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Materials for Applications: The Industrial Chemists' Viewpoint

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Materials for applications: the industrial chemists' viewpoint

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Many of the advances in displays during the past decade have been facilitated by the development of new mixtures, tailored to the application, in chemical companies that specialize in the production of liquid crystals. Problems that occur in this type of work are illustrated by the example of the development of mixtures for multiplexing 16–32 ways. The production of liquid crystals is discussed briefly.

Introduction

Companies that manufacture liquid crystals have made considerable contributions to the science of the subject and to the progress of displays. Merck began their work in 1968 at a time when few practical applications were known, and the materials they provided for experimental purposes helped to sustain the interest of research workers. The discovery that founded the display industry, the principle of the twisted nematic cell, was made in 1971 at Hoffmann La Roche and the cyanobiphenyls produced in 1973 were the first materials that made the production of low-voltage fast-switching displays possible. A decade of rapid progress has followed in which the succession of demands from the display industry for materials suitable for more sophisticated applications has been met by research into the chemistry and physics of liquid crystals. From the simplest static-driven watch display, the technology has advanced through three-way multiplexed displays for calculators, dot matrix displays, displays for operating over wide temperature ranges, coloured displays to the verge of high-information v.d.u.-type displays. Each application requires a liquid with different properties and each has been met from the products produced by the materials companies.

These developments occurred outside the display industry because companies with the capability to manufacture displays had little reason, before the l.c.d., to employ the physical and organic chemists necessary for research into liquid crystals, and even less incentive to invest in the chemical plant required for their manufacture. This situation remains largely unchanged today. Although there are some exceptions, most of the display industry continues to purchase its liquid crystal requirements. There is a natural industrial and technological boundary between the chemical companies that manufacture liquid crystals and the electronic companies that manufacture displays, and this gives the materials companies the opportunity to develop and sell their products.

Liquid crystals are examples of chemicals that the chemical industry describes as 'speciality chemicals', i.e. chemicals produced to be sold to a different industry for the sake of their properties rather than their structure. Speciality chemicals are attractive to the chemical industry because the prices they command are higher than those of commodity chemicals. On the other hand, their development is much more expensive because the chemical company must employ a group of experts in the speciality field that their business might not otherwise need. The expertise that these groups build up by their research, protected by patents, deters other chemical companies from competing in the business, and helps to preserve the position of those first in the field.

The sequence of events leading to the development and marketing of a new liquid crystal mixture forms a cycle of interactions illustrated in figure 1. The process may begin with a request from a customer for an improved material. More often it starts with the synthesis of a new chemical structure, and a hint, obtained from physical measurements, of properties superior to existing materials. In either case, the group concerned with making liquid crystal mixtures becomes involved, and if the efforts are successful the product is produced and marketed after suitable processes for manufacturing the chemicals have been devised. The research work of the materials companies on one side of the circle is well known from their papers and patents (and here we at BDH are very fortunate to be associated with work at Hull University and the Royal Signals and Radar Establishment) and their products are well known on the other. The segment in between is the subject of this paper.

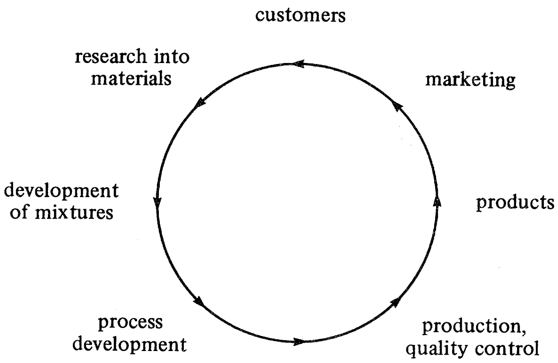


Figure 1

The preparation of liquid crystal mixtures

The properties that the device engineer seeks are shown in table 1. One property may be of dominating importance for a particular application – such as fast response times at low temperatures for displays to be used for automobile instrumentation – but other criteria always have to be fulfilled as well. The scientist in the materials company must build the appropriate combination of properties into the mixture.

