The bandwidth is defined as the blue start temperature minus the red start temperature. The **Color Play** of a TLC mixture is defined by specifying *either* the red start or the mid-green temperature **and** the bandwidth. For example, R35C1W describes a TLC mixture with a red start at 35°C and a bandwidth of 1°C, i.e. a blue start 1 ° higher, at 36°C; G100F2W describes a TLC mixture with a mid-green temperature at 100°F and a bandwidth (red start to blue start) of 2°F.

Temperature-insensitive (shear-sensitive) TLCs are defined by specifying the color and clearing point. The clearing point is the temperature above which the color disappears, also called the cholesteric liquid crystal to isotropic liquid (Ch-I) transition temperature. For example, R50C describes a red TLC mixture with a **Clearing Point** of 50°C.

Although individual compounds exhibit color change properties as high as 250°C (482°F) or more, for practical purposes the working temperature range for temperature-sensitive TLC mixtures currently available in commercial quantities is approximately - 30°C (- 22°F) to 115°C (239°F); temperature-insensitive formulations with clearing points between -20°C (-4°F) and 80°C (176°F) are also available.

As a point of warning, it should be noted that the color plays and clearing points of all TLC mixtures are very sensitive and susceptible to change during any processing step to which the materials are subjected, some more so than others. Extreme care should be exercised whenever the materials are handled.

1.2 APPLICATIONS

The color change properties of TLCs are produced by a very delicate arrangement of molecules and the materials are extremely sensitive. Color changes can be induced by many things in addition to temperature variations; these include shear, pressure, electric fields, magnetic fields and impurity doping among others. The materials thus have a great number of potential applications, however the majority are still related to their temperature sensitivity and this is by far the most important property of the materials from the applications viewpoint.

Numerous applications for the materials have been claimed in the patent and scientific literature over the years, although not all have been successfully commercialized. A representative selection is summarized below:

a) **General Temperature Indication/Digital Thermometers**
- Room/Household
- Refrigerator/Freezer
- Infant Bath/Bottle
- Aquarium
- Hot/Cold Warning Indicators

b) **Battery Testers and Other Voltage Measuring Devices**

c) **Temperature Indicators for Medical Applications**
- Forehead Thermometers/Fever Indicators
- Hypothermia Warning Indicators
- Drug Testing; Temperature Indicating Labels for Urine Specimen Authentication

d) **Medical Thermography**
- Sub-cutaneous Cancer Detection
- Diagnosis of Vascular Diseases
- Placenta Location
- Pharmacological Tests
- Skin Grafting and Vein Location
- Veterinary Applications
- Chiropractic Applications

e) **Radiation Detection**
- Infrared
- Microwave
- Ultraviolet
- Ultrasonic
- Electromagnetic

f) **Aesthetic**
- Advertising and Promotions
- Decoration
- Jewelry, Badges, Fabrics, Clothing and Other Novelties

g) **Ingredients in Cosmetic Formulations**

h) **Non-Destructive Testing/ Thermal Mapping**
- Surface and Sub-Surface Flaw Detection in Metals, Welded Metals, Bonded and Other Composite Structures
- Fault/Short Location in Electric Components and Electronic Circuits

i) **Aerospace and Engineering Research**
- Heat Transfer Studies
- Flow Visualization in Fluids and on Solid Surfaces in Airflows

j) **Gas/Liquid Level Indicators**

k) **Miscellaneous**
- Chemical and Gas Detectors
- Pressure Sensors
- Information Displays

The selection listed above is not exhaustive. Novel applications for the materials are continually under development and new patents are filed on a regular basis.

1.3 HALLCREST PRODUCT RANGE AND SERVICES

HALLCREST offers a wide range of products to satisfy the needs and demands of the market across the full spectrum of applications. The major product lines include temperature indicators, cosmetic raw materials and temperature-sensitive inks and coatings. A custom microencapsulation service is also offered for oils in general.

Standard product ranges are supplemented by a full custom-manufacturing service which allows products to be tailor-made and personalized to specific customer requirements. This applies to HALLCREST's complete catalog of products, from unsealed TLC mixtures through microencapsulated slurries and coatings to finished temperature indicating devices. Experienced personnel are on hand to discuss any aspect of thermochromic liquid crystal. microencapsulation and related technologies, as well as potential applications and optimized manufacturing procedures.

Major market areas include medical industrial cosmetic, promotional research and retail.

A well-equipped research and development laboratory is maintained and the company is engaged in its own ongoing Research and Development programs, aimed specifically at novel applications and new and improved production techniques. Close collaborations and working relationships with customers and suppliers are encouraged whenever possible. Consultative and contract research services are also offered.

2. APPLICATIONS AND THE TECHNOLOGY OF USE AND MANUFACTURE OF TLC PRODUCTS

2.1 Introduction

2.2 The Use of TLCs as Temperature Indicators

2.3 Microencapsulation

2.3.1 Introduction; Application to TLC Mixtures

2.3.2 Microencapsulation Techniques; Classification

2.3.3 Phase Separation Processes; Coacervation

2.3.4 Complex Coacervation

2.3.5 Summary

2.4 Coating Manufacture

2.5 Temperature Indicating Devices

2.5.1 Methods of Manufacture

2.5.2 How to Read TLC Thermometers and Interpret the Color Changes of TLC Temperature Indicators

2.5.3 Special Color Change Effects

2.6 The Use of TLCs and Their Products in Research and Testing Applications

2.7 The Use of TLCs as Raw Materials in Cosmetic Formulations

2.1 INTRODUCTION

Although there are many possible applications for TLC products (see section 1.2), HALLCREST's business can be split into three main areas. This segregation is primarily based on the different end uses of the TLC products in question. The different sales and marketing approaches necessary to develop each business area are also taken into account together with the different forms the products take and the different ways in which they are manufactured. The three business areas are as follows:

a) Temperature Indicating Applications

b) Cosmetic Ingredients

c) Products for Research and Testing

Temperature indicating applications include both temperature indicating devices and temperature-sensitive inks and coatings; cosmetic ingredients include both unsealed and microencapsulated TLC mixtures (and custom-microencapsulated non-TLC oil blends); products for research and testing include unsealed and microencapsulated TLC mixtures, ready-to-use coating formulations and coated polyester sheets.

Each of the three application areas will be discussed in turn, highlighting the technology necessary to produce optimized TLC products for use in each area. Some of the shortcomings of using unsealed TLC mixtures along with the associated importance of the microencapsulation process in the manufacture of accurate and reliable temperature indicators will be emphasized. Microencapsulation processes in general will be described and classified with particular attention being paid to the process called complex coacervation and its successful application to the microencapsulation of TLC mixtures.

2.2 THE USE OF THERMOCHROMIC LIQUID CRYSTALS AS TEMPERATURE INDICATORS

The unique properties of TLCs can only be used to advantage if they can be controlled and the materials made to behave predictably for a given period of time.

The chemicals themselves are essentially oils whether they are cholesteric or chiral nematic in origin, and the consistency of most unsealed TLC mixtures at their working temperatures varies between that of a thinnish oil (like cooking oil) and a viscous paste (like lanolin); they are difficult to use. In addition, films of unsealed TLC are very susceptible to degradation, particularly from UV light. and are also very sensitive to certain organic chemicals, especially fats, greases and common solvents.

In general the degree of stability offered by the materials as the neat. unsealed liquids falls far short of that required for the successful commercial exploitation of their unique properties in the majority of temperature indicating applications. The unsealed TLC liquids must be protected and stabilized if they are to be used successfully in applications requiring any degree of longevity and reproducibility of performance.

2.3 MICROENCAPSULATION

2.3.1 Introduction; Application to TLC Mixtures

To date, the microencapsulation process has been the most versatile, widely applicable and successful way of stabilizing, packaging and protecting TLC mixtures. The liquid crystal is isolated from the atmosphere by a protective barrier and, at the same time, converted into a comparatively easy-to-use form. In simple terms, a microcapsule is a small sphere with a uniform wall around it, and in the microencapsulation process tiny droplets of liquid crystal are surrounded with a continuous polymer coating to give discrete microcapsules. Microcapsule diameters are generally between a few microns and a few millimeters.

In addition to the stabilizing and protection benefits of microencapsulation, there are two additional specific advantages to packaging TLCs in this way:

a) Each individual droplet of liquid crystal is totally encased, inhibiting crystallization of the mixture, and preventing extrusion of the oily, unsealed TLC from coated or printed films

b) Microcapsules of different TLC formulations can be mixed together to produce coatings and films with multiple color plays.

2.3.2 Microencapsulation Techniques; Classification

Many different types of microencapsulation process exist. most of which have been disclosed in the patent literature. The large number of processes, some of which are very similar. and the large number of potential applications make some kind of classification/categorization desirable. Over the years, several different methods of classifying microencapsulation processes have been proposed. We have chosen the method described below, where a major division is based on the medium in which the microencapsulation process takes place.

Type I Processes are those in which a liquid is used as the suspending medium for the microcapsules. One of the key steps is the emulsification/dispersion of two or more immiscible phases.

Type II Processes are those in which a gas is the suspending medium for the microcapsules, where one of the most important steps is the atomization of a liquid phase.

Using this major division as the basis, microencapsulation techniques are classified and listed in table 1 below.

Type I	
Liquid Suspending Media;	**a) Oil-in-Water** **b) Water-in-Oil**
Interfacial Polymerization	
In-Situ Polymerization	
Solvent Evaporation	
Desolvation	
Simple Coacervation	
Complex Coacervation	
Polymer-Polymer Incompatibility	
Gelation	
Pressure Extrusion	
Liposomes and Surfactant Vesicles	

Type II	
Gas Suspending Media;	**a) Solvent** **b) Solvent Free**
Spray Drying/Freezing, etc.	
Fluidized Bed/Air Suspension Coatings	
Pan Coating (Formation)	
Co-extrusion	
Vacuum Coating	
Vapor Deposition	
Electrostatic Processes	
Centrifugal Processes	

Table I: Classification of Microencapsulation Techniques

The listing in table 1 gives an idea of the number and diversity of established, discrete, microencapsulation techniques, although many variations of each of the processes listed also exist. Several less important processes have been omitted and new techniques are continually under development. In addition, the nomenclature used varies from author to author and different names are used for the same techniques. All of this leads to some confusion, especially on the part of those trying to learn about microencapsulation for the first time, and further reading is strongly recommended for those who have an interest.

