

1

A LIQUID CRYSTAL DISPLAY ELEMENT,
METHOD OF MANUFACTURING AND STORING THE SAME
AND ELECTRONIC EQUIPMENT ON WHICH THE SAME IS MOUNTED

The present invention relates to a liquid crystal display element including flexible substrates; to methods of manufacturing and storing such liquid crystal display elements and electronic equipment on which such a liquid crystal display element is mounted.

As shown in Fig. 15, a liquid crystal display element typically comprises a pair of substrates (1) sandwiching between a liquid crystal medium (6). Orientating films (3) are disposed on the substrates for orientating liquid crystal molecules to provide the requisite display. Hitherto, the substrates have comprised glass but increasingly flexible substrates such as plastic films have been used and the flexible substrates have merely replaced the glass substrates during manufacture.

When manufacturing liquid crystal display elements with glass substrates, the glass substrate is relatively impervious and so there was no need to subject the substrates to any gas barrier treatment. The liquid crystals of the liquid crystal medium were not been monitored so as to control the solubility and degree of saturation of gas in the liquid crystal medium. The elements were stored at normal pressures and temperatures. Finally, when mounting such elements in electronic equipment, the elements were exposed so that external pressure could be applied directly to the elements.

However, when flexible substrates are used, problems have arisen with such elements. One change due to including flexible substrates was made and that was providing spacers (4), at least 100 to 150 spacers per mm² for initially determining the thickness of the element. Further problems arose because the

flexible substrates such as plastic films have permeability to gas or water vapour. Consequently, when the element is stored or used at ambient conditions (i.e. (normal pressure or temperature, usually 25°C at 1 atm) gas or water vapour permeates the flexible substrate and thus enters the liquid crystal medium. Eventually, the gas or water vapour may become saturated in the liquid crystal medium. Thus due to the inherent nature of the flexible substrates that they are likely to become deformed by an external force such as being pressed by a finger or dropped, bubbles may form inside the liquid crystal display element and thereby diminishing the quality of the display.

An object of the present invention is therefore to provide a liquid crystal display element including at least one flexible substrate which substantially obviates the aforementioned problem. A further object of the present invention is to provide a method of manufacturing and storing such a liquid crystal display element and to provide electronic equipment on which the same is mounted for minimising the possibility of bubbles forming in the liquid crystal display element.

According to the present invention there is provided a liquid crystal display element comprising

- a pair of flexible substrates including a gas barrier layer;
- orientation films disposed on one side of said substrates;
- an electrode layer disposed on the same side of one of the substrates;
- seal members for bonding together said substrates having the sides of said substrates facing each other;
- a number of spacers arranged between said substrates for providing a predetermined gap therebetween;
- a liquid crystal sealed in said gap; and
- means for providing polarisation, characterised by the end portions of the substrates being subjected to a gas barrier means.

The present invention provides a liquid crystal display element in which a pair of flexible substrates on which orientating films for orientating liquid crystal molecules are formed are bonded together by seal members with the aid of spacers so that the substrates face each other with a predetermined space therebetween, a liquid crystal being sealed in said space, wherein the end portions of the substrates of said liquid crystal display element are subjected to a gas barrier treatment.

The liquid crystal of the above liquid crystal display is employed which has oxygen saturation solubility of not less than $10 \mu\text{l/ml}$, a liquid crystal having nitrogen saturation solubility of not less than $10 \mu\text{l/ml}$ or a liquid crystal having saturation solubility of water vapour of not less than 100 ppm, and the degree to which either oxygen, nitrogen or water vapour, or a mixture thereof, is saturated in the liquid crystal immediately after the production of the above liquid crystal display element, is not more than 0.9.

The number of said spacers ranges from 150 to 300 per mm^2 , and hard coat layers having a pencil hardness of not less than "H" are formed between inner surfaces of said film substrates and said orientating films.

The above liquid crystal display element is produced by allowing it to stand at reduced pressure.

The above-described liquid crystal display element is stored at reduced pressure.

The structure of electronic equipment on which a liquid crystal display element is mounted is such that a guard plate having a thickness of not less than 0.5 mm is disposed over the above liquid crystal display element.