Table 1. Properties required in mixtures for display applications

temperature range
birefringence
response times
threshold voltage
sharpness of threshold
temperature dependence of threshold

The process of making mixtures is guided by theoretical considerations, by calculation and by prediction, but much remains to be determined experimentally. The measurement of dielectric anisotropy and elastic constants on individual components is a valuable guide to which to use for a particular application or how best to exploit the properties of a new material. However, such measurements never provide the complete answer to making a mixture because components will have to be used that have transition temperatures inconveniently high for the measurements to be made, and the properties of individual components do not add together in a predictable manner in the mixture. Moreover, non-ideal behaviour may occur in the mixture, such as the formation of an injected smectic phase when nematics of high positive and low positive or negative dielectric anisotropy are mixed.

In the example described in detail below, the development of mixtures for multiplexing 16–32 ways, the voltages provided by the electronic circuit that will drive the display determine the performance required of the liquid crystal. This subject was discussed by Needham (this symposium), who showed that the ratio $V_{\mathrm{ON}}/V_{\mathrm{OFF}}$ varies from about 1.3 for 16-way to 1.2 for 32-way multiplexing. She also showed that these voltages can be related to the performance of the liquid crystal via its electro-optic transmission curves and that $V_{50,10,20}/V_{90,45,20} = M'_{20} < V_{\mathrm{ON}}/V_{\mathrm{OFF}} < 1.3$ for 16-way or 1.2 for 32-way multiplexing when the voltages are measured in transmission. The voltage margin within which the liquid crystal must switch $(V_{\mathrm{ON}} - V_{\mathrm{OFF}})$ decreases with increasing level of multiplexing but increases with increasing supply voltage. Calculation of the voltage margin for 16–32-way multiplexing shows that the desired performance will be obtained only in mixtures with threshold voltage in the range 2–4 V, that is mixtures with a relatively low dielectric anisotropy. Clearly the threshold must be as sharp as possible.

Raynes *et al.* (1980) have shown that the sharpness of the capacitance threshold is inversely proportional to

$$\Delta\epsilon/\epsilon_{\perp} + \tfrac{5}{8}k_{33}/k_{11},$$

and a similar relation almost certainly applies to the optical threshold. The fraction $\Delta\epsilon/\epsilon_{\perp}$ is not a fruitful source for manipulation by varying the composition because $\Delta\epsilon$ is also a major factor in determining the threshold voltage and will be determined conversely by the necessity of keeping this in the range 2–4 V, whereas $\epsilon_{\perp}$ is decided mainly by the structure of the core of the molecule and is almost constant at 4–5 in common liquid crystals unless a lateral substituent is present. On the other hand, the ratio of elastic constants, k_{33}/k_{11} is known to decrease with increasing chain length in several homologous series of liquid crystals.

Thus analysis and calculation tell us that the materials most likely to be suitable for high-level multiplexing will have low dielectric anisotropy with a threshold in the range 2–4 V, with long chains at the end of the molecules to produce a favourable ratio of elastic constants and the sharpest possible optical threshold. Practical considerations add another constraint, in that it is advantageous to offer the device engineer two mixtures miscible in all proportions but with different threshold voltages so that he can tune the threshold exactly to match his cell and electronics.

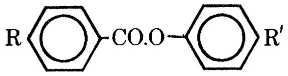


FIGURE 2. Structure of 4-alkylphenyl-4′-alkylbenzoic acid esters.

The class of liquid crystals chosen to fulfil these requirements was the 4-alkylphenyl-4′-alkylbenzoates (figure 2) because they are stable, have the lowest viscosity and highest birefringence among similar materials, are cheap to produce and have a proven record of performance in commercial liquid crystal mixtures. Their names are abbreviated to ME*XY* where *X* is the number of carbon atoms in the alkyl side chain attached to the acid part of the molecule and *Y* represents similarly the chain attached to the phenol.

The observation that started the development of these mixtures was made by D. G. McDonnell at R.S.R.E., who found that ME77 mixed with $5\,\%$ 2CB had an extremely sharp threshold (see table 2). This mixture froze at 22.5 °C, was nematic to 32 °C and had a monotropic transition to a smectic phase at 17 °C. The problem was to expand the nematic range to −10 to 60 °C while retaining the key property: the sharpness of the threshold.

