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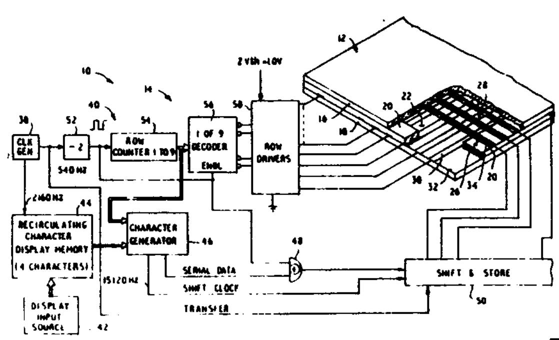
(54) **Matrix addressed electrochromic display device.**

(57) An electrochromic display device consists of orthogonal electrodes 26, 30 on the flat inner faces of a panel. The electrochromic composition in the panel, preferably a pyrazoline, has a threshold potential above which a display effect is achieved at a crossover point of the electrodes. The drive means 58 is of such low impedance and the electrodes are of such low resistance that the voltage levels at display sites (crossovers) are independent of whether or not a display is being effected at a display site. The display effect is temporary and is cyclically regenerated. The time average of voltage signals across unselected display sites is zero. Electrodes 28 consist of tin oxide and a central gold conductor 34 to decrease resistance. Electrodes 30 are of gold.



EP 0 000 616 A1

Croydon Printing Company Ltd.

TITLE MODIFIED
see front page

ELECTROCHROMIC DISPLAY DEVICE

This invention relates to an electrochromic display device comprising a pair of dielectric plates, at least one of which is transparent, sealed together to enclose an electrochromic redox composition, electrodes disposed on the inner faces of the plates so as to define display sites at each of which current may flow from an electrode on one face to an electrode on the other face, and drive means arranged to supply drive voltages selectively to individual electrodes.

Electrochromism is reviewed in the paper, Performance Characteristics of Electrochromic Displays, by Chang and Howard, published in the IEEE Transactions on Electron Devices, Vol ED-22, No. 9, September 1975 at pp 749 to 758. The type of display device with which this invention is concerned is described in this paper as employing electrochemichromic materials.

It is known to provide an electrochromic display in which a plurality of separate segments or display elements are individually energized to provide a desired display characteristic. One such arrangement is disclosed in U.S. Patent 4,008,950 to Chapman et al. However, such arrangements are relatively inconvenient for displays having a large number of display elements because individual control must be maintained over the energization of each display element.

An arrangement which avoids the necessity of separate electric connection to each display element is disclosed in U.S. Patent 3,864,589 to Schoot et al. In this arrangement a respective elongated electrochromic fluid cavity is provided for each of a plurality of rectilinear electrodes. A plurality of orthogonal electrodes are in contact with the fluid in each cavity. There is a common fluid-containing space above the cavities. This arrangement thus provides both a degree of electrical isolation of the individual display element cavities plus a simplified fluid filling procedure, and also provides coincident matrix selection of the individual display elements thereby reducing the complexity of the electrical drive circuitry.

Severe problems have heretofore limited practical applications of matrix addressed electrochromic displays. One is image diffusion and another is cross-talk or the effect which one display element has upon another. The patent to Schoot et al illustrates the two techniques which are most commonly used for minimising these effects. These are physical isolation of the individual display element cells and use of an electrochromic chemical system in which the coloured species deposits out on the electrode. While the use of a pool of electrochromic material as taught by Schoot et al reduces the manufacturing cost, the partial isolation used therein still maintains the manufacturing cost relatively high. The use of solid coloured materials limits the choice of the chemical systems which can be used and degrades the speed with which the cells can be coloured or erased. Furthermore, in addition to the direct conductivity of the electrochromic fluid between cells, another source of cross-talk is interaction between cells via the electrodes associated with the matrix. A coloured display cell in general has a different electrochemical potential difference across it than a clear cell. When these cells are connected together the coloured cell tends to drive or colour the clear cell. While eliminating the conductivity between cells, the Schoot et al arrangement still suffers from communication between the cells via the electrodes.

According to the invention, an electrochromic display device of the kind to which the invention relates is characterised in that, the inner faces of the dielectric plates are flat and each carry a set of display electrodes, the respective sets defining a matrix of display sites, the drive means is such as to supply to the display electrodes a voltage signal such that the potential difference between the electrodes at selected display sites only is at a level in excess of a given threshold, dependent on the electrochromic composition, and the drive means is of such low impedance and the electrodes of such low resistance that the voltage levels at display sites are independent of whether or not a display is being effected at a display site.

Preferably, the electrochromic composition is such that the display effect at a display site fades in the absence of a potential difference exceeding the given potential, and the drive means is arranged to supply cyclic pulse signals to selected display electrodes such that the display effect is regularly regenerated.

Preferably, the invention is further characterised in that, the drive means is arranged to supply voltage signals to electrodes such that the time average of the potential difference across unselected display sites is zero.

The preferred electrochomic composition includes a pyrazoline.

When the panel is driven by low impedance circuitry, the colouration decays spontaneously at each display element when the cross-point is not being held at a potential difference exceeding the threshold potential. The display is therefore driven in a periodic refreshed mode in which desired display elements are periodically refreshed to maintain colour and display elements which are not refreshed rapidly discolour.