In the above structure, the above liquid crystal display element and above guard plate are disposed with a space of not less than 0.5 mm.

Embodiments of the present invention will now be described with reference to the accompanying drawings of which:

Fig. 1 is a cross section of a liquid crystal display element according to the first embodiment of the present invention;

Fig. 2 is a cross section of a liquid crystal display element according to the second embodiment of the present invention;

Fig. 3 is a cross section of a liquid crystal display element according to the third embodiment of the present invention;

Fig. 4 is a cross section of a liquid crystal display element according to the fourth embodiment of the present invention;

Fig. 5 is a cross section of a liquid crystal display element showing the fifth embodiment of the present invention;

Fig. 6 is a graph illustrating the amount of time required for a bubble nucleus to disappear in accordance with a pressure test against the amount of time the display element has been allowed to stand;

Fig. 7 is a cross section illustrating vacuum packing in the fifteenth embodiment of the present invention;

Fig. 8 is a cross section illustrating several liquid crystal display elements being vacuum packed according to the sixteenth embodiment of the present invention;

Fig. 9 is an enlarged cross section illustrating part of the structure of a piece of electronic equipment by which a liquid crystal display element has been mounted;

Fig. 10 is an enlarged cross section of a gas barrier film according to the first embodiment of the present invention;

Fig. 11 is an enlarged cross section of a gas barrier film according to the sixth embodiment of the present invention;

Fig. 12 is a cross section of a pressure test tool illustrating a pressure test applied to a typical liquid crystal display element;

Fig. 13 is a cross section illustrating the nucleus of a bubble;

Fig. 14 is a cross section illustrating a bubble; and

Fig. 15 is a cross section of a conventional liquid display element.

Embodiment No. 1

With reference to Fig. 1, a liquid crystal display element is shown and comprises upper and lower substrates both utilising a gas barrier film. The element further comprises transparent electrodes 2 made of an ITO (Indium-tin oxide) film, an orientating film 3, a plurality of spacers 4, seal members 5 and a liquid crystal medium 6. A pair of polarising plates 7 are disposed on either side of the substrates with a reflecting plate 8 mounted on one of the polarising plates.

As the substrates 1 are flexible, the present invention includes means for applying a gas barrier treatment so as to reduce the gas permeability of the flexible substrates 1. The internal construction of one of the substrates 1 is shown in Fig. 10. With reference to Fig. 10, a film 9 typically a polycarbonate film is used as a supporting substrate. A gas barrier layer 10 is applied to both sides of the film 9. The gas barrier layer may comprise EVA (ethylene-vinyl acetate copolymer) or PVA (polyvinyl alcohol). The coating layer 11 sandwiches both the gas barrier 10 and substrate 9 therebetween. Typically, the coating layer comprises phenoxy resin and provides a pencil hardness of not less than H (H being a recognised hardness according to the Japanese Industrial Standards, JIS K5400 item 6.14). Please refer to Appendix A attached hereto for a definition of this term.

The method of manufacturing the liquid crystal display element according to the first embodiment of the present invention is as follows. The transparent electrodes 2 are applied to the substrate 1 including the gas barrier film by a low temperature sputtering process. A predetermined pattern is then formed by a photolithographic process. The orientation film 3 is then attached and cured to the

electrode pattern by offset printing. The orientation film is then rubbed with a cloth in the predetermined direction to instil the predetermined alignment. The seal members 5 are then printed on one substrate by a screen process printing. The seal members comprise an epoxy system adhesive containing gap materials mixed therein. Spacers 4 are then sprayed on the substrate using a wet spray process. The two substrates are then bonded together so as to face each other. The number of spacers sprayed is 150 per mm². Using a vacuum injecting process, liquid crystal 6 is injected into the space between the substrates. The portion where liquid crystal is injected, is then sealed by the epoxy system adhesive.