A number of reviews and books on microencapsulation have been published over the years, details of some of which are given in the bibliography at the end of this booklet.

2.3.3 Phase Separation Processes; Coacervation

Some methods of classifying microencapsulation techniques refer to **Phase Separation** as a distinct type. Phase separation processes are characterized by the initial suspension of the core material in a solution of the wall polymer(s). The wall material is then induced to separate as a liquid phase. This can be achieved by a number of different methods, either individually or in combination, including, for example, (i) the addition of a non-solvent for the wall polymer; (ii) decreasing the temperature, or (iii) adding another polymer that has a higher solubility in the solvent. In (iii). incompatibility between the polymers causes the first polymer to separate as another phase and the process is called **Polymer-Polymer Incompatibility** (see table 1). This is one of the two major phase separation microencapsulation processes; the other is **Coacervation**. When the wall polymer separates as a polymer-rich liquid phase, this phase is called a **Coacervate** and the process is called **Coacervation**. The term coacervation was first used the two Dutch scientists, Bungenberg de Jong and Kruyt. in 1930 [1], who derived the word from the Latin *acervus*. meaning heap. As the coacervate forms, it should ideally wet the suspended core particles/droplets and coalesce to form a continuous coating around each one individually. It is important that the core is not soluble in the wall polymer solvent and that the wall polymer itself does not partition strongly into the liquid core. The microcapsules must eventually be hardened and isolated. A schematic representation of microencapsulation by coacervation is shown in figure 2.

[1] H. G. Bungenberg de Jong and H. R. Kruyt. Kolloid-Z ., **50**.39 (1930)

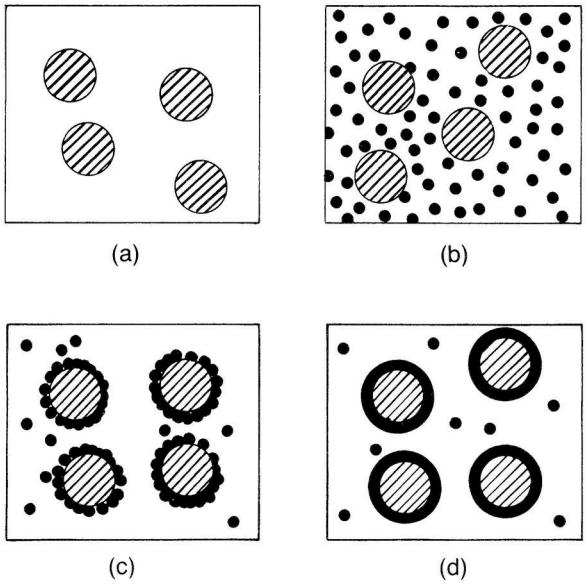


Figure 2: Schematic representation of microencapsulation by coacervation; (a) Dispersed droplets of core material in solution of wall polymer(s); (b) Beginning of coacervation – separation of microdroplets of coacervate from solution; (c) Gradual coating of core material droplets by microdroplets of coacervate; (d) Coalescence of coacervate to form continuous coating/wall around each droplet of core material.

2.3.4 Complex Coacervation

Coacervation takes place in dispersions/ solutions of hydrophilic colloids in water or aqueous solutions. The colloids can be either natural or synthetic.

Coacervates can be divided into 2 types; simple and complex. The major difference is the presence of a second (or third) colloid in complex coacervation systems.

The first commercially valuable microencapsulation process was based on complex coacervation and was developed by NCR Corporation for carbonless copy paper in the 1950s [2]. The coacervate was formed from the reaction product complex between gelatin and gum arabic. The largest market for microencapsulated products is still in carbonless copy applications.

Complex coacervation processes work well in the microencapsulation of water insoluble solids and oily liquids and are thus ideally suited for the microencapsulation of liquid crystal mixtures. Applied to TLC mixtures in general the complex coacervation process involves the addition of gelatin and gum arabic to a suspension of the liquid crystal in water at a certain pH at an elevated temperature (above 35°C (95°F)). The reaction vessel is maintained under constant agitation, which ensures that the TLC micro droplets are kept separate and minimizes agglomeration. The agitation can also be used to set (and maintain) particle size distribution. As the temperature is reduced and the pH is changed, the gelatin and gum arabic react to form a complex and viscous liquid micro droplets of polymer coacervate separate. (In the absence of the liquid crystal this is visible as a clouding of the previously almost clear sol.) As the coacervation continues, the fine coacervate micro droplets coalesce into larger ones and eventually wrap around the suspended TLC micro droplets to form a continuous wall of liquid coacervate around each individual TLC microsphere. Almost all the wall polymer in solution separates as a coherent coacervate phase and forms the microcapsule walls in this way. Finally, the mixture is rapidly cooled and the wall is hardened. A variety of physical and/or chemical methods can be used for hardening the wall. Precise control of the pH, temperature, agitation and dilution are important for optimized and reproducible results. Complex coacervation processes are discussed in detail in the references on microencapsulation listed in the bibliography at the end of this booklet. Additional information is also available from HALLCREST. Further reading is recommended for those who have an interest.

2.3.5 Summary

A large number of microencapsulation techniques are now available and new ones are continually under development. Most established techniques also have seemingly endless variations and it is possible that new or improved techniques will be applied successfully to the microencapsulation of TLC mixtures in the future. However, for the moment, complex coacervation systems still afford the best means of microencapsulating TLCs, whether they are chiral nematic, cholesteric or combination mixtures.

[2] B. K. Green. US Patent 2800458 (1953)
B. K. Green and L. Schleicher. US Patent 2800457 (1953)

In the manufacture of temperature indicating devices using established methods, microencapsulated TLC mixtures offer much improved stability and versatility over their unsealed precursors. The materials are, to a certain extent, both isolated from the deleterious effects of the atmosphere and UV light and protected from solvents and other harmful chemicals to which they would otherwise be directly exposed. The microencapsulation process has played an important part in the development of the markets for TLCs and their products.

2.4 COATING MANUFACTURE

The product of the microencapsulation process is an **Aqueous Slurry** of discrete TLC containing microcapsules. In this form, TLCs are essentially temperature-sensitive pigments, for incorporation into water-based coating formulations. The coatings can be optimized for application to a variety of surfaces by a number of different techniques. An optimized coating, when dry, should ideally support the liquid crystal in a uniform film with the minimum degradative effect on the intensity and purity of the selectively reflected light. Such coatings form the basis of HALLCREST's product range.

In addition to the manufacture of all of its own coatings for device manufacture and internal use, HALLCREST produces a full range of ready-to-use coatings for resale. Microencapsulated TLC slurries for coating manufacture are also available. Full details are given on the relevant data sheets.

2.5 TEMPERATURE INDICATING DEVICES

2.5.1 Methods of Manufacture

TLCs have been used in many temperature indicating applications. The majority of thermo chromic devices contain a thin film of the liquid crystal sandwiched between a transparent polymer substrate (sheet) and a black absorbing background. The standard method of producing such devices, which has evolved since the early 1970s, has been to produce a coating (ink) containing preferably microencapsulated TLC, and use a printing method to apply it to the supporting substrate. A black ink is then applied on top of the dry TLC coating, and color change effects are viewed from the reverse (uncoated) side of the sheet.

TLC inks and coatings can also be applied to the top surface of a variety of dark (preferably black) substrates. The substrate can be printed/painted with black (dark) areas before application of the TLC coating. In applications where the TLC has been front-face printed or coated, there is always the need for a clear overcoat or lacquer to be applied on top of the dry TLC coating. This clear overcoat should ideally exhibit strong UV absorbing properties; it also imparts additional abrasion resistance.

Recent technical advances in a number of different areas have resulted in Significant improvements in the quality, performance and longevity of front-face printed TLC temperature indicating products. The market for these types of products, particularly paper labels/stickers of one sort or another, is developing quickly.

2.5.2 How to Read TLC Thermometers and Interpret the Color Changes of TLC Temperature Indicators

2.5.2.1 Conventional Color Changes

The color change properties of unsealed temperature-sensitive TLC mixtures are described in section 1.1.3 earlier in this booklet. When the materials are microencapsulated, incorporated into coatings and printed, the colors reflected by the dried coating are modified slightly. These changes are only minor and arise as a result of the modification of the light as it passes through both the microcapsule wall and the polymer supporting the TLC micro-capsules in the thin dried film. Three colors predominate, a brownish red (tan) at low temperatures, changing to green and finally to blue as the temperature increases (all colors are again visualized against black backgrounds). The other colors seen in thin films of unsealed TLC mixtures are still visible on close inspection, but are far less pronounced.

2.5.2.2 Accurate TLC Thermometers

TLC thermometers/temperature indicators are usually comprised of a series of liquid crystal 'events', which change color in sequence as the temperature changes. Behind or adjacent to each number (temperature) on the TLC thermometer is an 'active' area coated with a precisely calibrated TLC mixture designed to change color at the temperature in question. For a given temperature event, a green color shows the exact temperature, a blue color shows the actual temperature is higher than indicated and a tan/brown color shows the actual temperature is lower than that indicated. If two consecutive events show colors simultaneously, one blue (the lower temperature of the two) and the other tan, the correct temperature is between the two. No two events should ever show green at the same time (temperature).

2.5.2.3 General Temperature Indicators

TLC temperature indicators do not necessarily have to take the form of an accurate 'thermometer'. Many different types of product can be made, some with just a single TLC event, some with many, and in a variety of shapes and sizes and not necessarily in the form of a strip, the most common shape for an accurate multi-event TLC temperature indicator. The 'active' TLC color change area can be printed in a variety of different shapes in addition to circles, squares or the numbers themselves, as is usual with strip thermometers. For example, symbols or messages can be made to appear/disappear at predetermined temperatures.

As indicated above in section 2.5.2.2, when a series of TLC events are included on the same product and accurate temperature indication is required, the green color (in the middle of the visible spectrum) is most commonly used to indicate the exact or correct temperature, in preference to any other color that may be visible.