TABLE 2. ELECTROOPTIC DATA FOR MIXTURES OF HIGH POSITIVE Δε COMPONENTS WITH MIXTURES OF ESTERS

	positive Δε component	ester mixture	$V_{90,0,20}$ / V r.m.s.	M_{20}	M'_{20}
1	5% 2CB	ME77	3.73	1.49	1.19
2	5% 2CB	TE2	2.83	1.57	1.22
3	5% 2CB	80% TE2, 20% MB75F	3.85	1.53	1.20
4	5% 2CB	72% TE2, 18% MB75F, 10% 3R33	3.67	1.56	1.22
5	12% 2CB 3% BB21	72% TE2, 18% MB75F, 10% 3R33	2.48	1.61	1.27
6	2% 2CB 3% BB21	72% TE2, 18% MB75F, 10% 3R33	3.89	1.55	1.22

The first property to receive attention was the freezing point, which is influenced strongly by the freezing point of the ester as the major constituent of the mixture. Other esters of a similar chain length had equally unfavourable melting points, and the only remaining possibility to depress the freezing point was to use a eutectic mixture of esters. At once the kind of compromise with which this type of work is fraught was encountered. Depression of melting point between homologues of similar chain length is generally small. Maximum depressions are obtained by maximum differences in chain length, and, because the chain cannot be lengthened beyond 7–8 carbon atoms owing to the occurrence of smectic phases, homologues of shorter chain length have to be used, which probably have less favourable elastic constants. The eutectic (TE2) of ME73, ME75 and ME77 was determined and found to freeze at −3 °C and be nematic to 28 °C. Electro-optic measurements on a mixture of this with 5 % 2CB (see table 1) show there has been some loss of sharpness, but shortening the average chain length has also reduced the threshold voltage.

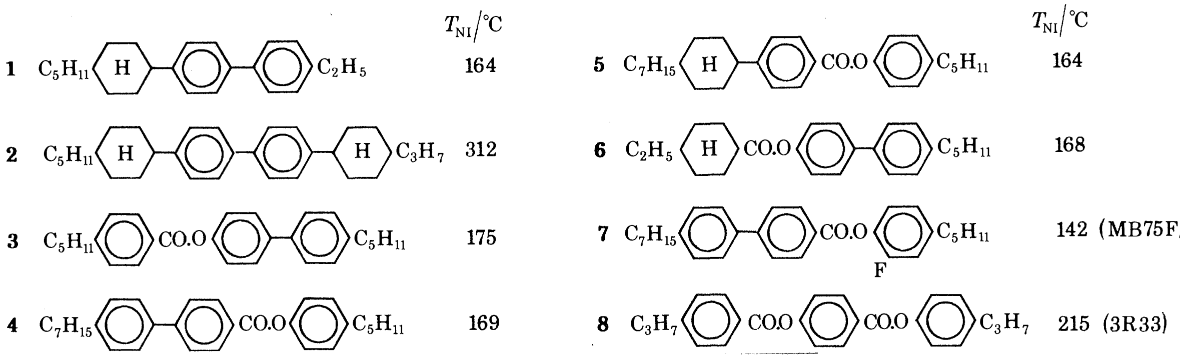


FIGURE 3. Low Δε, high T_{NI} components.

The next problem was to raise the N–I temperature (T_{NI}) to about 60 °C, for which purpose a component with low dielectric anisotropy but high T_{NI} was required. Several were studied (figure 3). The hydrocarbon molecules **1** and **2** were insufficiently soluble. The esters **3–6** either increased the viscosity too much or spoiled the threshold sharpness. Only MB75F and 3R33 seemed promising. The solubility of MB75F in TE2 was now determined and found to be about 20 % (figure 4), depressing the melting point to −8 °C and raising T_{NI} to 47 °C. 3R33 was found similarly to be about 10 % soluble in 80 % TE2 – 20 % MB75F, depressing the freezing point further to –10 °C, and raising T_{NI} to 58 °C. Measurement of the threshold on these mixtures after adding 5 % 2CB showed that little further deterioration in sharpness had occurred (see table 2).