The liquid crystal display element then undergoes further gas barrier treatment by the application of epoxy system adhesive 13 to both ends of the substrate which is then hardened. After polarising plates 7 are fixed to the upper and lower sides of the cell and the reflecting plate 8 mounted, the liquid crystal display element is finished. Such a liquid crystal display element utilizing a gas barrier means reduces the permeation of gas or water vapour into the liquid crystal by applying such to the end portions of the substrates or being welded by heat or the like.

For the purposes of this description, tests done on elements of the present invention were also conducted on a prior art liquid crystal display element as a comparison. In the prior art comparison, the element was comprised as above but without epoxy system adhesive being applied to the end portions of the substrate and then being hardened.

Tests were conducted using a tool 16 as shown in Fig. 12. The tool comprises a hard ball with a diameter of approximately 1cm and used to apply pressure of 2kgs for 3 seconds. Initially, both the liquid crystal display element according to the first embodiment and the comparison element were allowed to

stand at normal pressure and temperature. Then the pressure test was applied as above so as to form a nucleus 14 of a bubble as shown in Fig. 13. The bubble had a diameter of approximately $30\text{ }\mu\text{m}$. Both elements were then tested to measure the amount of time required for the nucleus 14 to disappear.

The results of the test are shown in Fig. 6. This is a graph giving the amount of time required for the nucleus to disappear plotted against the amount of time the display element is allowed to stand. In each case, if the element stands for greater length of time, then it takes a greater amount of time for the bubble nucleus to disappear. Fig. 6 shows the result of preparing 5 elements according to the first embodiment and five comparison elements. After 3000 hours have passed, a nucleus of a bubble is made in each of the ten elements. The amount of time required for the nucleus to disappear under normal pressure and temperature conditions is then measured. Each element is then left for 6000 hours. After 6000 hours, another nucleus of a bubble is made and again the amount of time required for the nucleus to disappear under normal pressure and temperature conditions is again monitored. This is repeated for all of the elements until 40,000 hours from the beginning of the test have passed. This results in a nucleus being made a total of six times in each element.

The values given for the liquid crystal display element of the first embodiment and a comparison element in Fig. 6 is thus the average of the five elements. Thus for example, the average of five elements being allowed to stand for 10,000 hours results in the bubble nucleus to disappear after just under 200 hours in the comparison product and in the present invention after 60 hours. After 20,000 hours, the bubble nucleus in the comparison element did not disappear but instead formed into another bubble 15 as shown in Fig. 14. Hence the bubble did not disappear. In contrast, the liquid crystal display element of the

first embodiment enabled the bubble nucleus to disappear even being allowed to stand for 40,000 hours.

Other embodiments of the present invention will now be described but it should be noted that the embodiments are not exclusionary and the features of one embodiment maybe applied with features from one or more of the other embodiments.

Embodiment No. 2

An element as described above in Embodiment No. 1 is shown in Fig. 2 with the modification that the polarising plates 7 and reflecting plate 8 were fixed to the substrates 1 prior to the epoxy adhesive been applied to both ends of the substrate and hence contacts the ends of the plates.

Embodiment No. 3

An element as described in Embodiment No. 1 is shown in Fig. 3 with the modification that the end portions were cut by a laser or a hot knife typically at a temperature of 250°C to seal the edges and adjacent substrates were then welded together to form a welding film 17.

Embodiment No. 4

As shown in Fig. 4, a liquid crystal display element similar to that described in Embodiment No. 1 forms this fourth embodiment. However, in this embodiment, the liquid crystal cell was totally immersed in the epoxy adhesive to form a film on the entire liquid crystal cell and then the polarising plates 7 were affixed thereto.

Embodiment No. 5

An element similar to Embodiment No. 1 is shown in Fig. 5. In this fifth embodiment, the ends of the substrates are immersed in the epoxy adhesive and the adhesive does not extend to the polarising plates 7.

Embodiment No. 6

In the sixth embodiment, the substrate 1 is constructed as shown in Fig. 11. In this embodiment, a polarising element film 12 is disposed between two polycarbonate films 9, the EVA films 10 and the phenoxy resin films 11. In this embodiment the substrate serves as a polariser and hence polarising plates 7 are not required. The epoxy resin may be applied in any manner as shown in Fig. 2 to 5.

