

TLC TECHNICAL NOTE (S) - STABILITY OF TLC MIXTURES

OXIDATIVE ATTACK ON UNSATURATED BONDING IN CHOLESTEROL DERIVATIVES

Any chemical containing isolated double bonds between carbon atoms is liable to attack on these bonds by oxygen. For cholesterol, there is one C=C bond between the 5 and 6 positions in the ring nucleus. In cholesterol derivatives, the side chain can also contain double bonds (e.g) the oleyl side chain (CH₃ (CH₂)₇CH=CH(CH₂)₈-) and also via the carbonate linkage (-O-C(=O)-O-).

Cholesterol deteriorates in the presence of air in the dark, a process which is accelerated under the influence of heat and light. The same instability is found in its derivatives, including those compounds commonly used in the formulation of cholesteric liquid crystal mixtures – esters, carbonates and halides. Aromatic derivatives are generally more stable than aliphatic.

Historically, problems encountered in trying to use the materials successfully have been compounded by the fact that the characteristics of the cholesteric liquid crystal phase which gives rise to its commercial usefulness also creates the stability and life time issues on which so much development time and effort has been spent over the years. Most of this work was carried out in a 10 year period from the late 1960s to the late 1970s. This was during the formative days of the industry which grew up around the use of cholesteric liquid crystals as color change temperature indicators.

Over the years, one compound in particular has been the subject of far more studies than any other. This is because of its high inherent instability and the fact that its properties make it one of the most widely used constituents of common commercial mixtures. Cholesteryl oleyl carbonate (OCC) contains all three sites of unsaturation in its molecule (oleyl side chain, carbonate link and cholesterol nucleus) and is therefore one of the least stable cholesterol derivatives. These studies (e.g. refs 1 – 4) have led to significant improvements in the performance and stability of cholesteric liquid crystals mixtures being made. They include the use of anti-oxidants, UV absorbers, crystallization inhibitors and other stabilizers as well as much higher levels of purification of the raw materials (e.g. refs 5 – 10).

OCC has historically been one of the principal components used by LCR Hallcrest across its range of LC mixtures and it still is today. The inherent instability of OCC led to an extensive search for possible replacements and several new compounds have been synthesised as a result. These include cholesteryl oleate (CO - which does not contain the carbonate link) and cholesteryl isostearyl carbonate (ISC - which does not contain the unsaturated C=C bond in the side chain. LCR Hallcrest also uses both of these compounds on a regular basis.

With respect to the high temperature TLC formulations that need to be used in the manufacture of temperature indicators working at elevated temperatures (above 50 deg C), the key to achieving optimized performance, appearance and stability in the finished devices is to use the most stable components in the LC formulations. Notwithstanding the advances that have already been made by the use of anti-oxidants, UV absorbers and other stabilizers, a switch from OCC to either CO or ISC will certainly provide further improvements to stability.

Further possibilities also exist on the formulation side by switching away from predominantly cholesterol-based LC mixtures to those based on non-sterol phenyl benzoate esters (e.g. refs 11 – 16), the use of which LCR Hallcrest is the acknowledged global leader. These materials are cholesteric LCs by the accepted definition but are not related to cholesterol or any other sterol and thus have different chemical and physical properties. Ideally, they need to be differentiated and the term “chiral nematic” is usually 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 (see Hallcrest Handbook of TLC Technology). It is also possible to mix chiral nematics with cholesterics to give formulations which have intermediate properties. There are many different ways of making LC mixtures with nominally identical color change transition temperatures.

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TLC-TN-S (04/09)

RT 005

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