2.5.3 Special Color Change Effects

The tan/red-green-blue color changes described previously refer to those seen in products using unadulterated, conventional, temperature-sensitive TLC mixtures. A variety of special, customized color-change effects can also be achieved. A number of methods are available and include the following:

a) Addition of dyes to conventional temperature-sensitive TLC mixtures and coatings containing them. This can be used to augment the traditionally weaker reflected colors (reds, oranges, yellows).

b) Using colored rather than colorless transparent polyester as the substrate. This produces, in effect, single color change products with properties similar to those that would be achieved by printing onto a colored light filter.

c) Using colored/dyed overcoats/varnishes, producing effects similar to b), above.

d) Over-printing 2 (or more) different TLC coatings on the same area to produce 'double (multi) color play' events. The red starts of the higher temperature TLC mixtures overlap with the blue tails of the lower temperature mixtures to produce additional unique color change effects.

e) Using temperature-insensitive TLC mixtures (see section 1.1.2) to produce single color change products. The usual (highest contrast) color change is green to black (against a black background) as the temperature is increased. Reversible and hysteretic (memory) TLC mixtures can be used.

The above list is intended as a guide to give an idea of some of the different ways in which the color change properties of TLC temperature indicators may be modified. Many possibilities exist, including those listed above, individually and in combination. These modifications extend the number of potential applications for the materials by increasing the options available.

2.6 THE USE OF TLCs AND THEIR PRODUCTS IN RESEARCH AND TESTING APPLICATIONS

The use of TLCs in engineering and aerospace research has become increasingly widespread during recent years. The main areas of application are currently in heat transfer and flow visualization studies, although the materials can also be used in virtually any work involving the indication of temperature fields and thermal mapping.

Following the increased publicity given to TLC products in the scientific literature by the engineering/aerospace research community, interest in the use of the materials in more general NDT and related applications has also been rekindled. The areas of research and testing where TLC products have established themselves and the products offered by HALLCREST most commonly used in each area are listed below:

a) **Heat Transfer Measurements**, and

b) **General NDT and Thermal Mapping** (in air or water)
- coated polyester sheets containing microencapsulated TLC mixtures; with, or without, adhesive-backing
- sprayable coatings containing microencapsulated chiral nematic and combination TLC mixtures
- sprayable black backing paints

c) **Flow Visualization Studies in Fluids**
- microencapsulated TLC slurries for use as tracer particles; chiral nematic, cholesteric or combination mixtures; microcapsule diameter and buoyancy characteristics can be controlled within limits
- unsealed chiral nematic and combination TLC liquids; can be emulsified directly in carrier fluid

d) **Flow Visualization Studies on Solid Surfaces**
- shear-sensitive, unsealed TLC mixtures; chiral nematic, cholesteric and combination
- sprayable black backing paints

A series of introductory kits is also available. Complete product and background information, including reviews of the published patent and scientific literature, are available on a series of data sheets dedicated to this application area.

2.7 THE USE OF TLCs AS RAW MATERIALS IN COSMETIC FORMULATIONS

Following the introduction of the first cosmetic product to contain an unsealed TLC mixture at the beginning of 1987 and its subsequent successful sales performance, the use of TLC mixtures as raw materials in the formulation of cosmetic products has become well established. Many products containing the materials have been developed and commercialized with varying degrees of success.

The initial application of TLCs to cosmetic formulations was in skin repair products, where strands of unsealed temperature- insensitive TLC mixtures were suspended in clear, water-based gels. The TLC strands gave these products their characteristic opalescent/ iridescent appearance. Other unique properties based on the chemistry and physics of TLCs have also been claimed.

As indicated above, in cosmetic applications, it is the bulk appearance of TLC mixtures, rather than their thin film light- reflecting properties, that is of most importance. Their characteristic opalescent/ mother-of-pearl appearance (caused predominantly by interference effects - see section 1.1.2) is unique and is probably the most significant factor behind the materials being used in this application area initially.

These attractive bulk light-reflecting properties of unsealed TLC mixtures have been extended to the microencapsulated form by modifying HALLCREST's existing microencapsulation technology to enable 'large' microcapsules with diameters up to 2000-3000 microns (2-3 mm) to be made. (This compares with microcapsule diameter distributions with means in the range 10-30 microns for normal use in the manufacture of temperature indicating devices.)

This custom-manufacture of microcapsules with 'large' diameters has been applied successfully to oily materials in general and HALLCREST also offers a full custom- microencapsulation service for oils/oil blends for cosmetic applications. In summary, considerable potential exists for the use of TLCs in the cosmetics industry, whether the materials are:

- temperature-insensitive or temperature-sensitive
- cholesteric, chiral nematic or combination
- unsealed, or in the microencapsulated form
- purely decorative or functional

Add to this the further potential offered by the application of the microencapsulation process to the packaging of custom-formulated oil blends, coupled with the versatility offered by the convenience of a complete custom-manufacturing service and it can be appreciated that the full range of HALLCREST products available to the cosmetic chemist affords a number of unique formulating opportunities.

Full details are available in a series of data and information sheets.

3. LIQUID CRYSTALS; THE CHEMISTRY AND PHYSICS OF THE CHOLESTERIC MESOPHASE

3.1 Introduction

3.2 The Liquid Crystalline State

- 3.2.1 Introduction
- 3.2.2 Brief History

3.3 Classification of Liquid Crystals

- 3.3.1 Introduction
- 3.3.2 Lyotropic and Thermotropic
- 3.3.3 Smectic. Nematic and Cholesteric

3.4 Structure of the Cholesteric Mesophase

- 3.4.1 Introduction
- 3.4.2 Right-handed and Left-handed Materials
- 3.4.3 Compensated Mixtures
- 3.4.4 Textures
- 3.4.5 Phase Transitions

3.5 Optical Properties of the Cholesteric Mesophase in its Planar Texture

- 3.5.1 Introduction
- 3.5.2 Birefringence
- 3.5.3 Optical Activity
- 3.5.4 Circular Dichroism
- 3.5.5 Bragg Scattering
- 3.5.6 The Modification of White Light as it Passes Through the Cholesteric Planar Texture; The Reflection of Bright Colors Which Change With Temperature

3.6 Control of the Color Change Properties of TLC Mixtures; Principles of Mixture Formulation

3.1 INTRODUCTION

The final part of this booklet is devoted to the science - the chemistry and physics - behind cholesteric liquid crystals. The liquid crystalline state is introduced and defined, with particular reference to the thermotropic class of materials. A brief history of thermotropic liquid crystals is given, going back to their discovery in the late nineteenth century and covering the most important technical and commercial advances over the last 100 plus years. An overview of the development of the present day industries based on both the electro-optic and thermo chromic applications of liquid crystals is also included. Emphasis is biased in favor of cholesteric liquid crystals throughout.

Liquid crystals are then classified, initially into lyotropic and thermotropic types and again into smectic, nematic and cholesteric structures. The cholesteric liquid crystalline state is discussed in some detail beginning with the structure of the mesophase itself and its various modifications and going on to cover the characteristic optical properties of the mesophase, leading to a description of how a beam of unpolarized white light is modified as it passes through the cholesteric planar texture.

Finally, for those who persevere, there is the reward of a discussion of the chemistry and physics of TLC mixture formulation describing some of the ways in which the color change properties of TLC mixtures can be controlled.

As a footnote it should be pointed out that the term "liquid crystal" used throughout this booklet refers solely to monomeric materials, and although the adjective "monomeric" has been omitted, its presence is implied. Polymeric liquid crystals also exist, and although the materials are the subject of much interest, both technically and commercially, the science and technology of liquid crystal polymers is not relevant here and is not discussed.

3.2 THE LIQUID CRYSTALLINE STATE

3.2.1 Introduction

Matter conventionally exists in three forms - solid, liquid and gas. Solids may be either crystalline or amorphous. THE LIQUID CRYSTALLINE (OR MESOMORPHIC) STATE IS INTERMEDIATE BETWEEN THAT OF A CRYSTALLINE SOLID AND AN ISOTROPIC LIQUID.

When a crystalline solid (with long range three-dimensional molecular order) is heated, it transforms, at its melting point into an isotropic liquid (with no long range molecular order), and, on cooling, the isotropic liquid reverts back to a crystalline solid. However, there are certain substances (generally organic in nature) which do not pass directly from a crystalline solid to an isotropic liquid, and vice versa. These materials adopt an intermediate structure with associated molecular order less than that of the crystalline state, but more than that of an isotropic liquid. They possess the mechanical properties of liquids (fluidity, surface tension) and the optical properties of crystalline solids (anisotropy to light birefringence) and are called LIQUID CRYSTALS. Other names commonly used for the materials are mesomorphs, rnesophcses. mesomorphic phases (mesomorphic - of intermediate form) and mesogens.

Although liquid crystals exhibit certain aspects of both the solid and liquid phases, the materials also possess their own unique properties that are not found in either solids or liquids individually. For example, their ordering properties can be controlled by electric and magnetic fields; some have optical activity of a magnitude without parallel in any solid, liquid or gas, and some change color as a result of the sensitivity of their structure to temperature. These unusual properties are the bases for practical applications, and of particular interest here are the color change and light-modifying properties of thermochromic (cholesteric) liquid crystals.

3.2.2 Brief History

Liquid crystals were discovered at the end of the nineteenth century. At the time, there was a protracted and often acrimonious debate concerning the right of discovery and relative claims of priority. However, both Otto Lehmann, a German physicist. and Freidrich Reinitzer, an Austrian botanist contributed considerable amounts of knowledge and each deserves recognition.

The initial observation and discovery of the liquid crystalline state is usually attributed to Reinitzer in 1888, although scientific papers written earlier in the nineteenth century describe materials with properties now know to be liquid crystalline. Reinitzer [1] prepared a number of esters of cholesterol in which he observed a new and unusual melting phenomenon of the compounds he studied. The most quoted example is cholesteryl benzoate, which appeared to have two melting points; the white crystalline solid melted sharply at 145°C, but the melt was definitely opaque; on further heating the opacity disappeared, again sharply, to give a clear liquid at 179°C. The original use of the term "liquid crystal" is credited to Lehmann. In his many publications of the time, Lehmann used terms like *Fliessende Krystalle* (flowing crystals) and *Flussige Krystalle* (fluid crystals) to describe the unusual phase that existed between the two melting points of not only cholesteryl benzoate, but also a large number of other compounds he studied. The term "flowing crystals" was used for the first time by Lehmann in 1889, "crystalline liquid" in 1890 and "liquid crystal" appeared for the first time in 1900[2]. The traditional use of this terminology has continued primarily because it has not been universally accepted that anything more suitable has been proposed, although there have been heated discussions on the subject over the years. There might also be some truth in the argument that the persistent use of this nomenclature may well originate from the inherent attraction in using the apparently contradictory terms liquid and crystal together.