When the aforementioned pressure test was applied to a liquid crystal display element according to the second to sixth embodiments, the same advantages were obtained as those according to the first embodiment.

Embodiment No. 7

The seventh embodiment is as described in the first embodiment but with a liquid crystal having an oxygen saturation solubility of not less than $10 \mu\text{l/ml}$, and preferably not less than $50 \mu\text{l/ml}$. The element was then allowed to stand for 200 days (i.e. 4800 hours). The pressure test as discussed above was then applied. In this case, no bubbles formed or small bubbles formed but disappeared quickly. Hereinafter, this is referred to as no abnormalities. However, if the liquid crystal had an oxygen saturation solubility of less than $10 \mu\text{l/ml}$, then a bubble 15 as shown in Fig. 14 was observed.

Embodiment No. 8

Again, a liquid crystal display element as described in the first embodiment was manufactured having a liquid crystal medium with a nitrogen saturation solubility of not less than $10 \mu\text{l/ml}$ and preferably not less than $50 \mu\text{l/ml}$. The element was again allowed to stand for 200 days or 4800 hours. When the same pressure test was performed, it was observed that no abnormalities occurred. However, if the saturation solubility of nitrogen was less than $10 \mu\text{l/ml}$, then a bubble formed in the display element.

Embodiment No. 9

A liquid crystal display element as described in the first embodiment again produced with a liquid crystal having a saturation solubility of water vapour of not less than 100 ppm and preferably not less than 300 ppm. The element was then allowed to stand for 200 days or 4800 hours. When the same pressure test was applied, it was observed that no abnormalities occurred in the element. However, if the saturation solubility of water vapour was less than 100 ppm, then a bubble formed in the liquid crystal display element.

Embodiment No. 10

An element as described in the first embodiment forms the subject of the tenth embodiment but controlling the degree to which either oxygen, nitrogen or water vapour or a mixture thereof was saturated in the liquid crystal immediately after the production of the liquid crystal display element. The degree was controlled to not more than 0.9 and preferably not more than 0.5. The degree is obtained as follows:

$$\frac{\text{solubility}}{\text{saturation solubility}} \begin{matrix} \text{(O}_2\text{)} \end{matrix} + \frac{\text{solubility}}{\text{saturation solubility}} \begin{matrix} \text{(N}_2\text{)} \end{matrix} + \frac{\text{solubility}}{\text{saturation solubility}} \begin{matrix} \text{(H}_2\text{O)} \end{matrix} \leq 0.9$$

The element was then allowed to stand for 200 days or 4800 hours. When applying the same test as applied above, no abnormalities occurred in the display element. If, however, the liquid crystal medium was saturated to more than one, bubbles formed in the liquid crystal display elements.

Embodiment No. 11

Three elements as described in the first embodiment were produced but with a different number of spacers sprayed onto the substrate. In each case, the elements were allowed to stand for 200 days or 4800 hours. Each element was

then subjected to the pressure test as described above. The different number of spacers was as follows: the first used 60 spacers per mm^2 , the second used 150 spacers per mm^2 and the third used 300 spacers per mm^2 . In the second and third element, no abnormalities occurred in the elements. However, the first having only 60 spacers per mm^2 formed a bubble such as shown in Fig. 14.

As a comparison, the same tests were conducted on the same elements as above but without the coating layer 11. In each case, irrespective of the number of spacers, bubbles as shown in Fig. 14 were formed.

Embodiment No. 12

A liquid crystal display element as described in the first embodiment was allowed to stand for 200 days or 4800 hours at normal pressure and temperature conditions. The element was then allowed to stand for 24 hours in a vacuum dryer under a reduced pressure of 50 torrs. When the pressure test as described above was applied, no abnormalities occurred in the element. However, if the same element was only allowed to stand for 200 days at normal pressure and temperature conditions and was not allowed to stand at the reduced pressure, this resulted in a bubble being formed as shown in Fig. 14.

