

TLC LITERATURE REVIEW (A) TECHNICAL BACKGROUND AND PRACTICAL ISSUES

This review was originally compiled as an aid to understanding the practical issues that have been encountered over the years by those interested in exploiting the unique properties of TLCs in commercial applications. It covers the problems associated with using TLCs as the unsealed liquids and the related need for stabilization and protection of the materials if they are to be used successfully. The various methods and technologies that have historically been used during manufacturing to impart additional stability and protection are described. These include the optimization of unsealed TLC mixtures by changing their composition and the use of microencapsulation techniques and polymer matrix dispersions to produce stable coating formulations.

PROBLEMS WITH USING TLCs AS THE UNSEALED LIQUIDS

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 lifetime of the product in which they are to be used).

In simple thermographic/thermal mapping/NDT applications when long-term stability is not important, the materials can be used as the unsealed liquids. However, they are not easy to use in this form. The consistency of most commercially available thermochromic liquid crystal formulations (at their working temperatures) varies between that of thin oil and a viscous paste; this makes it difficult to apply the materials onto a black background to give a thin uniform film. In addition, the liquid crystal, once applied, should remain inert and inactive. Problems encountered in trying to use the materials successfully are compounded by the fact that, to a certain extent, the characteristics of the cholesteric (chiral nematic) liquid crystal phase which gives it its commercial usefulness also create the stability and the life-time problems to which so much development time and effort has been applied over the years.

Unsealed TLC mixtures are generally applied in thin uniform films of 10-100 microns thickness. As a result, changes in color can be observed when only small amounts of energy are applied and response times can be fast. However, the resulting large surface area to volume ratio gives rise to a high susceptibility to degradation, whether from oxygen in the atmosphere, which can diffuse into the shallow film easily, UV radiation or dust and fiber particles.

Films of unsealed TLC are also very sensitive to certain chemicals, particularly fats, greases and many common organic solvents. The presence of small amounts (a few ppm) of these chemicals change the temperature at which a particular color is shown or, for fixed color systems (showing one color over a wide temperature range), change the color seen. Indeed, some TLC compounds and mixtures possess very good solvent properties themselves (particularly at high temperatures around 100°C) and have the ability to selectively extract certain harmful chemicals from various polymer sheets and coatings with which they are in contact, resulting in associated changes in their color/temperature profiles. In chemical analysis systems, such sensitivity is particularly useful (see, for example, reference (1)), but in other applications it is a serious drawback. Dust and fiber particles are readily trapped by viscous films of unsealed TLC. These can induce changes in the film from the colored, maximally reflecting, planar texture of the cholesteric mesophase to the colorless focal conic texture (2). High viscosity can also result in entrapment of the solvent which may have been used to apply the film initially. The volatile solvent eventually evaporates out, changing the color/ temperature characteristics of the film as it does so.

As a result of the effects described above, the lifetime of an unprotected, unsealed TLC film varies from a matter of hours to a few days, depending on the conditions to which the material is subjected. In "spray-on/wipe-off" thermal mapping/NDT applications this causes no problems, however, the majority of applications require a degree of stability far in excess of the lifetimes quoted above.

Numerous cholesteric TLC compositions have been recommended for thermographic/ temperature indicating applications in the literature (3-24, 159, 167-171). These include hysteretic (memory) and shear-sensitive (temperature insensitive) formulations. Significant improvements in the performance and stability of cholesteryl ester mixtures can be obtained by the addition of crystallization inhibitors, anti-oxidants and other stabilizers (7, 8, 12, 25-35, 163-166). The decomposition of cholesteryl ester mixtures and the effects of various inhibitors/stabilizers have been studied (36, 37).

Non sterol-based "chiral nematic" compounds (38-48) were made on a commercial scale for the first time in the 1980s. These materials are cholesteric liquid crystals by the accepted definition but are not related to cholesterol or any other sterol and therefore have different chemical and physical properties to cholesteryl esters. They need to be differentiated and the term "chiral nematic" is used to do this. Although the mechanism by which these materials change color is the same as cholesteryl esters, they can be used in different ways to achieve different effects (172). It is also possible to mix chiral nematics and cholesterics to give TLC formulations which have properties intermediate between those of the constituents. Compositions for useful TLC mixtures (cholesteric and chiral nematic) continued to appear in the open and patent literature well into the 1980s (e.g. (49-52, 173-175)).

In the bulk, unsealed, unstabilized form, chiral nematic mixtures are inherently more stable than their cholesteryl ester counterparts, but the materials are still far from being completely stable. The mechanism of chemical decomposition is different and unsealed chiral nematic TLC mixtures cannot be stabilized in the same way as cholesterics. However, it is possible to greatly increase the stability of both types of material in a number of different ways during the further processing steps necessary to put together a finished product or effect.

Ultimately, the stability or apparent stability of a TLC mixture is determined by many parameters including the following: (a) its functionality - essentially how temperature sensitive it is; (b) the form in which it is used; (c) its environment - the composition of the vehicle to which it is added / nature of the product in which it is incorporated; (d) the conditions to which it is exposed, during handling and when it is in the final product.

The actual composition of the unsealed TLC mixture is also an important factor, but not as overly important as it might appear to be initially. The ways in which the materials are used and the steps that are taken to improve stability in their working environment are probably equally important, if not more so.