[1] F. Reinitzer, Monatsh ., **9**, 421 (1888)

[2] 0. Lehmann, Verhandl. d. Deutschen Phys. Ges ., sitzung v. 16.3.1900. p.1 ,

For a long time after their initial discovery, interest in liquid crystals remained relatively low as no commercial applications for the materials were immediately apparent. In addition, the initial descriptive observations of Lehmann, Reinitzer and others were not fully understood, and it was not until Georges Friedel published his pioneering work *Les Etats Mesomorphes de la Matière* in 1922[3] that most questions could be answered with some certainty. The importance of Friedel's work cannot be understated. The accepted present-day classification and nomenclature of liquid crystals is based almost entirely on Friedel's observations with the polarizing microscope and the associated publications which span the first three decades of the twentieth century. Historically, the most important of Friedel's publications is the one referred to above, which introduces and defines the terms used today to describe the liquid crystalline state: smectic. nematic and cholesteric (see section 3.3.3). On the subject of nomenclature, it should be noted that Friedel was one of the principal opponents of the use of the term "liquid crystal" and preferred instead the term "mesophase" (derived from the Greek *mesos* meaning intermediate), arguing that the opaque melt was neither truly crystalline, nor truly liquid.

Following the lead set by Friedel, some progress was made and by the early 1930s liquid crystal research reached a level it was not to exceed for another 30 years. The next decade or so saw interest fall, with only a few researchers continuing to study the materials.

All of the properties of liquid crystals that are now used for applications were first observed by Lehmann around the turn of the century, however, it was not until the 1950s that attempts were made to apply liquid crystals for the first time. The first of these applications was the use of cholesteric liquid crystals to measure thermal patterns.

During the early and mid 1950s the work of George Gray at the University of Hull in England encouraged a number of other researchers around the world, and by the late 1950s enough further work had been done for liquid crystals to be the subject of a Faraday Society discussion (1958), and for the now well known article by Brown and Shaw to be published in *Chemical Reviews*[4]. This period of increased research effort included some important advances at Freiburg in Germany where liquid crystal research had been conducted since the 1920s. By the late 1950s, the revival of experimental interest in the materials was well established, and Westinghouse Corporation set up a research program, led by J.L. Fergason, centered initially around an investigation of the color change properties of cholesteric liquid crystals. An important turning point had been reached.

Since then, research and development efforts on liquid crystals, their properties and applications, has increased rapidly. George Gray's book Molecular structure and the Properties of Liquid Crystals was published in 1962 and the Liquid Crystal Institute at Kent State University was founded by Glenn H. Brown in 1965. Initial interest during the 1960s followed the lead set by Westinghouse, and concentrated mainly on cholesteric liquid crystals and their thermo chromic properties.

By the late 1960s, interest in nematic liquid crystals began to increase. The invention of the Twisted-Nematic (TN) display device and a series of breakthroughs on the materials side in the early 1970s led to the birth of the international display industry, based on the electro-optic properties of nematic liquid crystals. This industry grew significantly, both technically and commercially, during the late 1970s and early 1980s, and continues to grow rapidly today. New and improved display technologies are continually being developed and now include the use of smectic liquid crystal mixtures in complex, high information content displays. Liquid crystal-based electro-optic displays are now the subject of extensive worldwide research and development effort, and only displays based on cathode-ray tubes currently have a larger share of the international display market. Novel applications for electro-optic liquid crystals currently under development could greatly increase the world market for raw materials over the next few years if commercialized successfully.

[3] G. Friedel. Ann. Phys. (Paris), **18**. 273 (1922)

[4] G. H. Brown and W. G. Shaw. Chem. Rev., **57**. 1049 (1957)

Cholesteric liquid crystals were first used commercially in reasonable volume in the early 1970s, where the market for the materials was initially almost solely dependent on the use of cholesterol derivatives in the manufacture of temperature indicating devices.

This market was subject to a number of up and down cycles during the 1970s and early 1980s, but remained at a comparatively low level compared to the booming market for electro-optic liquid crystals. This was primarily due to the fact that a number of promising potential large volume applications for the materials failed to materialize for a variety of reasons, some of which were technical. These technical shortcomings related either to the properties of the cholesterol derivatives themselves or to the technology of how the materials had to be used.

The commercial introduction of the first non-sterol related cholesteric liquid crystals in 1982 offered the established industry a wide range of new opportunities. The availability of new raw materials with different chemical and physical properties allowed a number of Significant advances to be made in the technology of device manufacture and also enabled some of the potential applications which had not been realizable with cholesterol derivatives to be resurrected and successfully commercialized. A period of learning covering several years passed during which time the properties of the new raw materials were fully evaluated and modifications made to the manufacturing processes necessary for their optimized use. The increased interest in research and development prompted by the availability of new raw materials had a spill-over effect onto the cholesterol derivatives and the properties of cholesteric liquid crystals in general were evaluated in a new light. A number of new application areas for both types of raw materials have subsequently been developed. Since 1986 major new markets have arisen in the cosmetics area (for both sterol and non-sterol derived materials, individually and in combination) and in the large volume production of thermo chromic printing inks (initially for non-sterol derivatives). Considerable commercial potential also exists for TLC mixtures containing both sterol and non- sterol materials together in the same formulation, and the first sales have already been made. In the future, the use of these "combination" mixtures is likely to lead to the successful commercialization of a number of new application areas as the respective advantages of both major groups of raw materials can be combined in one formulation. Demand for both sterol and non-sterol derived raw materials has grown dramatically since 1987 and is expected to continue to do so, at an ever increasing rate, for the foreseeable future.

From their comparatively humble beginnings as little more than chemical curiosities, liquid crystals, in one form or another, now feature in the everyday lives of most people; in the numerical and information displays of watches, calculators, lap-top computers and other electronic instruments; as the color change chemicals in digital thermometers, battery testers and a variety of other temperature indicators, promotional and novelty products; as the eye-catching iridescent strands, swirls and droplets in skin care and other cosmetic products.

Following the dramatic increase in the number of consumer products utilizing liquid crystal technology reaching the market over the last few years, present day predictions suggest that liquid crystals are likely to play an ever-increasing role in our day-to-day lives in the future. Thermochromic liquid crystal products may well lead the way.

3.3 CLASSIFICATION OF LIQUID CRYSTALS

3.3.1 Introduction

Many different types of liquid crystal exist. A major division arises as a result of the two different ways in which the molecular order of the parent solid can be broken down. These two main classes can then be subdivided into a number of additional distinct types on the bases of their different structures and properties.

THERMOCHROMIC LIQUID CRYSTALS, AS DESCRIBED IN THIS BOOKLET AND AS SUPPLIED BY HALLCREST, ARE THERMOTROPIC IN ORIGIN AND HAVE CHIRAL (TWISTED) STRUCTURES

3.3.2 Lyotropic and Thermotropic

Liquid crystals can be divided into two main classes according to the principal means of breaking down the complete molecular order of the parent solid. This is the major division among liquid crystals; the two types are called **Lyotropic** and **Thermotropic**.

Lyotropic liquid crystals result from the action of a solvent. When certain compounds are treated with a solvent. a true solution is not obtained and the resulting state possesses characteristics of the liquid crystalline phase. Lyotropic mesophases can be destroyed or converted into isotropic liquids by an excess of solvent or by heating to sufficiently high temperatures. Soaps, various detergents and polypeptides are materials that form lyotropic liquid crystals. These materials are more important from a biological viewpoint. and will not be discussed here.

Thermotropic liquid crystals are thermally activated mesophases and result from the melting of mesogenic (liquid crystal forming) solids by heating the materials to a temperature above which the crystalline lattice is no longer stable.

This class is further subdivided into **enantiotropic** and **monotropic** types. The enantiotropic type is formed by either heating the crystalline solid or by cooling the isotropic liquid, and has a definite temperature range of stability as the transitions occur at the same temperatures on both heating and cooling. The monotropic mesophase is not stable with respect to the solid, and can be obtained only by supercooling the isotropic liquid. The temperature at which the isotropic liquid becomes liquid crystalline is reproducible. An example is given in figure 3.

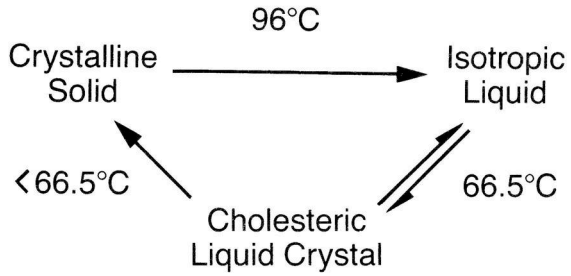


Figure 3: Phase transitions of cholesterol chloride showing existence of monotropic mesophase.

At the melting point of a material with enantiotropic liquid crystalline properties, the thermal energy is not enough to convert the crystalline solid to a completely disordered state. There is sufficient residual attraction between the constituent molecules to maintain an ordered state. With a further increase in temperature, the liquid crystal is converted to the isotropic liquid. This conversion from crystalline solid to isotropic liquid through the liquid crystal phase may be viewed as stepwise melting.

3.3.3 Smectic, Nematic and Cholesteric (Chiral Nematic)

The following classification is usually applied to thermotropic liquid crystals. However, analogues of the smectic. nematic and cholesteric do exist in lyotropic mesophases along with a number of other structures. Thermotropic systems only will be discussed here.