Embodiment No. 13

A liquid crystal display element as described in the first embodiment was mounted on a piece of electronic equipment and used for more than 200 days or 4800 hours. An impact of some kind was then applied to the element thereby forming a bubble. The element was then pressurised to less than $3\text{kg}/\text{cm}^2$ in a pressurising tank for 50 hours so as to cause the bubble to disappear. The element then stood for 24 hours in a vacuum dryer under a reduced pressure of 50 torrs. When the pressure test was applied, no abnormalities occurred.

Embodiment No. 14.

An element as described in the first embodiment was placed in a vacuum dryer under a reduced pressure of 50 torrs immediately after it had been produced. The element was allowed to stand in this condition for 200 days or 4800 hours. In comparison, another element was allowed to stand for 200 days at normal pressure. When the pressure test was applied as described above, no abnormalities occurred in the element stored at the reduced pressure but bubbles as shown in Fig. 14 were formed in the element stored only at the normal pressure.

Embodiment No. 15

As shown in Fig. 7, an element as described in the first embodiment was vacuum packed using a film 23 which also provided a gas barrier. The same advantages of those attained in the first embodiment were also obtained.

Embodiment No. 16

Fig. 8 illustrates a number of elements 19 being arranged side by side on a tray 18 and vacuum packed by a film 23 having gas barrier characteristics. The same advantages as those attained in first embodiment were also obtained.

Embodiment No. 17

A liquid crystal display element as described in Embodiment No.1 was mounted on a piece of electronic equipment, such as a desktop computer, as shown in Fig. 9. The element 19 was disposed behind a transparent guard plate 20 which was clamped by an external frame 21. A decorative plate 22 was disposed thereover.

The thickness l of the guard plate and the space d between liquid crystal display element 19 and the guard plate 20 were varied. A pressure test such as the one described above was applied to the electronic equipment in a direction

perpendicular to the guard plate 20. The results of the pressure tests are as shown in table 1.

Table 1

Space d (mm)	Thickness l of guard plate (mm)				
	0.2	0.3	0.5	0.7	1.0
0.0	Bubble formation	Bubble formation	Unchanged	Unchanged	Unchanged
0.2	Bubble formation	Bubble formation	Unchanged	Unchanged	Unchanged
0.5	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged
0.8	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged

In the above table, bubble formation indicates a bubble being formed in the element as shown in Fig. 14. As is apparent from table 1, the optimum thickness of the guard plate was not less than 0.5 mm. The optimum space between the guard plate and liquid crystal display element was not less than 0.5 mm.

The element may be mounted on other pieces of electronic equipment such as pocket beepers, electronic pocket notebooks, measuring instruments, telephone handsets, facsimile machines, IC cards or personal computers.

As has been described above, the liquid crystal display element is described as having a pair of flexible substrates. The end portions of the substrates are treated so that the permeation of gas or water vapour into the liquid crystal is reduced. The end portions may be submerged in epoxy resin or subjected to heat.

The amount of time taken for gas or water vapour to be saturated in the liquid crystal resulting in the element being likely to produce bubbles has been increased by the present invention. The increase is achieved by using a liquid crystal which has an oxygen saturation solubility of not less than $10 \mu\text{l/ml}$, a

nitrogen saturation solubility of not less than 10 μ l/ml or a saturation solubility of water vapour of not less than 100 ppm. Furthermore, if the oxygen, nitrogen or water vapour or a mixture thereof is saturated in the liquid crystal immediately after the production of the element is controlled to less than 0.9, then the same can be achieved.

The number of spacers provided in the element vary in the range from 150 to 300 per mm^2 . A coating layer having a pencil hardness of not less than H is formed on the inner surfaces of the substrate next to the orientation film. This further reduces the formation of bubbles caused by an external force.

When manufacturing the element, if it is allowed to stand at a reduced pressure, then the amount of gas or water vapour that can permeate into the liquid crystal is decreased. Consequently, if the element is stored at a reduced pressure, then this decreases the permeation of gas or water vapour.

When such an element is mounted on a piece of electronic equipment, if the guard plate disposed over the liquid crystal display element has a thickness of 0.5 mm or more and the distance between the guard plate and the element is at least 0.5 mm or more, then the likelihood of bubbles forming can be diminished.