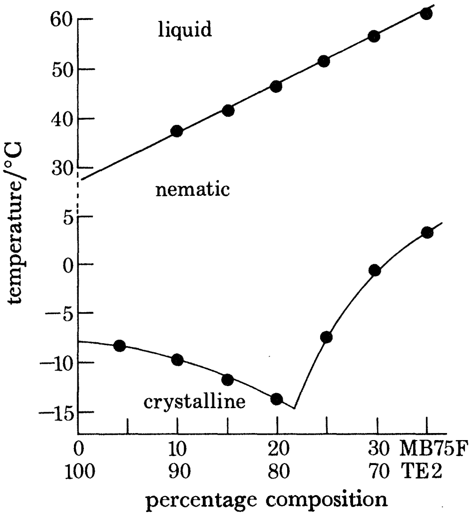
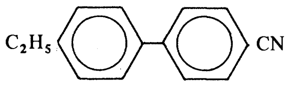
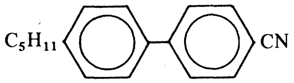
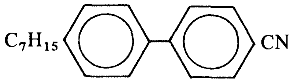
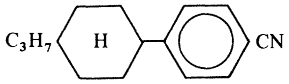
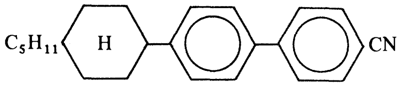
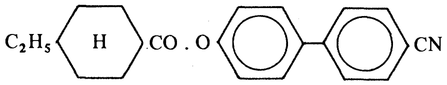
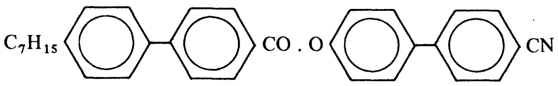


FIGURE 4. Part of the phase diagram of TE2 and MB75F.

TABLE 3. S–N TRANSITION TEMPERATURES OF 5 % OF HIGH POSITIVE $\Delta\epsilon$ COMPONENTS WITH 95 % OF A MIXTURE OF 72 % TE2, 18 % MB75F AND 10 % 3R33

positive $\Delta\epsilon$ component	abbreviation	S–N temperature / °C
	2CB	–7.4
	5CB	+11.1
	7CB	+16.7
	PCH3	+5.7
	BICH 5	+25.2
	CHE	+15.2
	BB21	–13.6

Attention was next directed towards conferring on the mixture the positive dielectric anisotropy necessary to produce threshold voltages in the required range. Here positive materials with long chains are desirable (such as 7CB) for maximum benefit to the elastic constant ratio, and several were tested at 5 % by mass for their effect in generating injected smectic phases (see table 3). 2CB and BB21 stand out as best, perhaps because of their disparate lengths in comparison with the smectic layers. By adding the appropriate combination of these, two mixtures with all the required properties were obtained (see examples 5 and 6 in table 2). Unfortunately when these were then mixed together as intended by the user, an injected smectic phase was found to occur at intermediate compositions. Therefore the last resource to suppress such phases had to be deployed, which is to add a small quantity of a material with short chains at each end: 5 % ME15 in this case. The resulting mixtures, E130 and E140, could now be mixed together without producing a smectic phase stable above −15 °C, and their properties, some of which were measured by E. P. Raynes and M. J. Bradshaw at R.S.R.E. are shown in table 4. E130 is suitable for 16-way multiplexing and E140 for 32-way, allowing for the increase in sharpness observed in reflexion in cells with less than 90° twist (Needham, this symposium).

TABLE 4. PROPERTIES OF E130 AND E140

	E130	E140
$T_{NI}/°C$	64.3	63.0
$T_{SN}/°C$	< -20	< -20
birefringence (at 589.6 nm, 20 °C)	0.154	0.147
$V_{90,0,20}/V$	2.38	3.80
M_{20}	1.63	1.58
M'_{20}	1.27	1.22
$\epsilon_{\perp}$ at 20 °C	4.57	4.19
$\epsilon_{\parallel}$ at 20 °C	9.09	5.71
$\Delta\epsilon$ at 20 °C	4.52	1.52
k_{11} at 20 °C/10^{-12} N	14.1	16.6
k_{33} at 20 °C/10^{-12} N	11.9	13.7
k_{33}/k_{11} at 20 °C	0.84	0.83

This example of the development of liquid crystal mixtures has been recounted at some length to demonstrate the limited but valuable part played in the process by calculation and prediction, and the decisive contribution made by experiment. Gradually knowledge is accumulated of the behaviour of individual components in the system under study, and this in turn leads to mixtures with better properties. The progressive improvement of the low-viscosity broad-range mixture ZLI 1565 at Merck is an excellent example of the same process.