Thermotropic liquid crystals can be further classified according to either their optical properties or their structures. Three distinct types can be distinguished from their differing optical properties and have historically been called **Smectic, Nematic** and **Cholesteric**. From a structural viewpoint however, it can be argued that there are only two basic types of liquid crystal **Smectic** and **Nematic**. Cholesteric liquid crystals, although optically unique, have physical properties which make it necessary to classify them thermodynamically as nematic. Thus, strictly speaking, cholesteric liquid crystals are a special type of nematic. The distinction between smectic and nematic is based on the extent and nature of the residual molecular ordering. Molecules that form liquid crystal phases are generally elongated and relatively rigid, somewhat similar in shape to cigars. Discotic (disc-like) liquid crystalline structures also exist and are comprised of large plate-like molecules; these are much less common. Discussion here is limited to long, thin, cigar-shaped molecules.

Smectic mesophases are characterized not only by the long axes of the molecules being parallel but also by a layering of the molecular centers of gravity in two-dimensional planes or sheets; the molecular centers of gravity are mobile in two directions and a characteristic layered structure results (see figure 4). The arrangement shown in figure 4 is only one of more than 10 different smectic phases identified to date. The smectic mesophase is the most solid-like of the liquid crystal modifications.

In the **Nematic** phase, the degree of randomness of the molecules is greater than in smectics. The long axes again remain substantially parallel but the centers of gravity are mobile in three directions (rather than two), and no discrete molecular layers can be identified (see figure 5). The average molecular direction is defined by a unit director.

The separate classification of **Cholesterics** or **Chiral Nematics** derives in principle from the unusual optical properties of the structure, which were also originally responsible for the discovery of the liquid crystalline state in 1888.

The materials are extremely optically active (they rotate the plane of linearly polarized light), much more so than can be accounted for on the basis of the constituent molecules alone, and they have a natural twisted structure. Within the nematic phase, it is thus necessary to differentiate between twisted (cholesteric or chiral nematic) and non-twisted (usually referred to as simply nematic) structures. This classification of a cholesteric as a special type of nematic is also discussed earlier.

When an optically-active material forms a nematic phase, the preferred direction of the long axes of the molecules (the molecular director) in a uniformly oriented sample is not constant as it would be in a regular (non- optically active) nematic. Passing through the sample in the direction of the optic axis (at right angles to the long molecular axes), the molecular director displays a continuous twist from one layer of molecules to the next. Within each plane molecular layer, the parallel alignment of the molecules is like that of a nematic. However, in order to spatially accommodate the functional (side) groups which extend out of the plane of the essentially flat constituent molecules, each layer must be slightly twisted with respect to those adjacent to it. The effect is cumulative and an overall helicoidal architecture results (see figure 6). On a larger scale, the molecular director traces out a helix in space. This is better shown in figure 7, which gives a different view of the twisted cholesteric structure. Because of this twist encumbrance, cholesterics/chiral nematics are generally more viscous than nematics, but are still more mobile than smectics.

The first compounds to exhibit these properties, in fact the first recognized liquid crystalline materials, were derivatives of cholesterol and the mesophase has historically been called **Cholesteric**. However, this can be misleading as many optically-active chemicals and mixtures containing them, which are not related to cholesterol or other sterols, also show the cholesteric liquid crystal structure. During the late 1980s, the use of these non-sterol related chemicals increased dramatically, and the once-cholesteryl ester dominated industry , has changed considerably from the raw materials viewpoint in recent years. For a complete understanding of the technology surrounding the present -day use of cholesteric liquid crystals, it is now more important than ever to differentiate non- sterol related materials from those derived from sterols. Although the mechanism by which the two types of materials reflect light and change color is the same, they exhibit different chemical and physical properties and can be used in different ways to achieve different effects. Each class offers relative advantages and disadvantages in respect of different applications and manufacturing methods. The non-sterol related cholesterics will be referred to as **Chiral Nematics**, a term that was first used in 19731. This differentiation of cholesterics. chiral nematics and mixtures of the two (called **Combination** mixtures) is discussed in more detail at the beginning of this booklet (see section 1.1.1).

A schematic representation of the classification of liquid crystals is shown in figure 8.

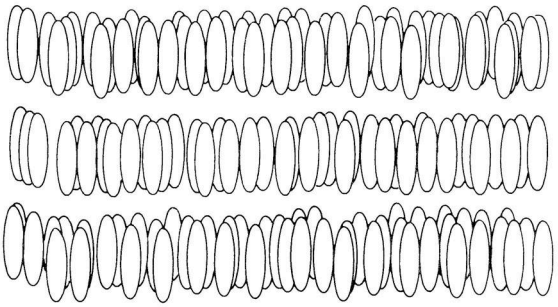


Figure 4: The smectic liquid crystal structure.

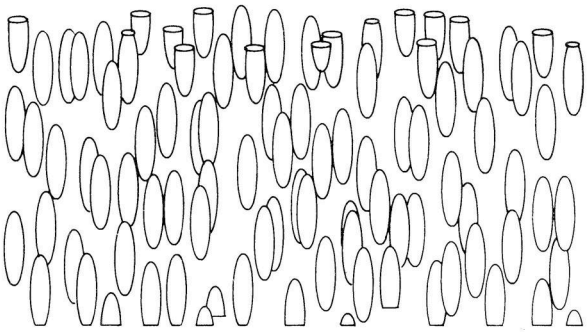


Figure 5: The nematic liquid crystal structure

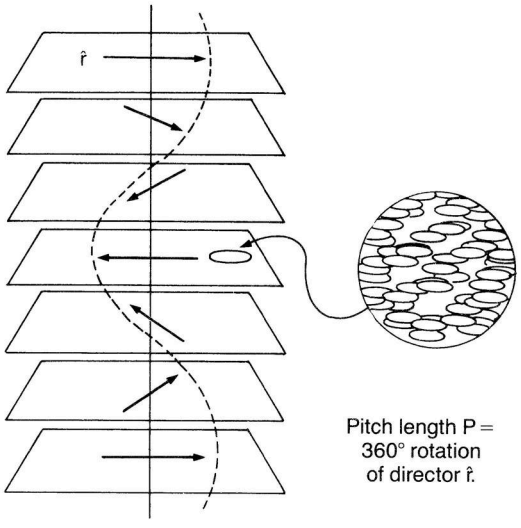


Figure 6: The cholesteric (chiral nematic) liquid crystal structure. The director (arrow) traces out a helical path within the medium.

As a footnote, it should be mentioned that twisted, tilted smectics also exist and behave optically as cholesterics. These phases are known as **Chiral Smectics** and they can also be used in the formulation of TLC mixtures, although their use, to date, has been rare

In this booklet and other HALLCREST technical information the term **Cholesteric** will normally be used to describe the mesophase. **Chiral Nematic** and **Combination** will be used only in relation to the chemical composition of TLC mixtures. **Cholesteric** may also be used to describe TLC mixtures containing only sterol derivatives, but in these instances every effort will be made to qualify its use

[1] D. Dolphin. Z. Muljiani. J. Cheng and R. B. Meyer J. Chem. Phys., **58.** 413 (1973)

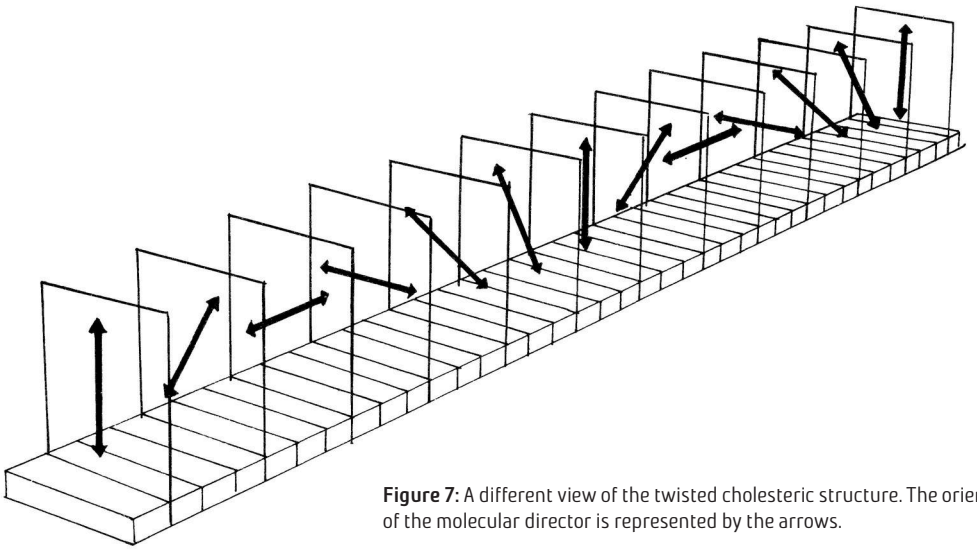


Figure 7: A different view of the twisted cholesteric structure. The orientation of the molecular director is represented by the arrows.

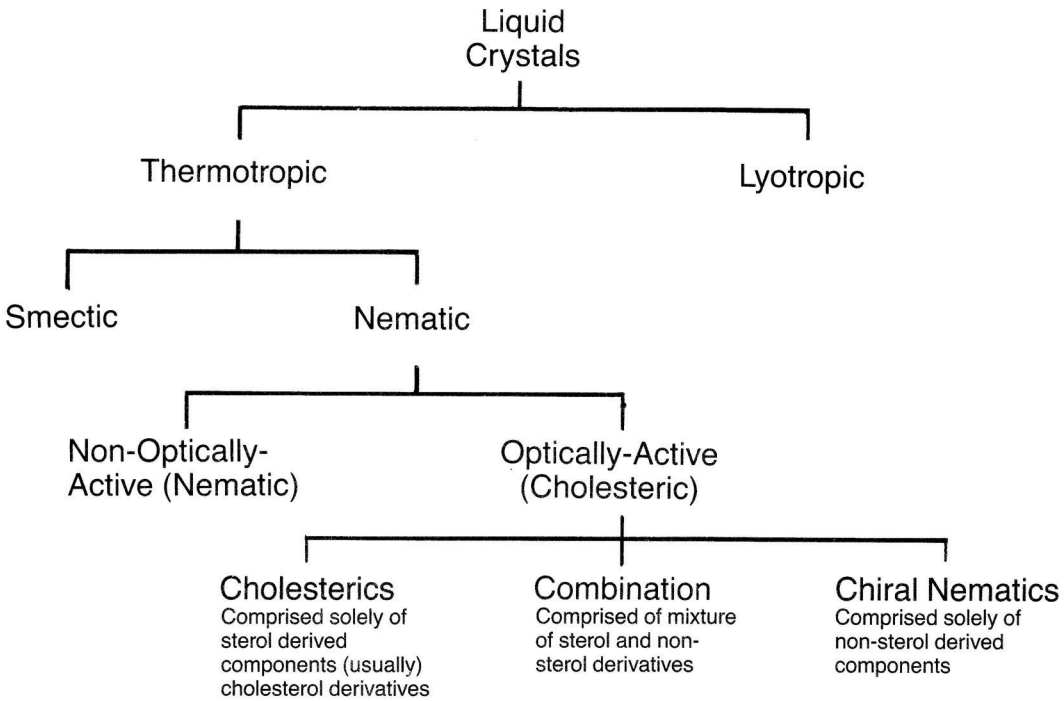


Figure 8: Schematic representation of the classification of liquid crystals.