Hence, the present invention is able to provide a highly reliable liquid crystal display element which obviates poor display performance caused by bubbles through the elimination of bubble formation.

The foregoing description of the embodiments of the present invention have been given by way of example only and it will be appreciated by a person skilled in the art that modifications may be made without departing from the scope of the present invention.

APPENDIX A

Pencil hardness is an indication of the scratch resistance of the hard coat film when the film is scratched by pencils having different densities. The scratch test method and criterion for judgement are prescribed by Japanese Industrial Standard (JIS) K-5400 item 6.14 published in 1988. As the value of the scratch resistance, the density symbol of the pencil having the next highest density to the one having scratched the hard coat film is used.

The following is the classification of pencil densities prescribed by Japanese Industrial Standard (JIS) S-6005 published in 1992.

9H, 8H, 7H, 6H, 5H, 4H, 3H, 2H, H, F, HB, B, 2B, 3B, 4B, 5B, 6B

The above classification is based on the density only because the hardness is difficult to measure, and expresses numerically. However, the classification shows the hardness of pencil as well because the density and the hardness correlate with each other.

The following table shows the bending strength equivalent to each density mentioned above. (According to JIS 6005 published in 1992).

<u>Density symbols</u>	<u>Bending stress (MPa)</u>
9H - 7H	78.5 or more
6H and 5H	68.6 or more
4H - H	58.5 or more
F and HB	49.0 or more
B	39.2 or more
2B and 3B	29.4 or more
4B	24.5 or more
5B and 6B	19.6 or more

Hence, the coating layer having a pencil hardness of not less than H can be defined as a surface hardness greater than or equal to a pencil having a bending stress of 50MPa.



CLAIMS

1. A liquid crystal display element (19) comprising
a pair of flexible substrates (1) including a gas barrier layer (10);
orientation films (3) disposed on one side of said substrates;
an electrode layer (2) disposed on the same side of one of the substrates;
seal members (5) for bonding together said substrates having the sides of
said substrates facing each other;
a number of spacers (4) arranged between said substrates for providing a
predetermined gap therebetween;
a liquid crystal (6) sealed in said gap; and
means (7,12) for providing polarisation, characterised by the end portions
of the substrates being subjected to a gas barrier means(13,17).
2. A liquid crystal display element according to claim 1, wherein the liquid
crystal has an oxygen saturation solubility of not less than 10 μ /ml, and/or
nitrogen saturation solubility of not less than 10 μ /ml and/or a water vapour
saturation solubility of not less than 100 ppm.
3. A liquid crystal display element according to claim 1 or 2, wherein the
degree to which either oxygen, nitrogen or water vapour, or a mixture thereof, is
saturated in the liquid crystal immediately after the production of said liquid
crystal display element, is not more than 0.9.
4. A liquid crystal display element according to any one of claims 1 to 3,
wherein the number of said spacers ranges from 150 to 300 per mm².



5. A liquid crystal display element according to any one of claims 1 to 4, wherein each substrate comprises a number of layers including a coating layer (11) sandwiching the remaining layers therebetween having a surface hardness greater than or equal to a pencil having a bending stress of 50MPa.
6. A method of manufacturing a liquid crystal display element as claimed in any one of claims 1 to 5 characterised by subjecting the end portion of the substrates (1) to a gas barrier means (13, 17).
7. A method of manufacturing a liquid crystal display element as claimed in claim 6, further comprising maintaining the liquid crystal display element at a reduced pressure.
8. A method of storing a liquid crystal display element as claimed in any one of claims 1 to 5, comprising storing the liquid crystal display element at a reduced pressure.
9. Electronic equipment having a liquid crystal display element as claimed in any one of claims 1 to 5.
10. Electronic equipment as claimed in claim 9 further comprising a guard plate 20 disposed over said liquid crystal display elements having a thickness l of not less than 0.5 mm .
11. Electronic equipment as claimed in claim 9 or 10 in which the distance d between the guard plate and the element is not less than 0.5 mm.