PROCESS RESEARCH AND DEVELOPMENT

Once the decision has been taken to use a particular component in a mixture, it has to be manufactured in the appropriate quantity. When originally synthesized in the laboratory, the route most convenient for the research chemist will have been used. The industrial chemist, on the other hand, seeks the cheapest synthesis, although the options available are limited by several considerations.

1. The raw material must be available from more than one source in case of a breakdown in supplies from a single manufacturer.
2. Solvents or reagents that are dangerously inflammable or toxic must be avoided.

3. The composition of the aqueous effluent that will be discharged after treatment into sewer or river is subject to strict control, and chemicals that are difficult to treat or will interfere in the treatment of others have to be avoided. Similar control must be exercised over gaseous effluent.

4. The chemical steps in the manufacturing process must be accommodated in existing plant if possible to avoid the necessity for capital expenditure on new equipment, at least until present spare capacity is used fully. Extremes of temperature and pressure have to be avoided.

Fortunately, organic chemistry is a sufficiently flexible science to allow these difficulties to be overcome. The development of an alternative synthesis of 4-alkoxy-4′-cyanobiphenyls (figure 5) to the original used by Gray *et al.* (1974), one that avoids the objectionable intermediate 4-nitrobiphenyl, is an example from the history of cyanobiphenyls.

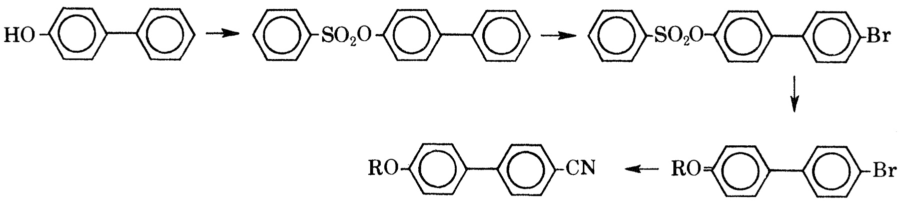


FIGURE 5. Synthesis of 4-alkoxy-4′-cyanobiphenyls used for their production.

Research into methods of manufacture is performed in all the companies supplying liquid crystals, and the scale of the effort may be comparable with that devoted to making mixtures. The discovery of new structures continually poses new problems that have to be solved under stress, because of the desire to commercialize the discovery quickly. The work rarely receives any publicity yet it determines the profitability of the chemical and thus plays a vital part in the sequence by which liquid crystals reach the customer.

PRODUCTION OF LIQUID CRYSTALS

The present annual production of liquid crystals is 6–7 t throughout the world. This quantity is divided among many components, of which 5CB is probably the largest single item, although less than 10 % of the total. Production is carried out batchwise in enamel-lined or stainless steel reactors of the type used generally for the manufacture of organic chemicals. The high purity of the products is achieved by rigorous quality control over the raw materials, by purifying intermediates so that impurities are not carried over from one stage to the next, and by lengthy purification of the final liquid crystal, including treatment to remove ions and raise the resistivity. The syntheses often involve many steps, and the total time of processing may be 3–4 months. This makes the organization of production a complicated matter, particularly as many components have to be manufactured simultaneously.

The materials companies and the display manufacturers have collaborated over the past decade to create a new technology, and many of the advances have originated in the chemical side. The display companies get the best of the bargain because their output has more than 10 times the value of the liquid crystal they use, but the materials companies will continue to meet the challenge of providing better liquid crystals as long as markets can be found for their products.

The experimental work was carried out by Mr P. Balkwill, Mr A. Pearson and Dr I. C. Sage. It was carried out under contract to the Ministry of Defence.

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