3.4 STRUCTURE OF THE CHOLESTERIC MESOPHASE

3.4.1 Introduction

Cholesteric mesophases are comprised of helical aggregates of molecules. The longitudinal dimensions (along the axis of the helix) of these aggregates are of the order of the wavelength of visible light. Such structures may be envisaged as being comprised of sheets of molecules (see figure 6). Within each sheet, the molecules behave as in the nematic phase and have an average direction defined by a unit director, 1'. To quantify the degree of twist, the parameter 'pitch length: P. of the helix is defined by convention as the longitudinal distance through which this director has to pass to make one complete 3600 revolution. (Using this concept of 'pitch', a nematic can, in effect, be viewed as being the same as a cholesteric with infinite pitch.) Thus, each molecule is skewed at some angle, e, with respect to its neighbors in the adjacent sheets, immediately above and below. This angle is called the 'displacement angle'. Two such helical arrangements are possible, right-handed and left-handed (see figure 9). In a given cholesteric composition, one will have a lower energy than the other, and form in preference. The helix sense is defined by examining the sense of the circle described by a given end of the molecule in a direction toward the observer.

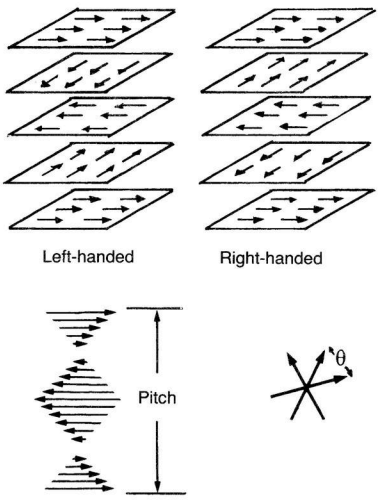


Figure 9: Left and right-handed helical structures showing pitch. P. and displacement angle. a.

3.4.2 Right-handed and Left-handed Materials

Cholesteric mesophases are labeled as being right-handed (RH; dextro) or left- handed (LH; laevo) on the basis of the sense of reflected light. Since the helices transmit light of the same sense of rotation as the helix itself (i.e., a helix which rotates to the right will not affect right circularly polarized light, but will reflect left circularly polarized light), a cholesteric mesophase with a right handed helix is defined as left-handed because it reflects left circularly polarized light.

According to this definition, most cholesteryl esters are right-handed, but cholesteryl halides are left-handed. The chiral nematic formulations supplied by HALLCREST are left-handed. Combination mixtures can be made to reflect either right or left circularly polarized light by varying their composition. Further control of the properties of combination mixtures is afforded by 'compensation effects' which can be used to varying extents (see next section).

3.4.3 Compensated Mixtures

Compensated cholesteric mixtures result when right and left-handed compounds or mixtures of compounds are combined to produce a mixture with no net handedness (i.e. infinite pitch) at a given temperature. At this temperature, the mixture behaves optically as a nematic. However. above and below the temperature in question, the mixture exhibits cholesteric behavior of opposite handedness. This situation is similar to that which exists in racemic compounds where a 1: 1 mixture of two enantiomers (non-superimposable mirror image stereo isomers) possesses no net optical activity and the individual enantiomers possess equal but opposite-signed optical activity. The principle of compensation is important in TLC mixture formation which is discussed in some detail in section 3.6.

3.4.4 Textures

Cholesteric mesophases can exist in a number of different textures (forms which have different characteristic appearances). The **Focal Conic** and **Planar** (or **Grandjean**) textures are the most important and these differ essentially only in the degree and direction of ordering relative to the observer. If the helices are at a 90° angle to incident light the **Focal Conic** or **Undisturbed** (since it forms upon cooling from the isotropic liquid without perturbation) texture results. This texture is birefringent but optically inactive. In this form, the cholesteric mesophase scatters light diffusely and appears milky and not brightly colored when viewed against a dark background. In the **Planar** texture (also called the **Grandjean** or **Disturbed** texture), which can be formed from the focal conic by mechanical shear, the helices are more or less all aligned with their axes parallel to incident light. This is the texture that exhibits the unique optical effects usually associated with the cholesteric mesophase-iridescence, optical activity, circular dichroism and selective reflection of white light to show brilliant colors. These properties are discussed in more detail in section 3.5. A schematic representation of the focal conic and planar textures is shown in figure 10.

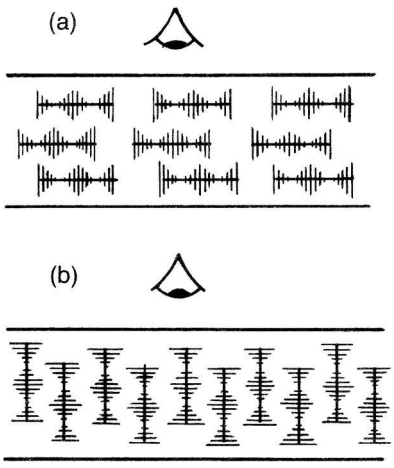


Figure 10: Orientations of helical and molecular axes relative to observer for (a) Focal-conic texture and (b) Planar texture.

Other textures also exist. Collectively, these have historically been called 'unexplored textures'. Most information is known about the texture variously described as **Homeotropic** or the **Blue Phase**, which often, but not always, intervenes prior to the focal conic texture on cooling the isotropic. The texture is transparent has only slight birefringence and no optical activity. The orientation of the structure is still not completely understood. Effects associated with these 'unexplored textures' have traditionally been the least understood properties of cholesteric mesophases. However, blue phases in particular have been the target of much increased research effort during recent years and new publications appear in the scientific literature on a regular basis.

Although certain 'unexplored textures' may still exist, the two most stable and prevailing textures of the cholesteric mesophase. the focal conic and the planar, have the same helical structure. Identification of the cholesteric mesophase is, therefore, possible even if selective reflection is not apparent.

For practical purposes, the only textures of interest to HALLCREST and of relevance to the topics discussed in this booklet are the focal conic and the planar. Of these, the properties of the planar texture are those which are normally viewed as being characteristic of the cholesteric mesophase and which also currently dominate the technology of the use and manufacture of TLC products.

3.4.5 Phase Transitions

Liquid crystal mixtures and compounds having a cholesteric phase can also commonly exhibit smectic mesophases at lower temperatures. (This is also true for nematics.) The conversions from the crystalline solid or isotropic liquid to the liquid crystalline state are true phase changes, as are the interconversions of the smectic and cholesteric (and smectic and nematic) mesophases. These transformations are all completely thermally reversible. In the case of the mesophase to crystalline solid transition, supercooling is possible and is usually observed. Transitions between the other phases (smectic, cholesteric and isotropic liquid) cannot be supercooled, although some hysteresis may occur.

A transition between cholesteric and nematic mesophases has never been accomplished by simply changing the temperature of a pure compound or mixture of chemicals. Cholesteric and nematic mesophases cannot be made to co-exist in a single composition without the intervention of an external electric or magnetic field - the structures of the two are qualitatively the same. Mixing of the two mesophases gives rise to a cholesteric. A nematic can be converted to a cholesteric simply by the addition of an optically-active dopant which does not necessarily itself have to exhibit cholesteric liquid crystal properties. The cholesteric mesophase can be converted to a 'pseudonematic' by the application of an external electric or magnetic field. This, in effect progressively unwinds the helix, increasing the pitch as it does so, until. in the limit the pitch length becomes infinite and the structure exhibits properties of the nematic mesophase. Reversion to the cholesteric occurs on removal of the external field.

A schematic representation of the various phase changes described above and commonly experienced by cholesteric (and nematic) liquid crystals is shown in figure 11.