STABILIZATION AND PROTECTION TECHNIQUES

Microencapsulation

The first step in stabilizing TLC formulations is to isolate the liquid crystal from the atmosphere by a protective barrier and preferably, at the same time, to convert it into an easily-to-use form. If the primary protection against degradation is provided by some sort of physical packaging, then secondary protection can be achieved by incorporating stabilizing (UV absorbing) properties into the materials used in conjunction with the liquid crystals to make devices. The clear polymer substrates to which the packaged TLC is applied and the polymer systems (ink or paints) which either contain the packaged TLC or are applied to it to protect it, are the best examples of hosts for stabilizers.

Generally speaking, contact with organic material (e.g. enclosure within foils, dispersions in polymers and plastics and microencapsulation) always brings with it the danger that soluble or diffusible substances can alter the color/temperature characteristics of the liquid crystal material. To date, the microencapsulation process seems to be the most versatile, widely applicable and successful way of packaging TLC. Slurries containing microencapsulated TLC are generally aqueous and need to be made into inks or paints before they can be applied successfully in device manufacture. Good TLC inks usually contain a number of water-based polymer/resin components in addition to the microencapsulated TLC and are optimized for the particular method of lay-down to be used. To date, screen printing has been the most successful means of laying down TLC inks commercially, although many other printing and coating processes are claimed in the literature.

As mentioned above, the microencapsulation process is especially well suited to protect TLCs (53-65, 176). The following procedure is a typical example (54): 1.25g of acid-extracted pigskin gelatin and 1.25g of gum arabic are stirred with 125g of distilled water at 55°C to yield a solution of about pH 4.5. When the solution has formed, the pH is adjusted to 6.0 by the drop-wise addition of 20% (by weight) aqueous sodium hydroxide solution. Then the cholesteric mixture consisting of 2g cholesteryl chloride, 8g cholesteryl nonanoate and 1g MBBA is added and emulsified to an average droplet size of 5 to 30 microns. By the drop-wise addition of 14% (by weight) aqueous acetic acid solution, the pH is slowly reduced to finally reach about 5, whereby the polymeric material is phased out to deposit on the liquid crystal droplets. The system is then chilled to 10°C under continuous agitation, and 0.06 ml of a 25% (by weight) aqueous solution of pentanediol, a chemical hardening agent for the gelatin, is added. After 12 hours stirring while slowly returning to room temperature, the capsule walls are firm and sufficiently hardened to be sieved through a wire mesh sieve. If a silver halide is incorporated in a similar procedure, photosensitive liquid crystal microcapsules can be obtained (62, 66, 67). A number of books and review articles provide both comprehensive summaries and detailed accounts of microencapsulation techniques (e.g. (68-72)).

Once microencapsulated, the TLC mixture can be incorporated into a coating formulation optimized for the application method to be used either in device manufacture or to achieve the desired color change effect.

Polymer Matrix Dispersions

It is possible to disperse the TLC mixture straight into a resin system without first microencapsulating it. Coatings made in this way are referred to as polymer (matrix) dispersions although confusion does exist as some people also refer to such

systems as encapsulated liquid crystal systems. Thermosetting resins (e.g. acrylic (135-139) and melamine resins (140)), polyvinyl alcohol (141-143) and other emulsion media (135, 139, 144-155) have all been suggested as components for polymer dispersion coatings, the structures and optical properties of examples of which have been studied (156-158). However, such dispersions containing non-microencapsulated liquid crystal mixtures are generally not as stable and have not been used as successfully in commercial thermochromic applications as coatings containing microencapsulated material.

Coating Formulations

Further processing of microencapsulated and non-microencapsulated TLC mixtures towards temperature indicating devices and applications includes ink (4, 73, 74, 76-79, 178), paint (80, 81, 179, 180) and general coating formulations (75, 177, 181-185), sprays (82, 83) film-forming pastes (84, 143, 186) and coated films/sheets (85-94, 187-189). Multi-coat systems are also described (83, 95, 96). Incorporation into or onto elastic membranes can offer microcapsules further protection (97, 98, 191). Response times of various commercially available TLC films and coating materials have been measured (99, 192). Electro-optical display devices containing microencapsulated cholesterics are claimed (100-104) and the preparation of vitrified nematic and chiral nematic (cholesteric) LC films (105, 106) and of decorative iridescent coatings have also been described (107-110). The use of dyes in LC mixtures (111), in coating formulations (112) and in overcoats as color filters (113) has also been covered. The literature includes reference to decorative coated plastic sheets for use as substrates (114) and protection against degradation by UV radiation can be built into clear polymer substrates optimized for use with TLC coating formulations (115).

Other Protection Methods

In addition to microencapsulation and coating formulations incorporating microencapsulated and polymer dispersed CLC mixtures, a number of other techniques for packaging, protecting and utilizing TLCs have been developed. The materials can be sandwiched between two plastic sheets (a transparent cover and a black substrate) or can be protected by similar procedures (116-124). The influence of polymer surfaces on the textures has been studied (125). Textile fabrics coated with CLC are described (126-130, 190), as are TLC filled hollow fibers that can reversibly change color with temperature (96, 131, 132). Yarns with temperature sensitive colors have been obtained in the following way (133). A polyester sheet is gravure coated with a black ink, gravure coated with a mixture of 30% aqueous polyacrylamide and 30% aqueous slurry of a microencapsulated TLC, and top-coated with a solution of maleic acid-vinyl acetate-vinyl chloride graft co-polymer. The film is slit to 0.4mm and wound round a 120 denier yarn. Other patents also exist (134).

Publications covering the subject matter of this review continued to appear in the open and patent literature into the mid 1990s, but at a much reduced rate. Since then, the rate of publication of relevant articles has continued to decrease, highlighting the importance of the 25 year period from the mid 1960s to the late 1980s as the golden era for advances in TLC technology.

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