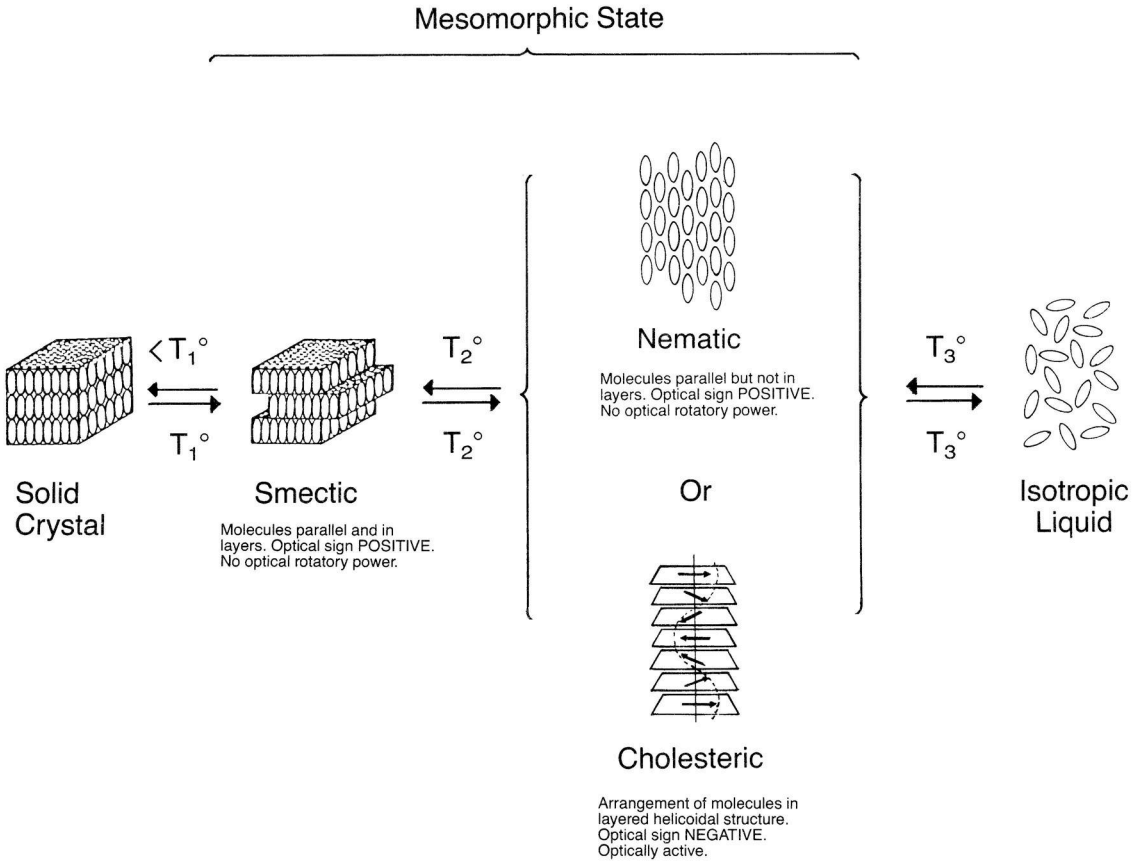


Figure 11: Schematic representation of the phase changes commonly experienced by cholesteric (and nematic) liquid crystals

3.5 OPTICAL PROPERTIES OF THE CHOLESTERIC MESOPHASE IN ITS PLANAR TEXTURE

3.5.1 Introduction

When the cholesteric mesophase is in the planar texture and the helical pitch length is of the order of the wavelength of visible light, the most striking (and those normally considered to be characteristic) properties of the phase can be observed. Applied as thin films, cholesteric liquid crystals selectively reflect bright, almost pure colors which can be made to change as the temperature changes. In the bulk, interference effects modify the appearance to one of iridescent reflection/scattering (not unlike liquid mother-of-pearl), the predominant reflected colors also being able to be made temperature-sensitive.

It should be noted that the absence of these reflected colors does not necessarily preclude the existence of the cholesteric mesophase. For example, the selective reflection may not be observed because it occurs in the infra-red (or somewhere else outside the visible region) or, alternatively, because the sample may not be in the state of alignment that exhibits selective reflection (i.e. in the focal conic rather than the planar texture).

The cholesteric planar texture possesses a number of properties which give rise to the unique optical effects referred to above:

a) it is birefringent; uniaxial and optically negative

b) it is optically active with rotatory powers many times that of normal optically- active materials

c) it is circularly dichroic and can be made to affect both right and left circularly polarized components of light

d) it scatters incident white light in a similar way to the scattering of much shorter wavelength X-rays by solid crystals

Each of these four properties will be discussed in turn, individually, with particular reference to the way in which they modify light. The various individual effects will then be combined to give a cumulative picture of how a beam of unpolarized incident white light is modified as it passes through the cholesteric planar structure.

3.5.2 Birefringence

Birefringence is a basic property of all liquid crystals. It is intrinsic to their anisotropy. The effect in the cholesteric mesophase is represented schematically in figure 12a. For any anisotropic material there are only certain directions at right angles to each other in which the vibrations of a light wave can be transmitted through the material. These 'privileged' directions or planes have different orientations with respect to the molecular alignment and light will be transmitted along them with different velocities. Because the refractive index for a material is a function of the velocity at which light is transmitted through it, the result is that the material has different refractive indices for light waves propagated along the different privileged directions. Thus, for unpolarized light (which may be regarded as being composed of equal amounts of plane polarized light vibrating in the plane of this paper, and plane polarized light vibrating at right angles to the plane of this paper) entering the liquid crystal. there will be a splitting effect. One plane polarized component will be transmitted along one of the privileged directions with a certain refractive index, and the other along the privileged direction at right angles to the first with a different index of refraction. Because of the transverse nature of light waves, the component of refractive index which affects light propagating in a given direction is, in fact, the component at right angles to the direction of propagation. The initial beam will be split into two beams, each linearly polarized, which emerge parallel to each other, but with their planes of polarization at right angles. This phenomenon of double refraction is known as birefringence.

Birefringent materials can be either optically positive or negative. For optically positive materials, light travels faster along the optic axis (the refractive index acting on light traveling along this axis is lower or the refractive index in the direction of the axis itself is higher) than it does at right angles to it. The opposite is true for optically negative materials. Cholesteric mesophases are uniaxial and optically negative; their optic axis is the central axis of the helix and not the long molecular axis, as is the case with nematics and smectics. which are optically positive. The optic axis of a cholesteric is thus at right angles to the local optic axes of the constituent nematic layers.

3.5.3 Optical Activity

Another property of the cholesteric planar texture is its extremely high **Optical Activity**, exhibiting optical rotatory powers many times that of common optically active materials. The plane of polarization of plane polarized light is typically rotated through thousands of degrees per millimeter thickness of liquid crystal (figure 12b). Values of optical rotatory power of this magnitude cannot be caused simply by optical activity alone and must be explained in terms of the ordered, helical molecular arrangement in the cholesteric mesophase.

3.5.4 Circular Dichroism

The structure is also **Circularly Dichroic**. Dichroism is a term more commonly used to describe the properties of certain dyes which absorb a component of unpolarized light vibrating in one plane but not the components vibrating in other planes. A similar effect is observed with cholesteric liquid crystals and circularly polarized light.

At a given wavelength, incident light is resolved by the cholesteric structure into its two circularly polarized components, one right-handed, the other left-handed (figure 12c). At this wavelength, one handedness of circularly polarized light is completely reflected while its complement is completely transmitted. This wavelength depends on (i) the helical pitch of the material which, in turn, is a function of the composition and temperature of the mesophase. and (ii) the angle of incidence of the light. The polarization of both components remains unaltered. With normal reflecting surfaces (mirrors, etc.) the sense of the circularly polarized light is reversed on reflection, whereas with cholesteric liquid crystals the original sense of rotation is retained in the reflected light. Either the right or the left- handed component can be affected in this way.

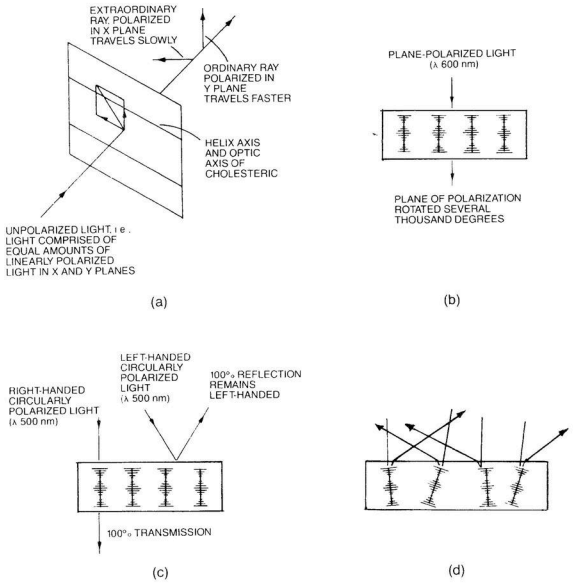


Figure 12: Optical properties of a hypothetical TLC with right-handed helical structure and pitch corresponding to a reflected wavelength of 500nm; (a) birefringence-definition of negative optic axis, (b) rotation of plane polarized incident light, (c) circular dichroism, and (d) Bragg-type scattering of non-normal incident light.

3.5.5 Bragg Scattering

The periodic layered structure of the cholesteric mesophase allows it to behave as a three-dimensional diffraction grating for light of visible wavelengths and show similar behavior to the Bragg Scattering effects observed in crystalline solids with much shorter wavelength X-rays. This Bragg-type scattering gives rise to the characteristic iridescent colors (figure 12d). The colors vary with the nature (composition) of the sample, the temperature, and the angles of incidence and observation. The relationship between the wavelength of the reflected light and the angle of the incident beam normal to the surface of the mesophase can be described approximately by the Bragg diffraction equation

$$\lambda o = 2d\ \bar{n} \sin\ \phi$$

where $\bar{n}$ is the mean refractive index
2d is equal to P. the cholesteric helical pitch length
ϕ is the angle of incidence normal to the surface of the mesophase
λo is the wavelength of the selectively reflected light (the reflected wavelength)

Different cholesteric compounds have different pitch lengths with different temperature dependencies and it is possible to make a wide variety of cholesteric liquid crystal formulations which reflect different colored light that changes at varying rates (or not at all) as the temperature changes, and where the wavelength of maximum reflection (the reflected wavelength) at any one temperature can vary from the infra-red region of the electromagnetic spectrum (or above) through the visible to the ultra-violet (or below). Many possibilities exist. Useful commercial cholesteric liquid crystal compositions may contain compounds which individually show nematic properties or, in some cases, no liquid crystal properties at all.

3.5.6 The Modification of White Light as It Passes Through the Cholesteric Planar Texture; The Reflection of Bright Colors Which Change With Temperature

The various individual effects of birefringence, optical activity, circular dichroism and Bragg Scattering can be combined to give the following description of how a beam of unpolarized white light is modified as it passes through the cholesteric planar texture.

When a beam of unpolarized white light enters the planar texture, it is selectively polarized. The extent and nature of the polarization and the subsequent modification of the resultant waveform depends on the wavelength.

On entering the cholesteric, unpolarized white light is split into its two linearly polarized components. Light of wavelengths much shorter than the reflected wavelength remains linearly polarized and is transmitted as such. However, as it passes through the mesophase, its plane of polarization is rotated (in the direction of the helix) many thousands of times. The rotatory power of cholesteric liquid crystals is extremely high- several hundred thousand degrees per millimeter for light in the visible region.

As the wavelength increases, the plane polarized light becomes increasingly circularly polarized (into its right and left- handed components, one wave spiraling in the same sense as the helix, the other spiraling in the opposite sense), and passes through a range of elliptical polarizations. The long axis/short axis ratio of the ellipse decreases towards unity with increasing wavelength, until. at the reflected wavelength, the light is fully circularly polarized.

Simultaneously, as the wavelength increases and the circular nature of the polarization of the light increases, the optical rotation of the polarized light decreases until the wavelength reaches a value nearly equal to the reflected wavelength. As the wavelength further approaches the reflected wavelength, the rotation of one circularly polarized component increases rapidly as it senses more strongly the helical molecular structure (as shown in figure 13a for a hypothetical cholesteric with a pitch corresponding to a reflected wavelength of 500 nm). The reflectivity of this component similarly increases rapidly (figure 13b) becoming 100 when the wavelength equals the reflected wavelength. At this wavelength, the remaining transmitted light is entirely circularly polarized in the opposite sense. As the wavelength continues to increase to become greater than the reflected wavelength, the reflectivity decreases again and the rotatory power, which is now strong in the opposite sense to before, also diminishes. The narrowness of this region of total reflectivity causes the reflected color to appear very pure.

The above description covers the main effects of the optical properties of the cholesteric mesophase on incident unpolarized white light. Additional structure is added to the reflectivity when the sample is very thin or when the helical structure is distorted by the influence of external fields. For light waves propagated at angles to the helical axis, the reflected wavelength decreases with increasing angle and this effect is explained by Bragg theory. In most commercial temperature indicating applications, because only a very small percentage of incident light is reflected by the liquid crystal, the materials must be viewed against an absorbing (preferably black) background for optimum visualization of their color change properties.

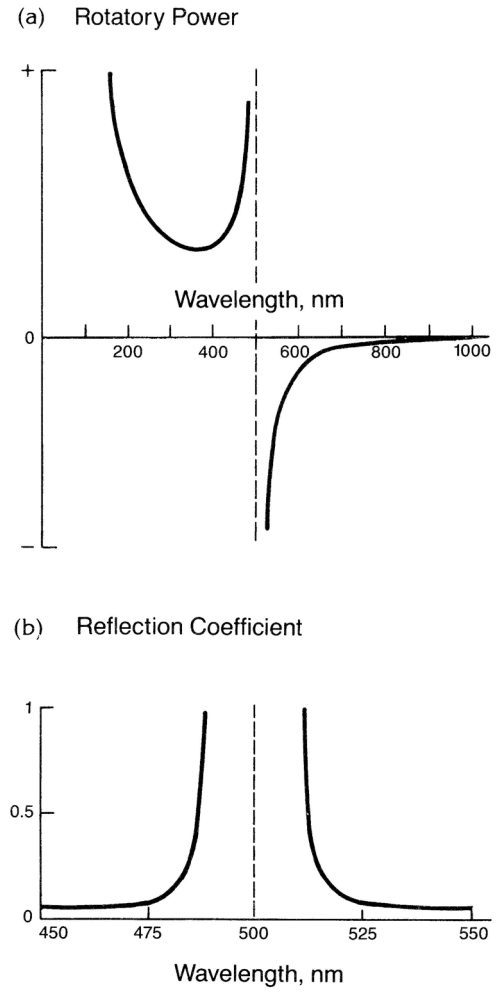


Figure 13: The wavelength dependence of (a) rotation of plane of polarization and (b) reflection coefficient, in a hypothetical TLC with a pitch corresponding to a reflected wavelength of 500nm.

3.6 CONTROL OF THE COLOR CHANGE PROPERTIES OF TLC MIXTURES; PRINCIPLES OF MIXTURE FORMULATION

The temperature interval over which the cholesteric mesophase exists is limited at the top end by a transition to the isotropic liquid and at the low temperature end by a transition to either the solid state or the smectic mesophase. This is true for single compounds and for mixtures; in mixtures, total solidification is usually proceeded by selective crystallization of the least soluble/highest melting components.

The presence or absence of the smectic mesophase plays an important part in determining the color reflecting properties of the mixture. The twist of the cholesteric helix decreases rapidly as the temperature decreases towards the point of transition to the smectic state. The helical structure apparently untwists before it undergoes this phase transition. It is in this pretransitional region, just before it undergoes the change to the smectic. that the cholesteric mesophase exhibits selective reflection of extremely high temperature dependence (the reflected wavelength changes very quickly (greatly) with small temperature changes). The influence of these pretransitional effects on the temperature dependence of the reflected wavelength far exceeds that of any other physical or chemical change that the cholesteric mesophase might inherently experience. The presence of a smectic mesophase immediately below the cholesteric therefore has a pronounced effect on the properties of the resultant mixture. It essentially determines whether the mixture is predominantly temperature- sensitive or temperature-insensitive over a given temperature range.

Away from the pretransitional region (if a smectic phase exists) the cholesteric structure is also sensitive to temperature changes. Three possibilities exist; the reflected wavelength can increase, decrease or remain unchanged as the temperature increases. These changes can be explained by considering the thermal motion of the molecules comprising the mesophase. As the temperature increases, the thermal motion of the molecules increases resulting in an increase in their molar volume which can affect the helical structure in two opposing ways (see figure 14):

a) the intermolecular distance along the helical axis (the distance between adjacent molecular layers) increases, tending to increase the pitch and reflected wavelength
b) the displacement angle between the long axes of adjacent molecules (8 in figure 14) in the helical stack increases, tending to decrease the pitch and reflected wavelength

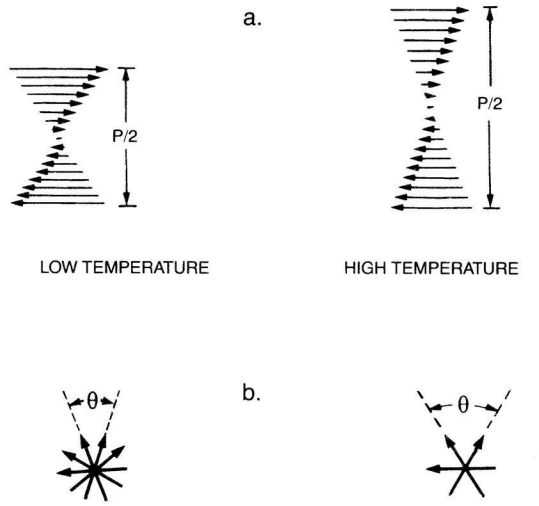


Figure 14: Possible effects of temperature on pitch; (a) alteration of spacing between molecular layers resulting in an increase of pitch with increase in temperature, and (b) alteration of displacement angle, e, resulting in a decrease of pitch with increase in temperature.

In individual chemical compounds b) usually dominates over a) and in almost all pure cholesteric and chiral nematic compounds studied to date, the pitch and reflected wavelength decrease with increasing temperature. Only a very small change in displacement angle (about one tenth of one degree) causes the reflected wavelength to move from one end of the visible spectrum to the other.

This dominance of b) over a) is also true for almost all commercial temperature- sensitive TLC mixtures, giving rise to the well- established characteristic color change sequence of red at low temperatures, through the visible spectrum (orange, yellow, green, etc.) to blue at high temperatures (see section 1.1.2).

With the wide range of chemical compounds now available for mixture formulation, many possibilities exist and mixtures with a variety of temperature- sensitive and temperature-insensitive color reflecting properties can be made. Combination of chiral nematics and cholesterics of opposite handedness in the same formulations and mixtures of these with nematics and non-liquid crystal forming compounds can give rise to TLC mixtures which show a variety of anomalous color change/temperature responses including mixtures where the pitch (and reflected wavelength) increases with increasing temperature and produces a reversed color play (blue at low temperatures towards red at higher temperatures). For a number of reasons, reversed color play TLC formulations have not yet found commercial applications.

The most common color-change properties of TLC mixtures, temperature- sensitive and temperature-insensitive, together with the associated phase changes are shown schematically in figure 15. For temperature-insensitive (clearing point) mixtures used in temperature indicating applications the most common reflected color is green. However, other colors can also readily be made and are, indeed, used extensively in cosmetic and research applications.

Precise control can be exercised over the properties which can be imparted to TLC mixtures by the experienced formulator. The number of useful raw materials available in commercial quantities is now greater than ever before. The options offered by the choice of cholesterics and chiral nematics, components with right and left-handed helical structures, non-optically active nematics and racemates, smectics and a number of chemicals, which on their own show no liquid crystalline properties, allow a degree of control that has not been available previously. Many possibilities exist.

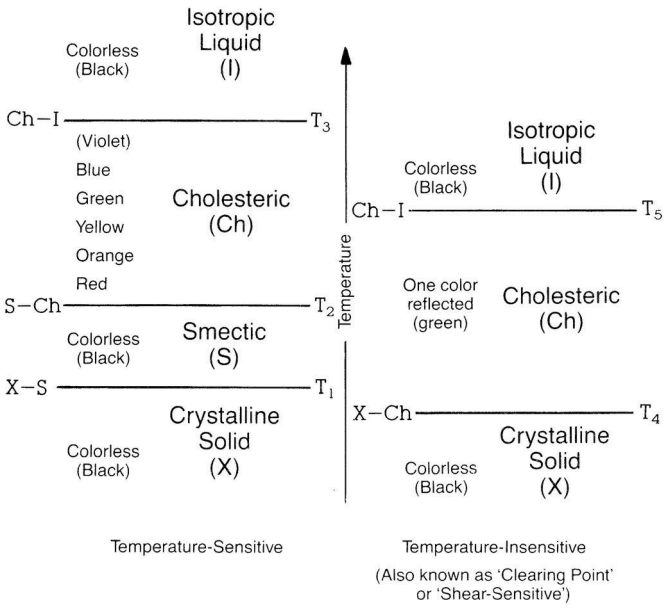


Figure 15: Most common color change properties of TLC mixtures showing associated phase changes and transition temperatures. Temperature-sensitive: T_1= X-S, crystalline solid to smectic LC. T_2 = S-Ch, smectic LC to cholesteric LC. T_3 = Ch - I cholesteric LC to isotropic liquid. Temperature-insensitive: T_4 = X-Ch, crystalline solid to cholesteric LC. T_5 = Ch - I cholesteric LC to isotropic liquid. Some hysteresis may occur on transitions to the crystalline solid.

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