Even though the coloured species may be soluble and thus free to diffuse throughout the display area, the spontaneous decay characteristic limits the diffusion to a distance comparable to the thickness of the cell. Since the cell can be thin compared to the width of a display element, there is no loss of image resolution due to diffusion.

The spontaneous decay rate of the chrominance depends on the voltage across the cell when the cell is not selected or driven above threshold. This voltage will vary in general with the information being displayed and causes chrominance variations. By using a special column and row drive technique in which the time average voltages appearing at display elements in unselected rows is always zero, this variation is eliminated.

The invention will further be explained by way of example with reference to the drawings in which:

Fig. 1 is a partly schematic and partly broken away perspective representation of a display device in accordance with the invention;

Fig. 2 is a schematic representation of the output stage of a low impedance row driver circuit in accordance with the invention;

Fig. 3 is a schematic representation of the output stage of a low impedance column driver circuit in accordance with the invention;

Fig. 4 is a graphical representation of the different waveforms that exist in the display device in accordance with the invention.

Referring to Fig. 1, an electrochromic display device 10 in accordance with the invention includes a display panel 12 and drive circuitry 14 coupled to drive the panel 12 in a matrix refresh mode of operation. The display panel 12 includes two clear glass plates 16, 18 disposed in closely spaced parallel opposed relationship and separated by a peripherally extending spacer 20 which sealingly engages the glass plates 16, 18 about their peripheries to maintain them in a desired spaced relationship and provide an interior cavity 22 between the two spaced apart plates 16, 18. The cavity 22 is filled with an electrochromic fluid which has a threshold voltage characteristic for electrocolouration and preferably has a relatively high resistivity.

A plurality of vertically extending or column electrodes 26 are disposed in parallel spaced relationship on the facing interior surface of upper clear glass plate 16 and a plurality of row electrodes 30 are disposed on a facing interior surface 32 of glass plate 18, which may or may not be transparent. The electrodes 26 and 30 extend through the display region and define a matrix of display sites, each site being disposed at a different crosspoint of a column electrode 26 and a row electrode 30. While the number and relative spacing of the column and row electrodes 26, 30 may depend upon a particular application for which the display panel 12 is designed, in the present instance the panel is suitable for the display of four data characters each represented by a display site array of 7 x 9 crosspoints. There are thus nine row electrodes 30 extending horizontally through the display region of panel 12 and 28 column electrodes 26 extending vertically through the display region of the panel 12. The size and shape of each display site is determined by the size and shape of the cross-over of the row and column electrode defining the site. The electrodes 26, 30 are thus made relatively wide with respect to the spacing between adjacent electrodes.

In the present example each column electrode 26 has a width of 0.508 mm (20 mils) and a spacing of 0.0762 mm (3 mils) is provided between adjacent column electrodes for a single character with a spacing of 1.168 mm (46 mils) being provided between the adjacent columns for adjacent characters. The row electrodes 30 have a width of 0.635 mm (25 mils) with a spacing of 0.0762 mm (3 mils) between adjacent electrodes. This results in a character height of 6.325 mm (0.249 inch) and a character width of 4.013 mm (0.158 inch). The column electrodes 26 are formed by selectively etching a Nesa coating on the interior surface 28 of glass plate 16 using conventional etching techniques. In addition, a fine gold conductor 34 is formed along each column electrode 26 in electrical communication therewith. The high conductivity gold electrode 34 affords each of the electrodes 26 a low resistance to permit cross-talk between display elements to be essentially eliminated by allowing the voltage at all locations along each electrode 26 to be controlled by the electronic circuitry and be substantially independent of the information being displayed. At the same time, the gold electrode 34 is sufficiently narrow that it is almost invisible and has very little effect on the viewing of displayed information.

The row electrodes 30 on the surface of glass plate 18 could be constructed in the same way as the column electrodes 26, but because they couple more display elements and thus carry more current and because they need not be optically clear, it is preferable that the row electrodes 30 be formed of a highly conductive material which is inert to the electrochromatic fluid such as gold or platinum. An underlayer of chrome is used to promote adhesion of gold to the glass surface 32. The specular reflection of the gold electrodes is preferably reduced by light sandblasting.

A number of competing factors are involved in determining the optimum spacing between the glass plates 16, 18 and the chemical composition of the electrochromic fluid. In general, it is desirable that the display elements show a high rate of increase of colouration at the energisation voltage and a decay rate response time constant which is relatively long for purposes of best colouration but short enough that the information content of the display may be readily changed.

The primary effect of spacing between glass plates is on the response time of the display. As a crosspoint is driven above threshold, coloured species are created at the electrode and begin to diffuse into the cell. This process continues until an equiblibrium is reached where the rate at which coloured species are produced equals the rate at which they disappear, either through bulk processes in the volume of the electrochromic liquid or by decolouration at an electrode. The time required to reach this equilibrium or the display response time is proportional to the diffusion time of a molecule across the cell thickness. Thus for fast response the spacing should be small. It is further desirable to keep the spacing small to reduce "blooming" of the image from the electrode, since the distance a coloured molecule will diffuse away from the electrode before it becomes decoloured by bulk processes may also be proportional to the spacing between plates. On the other hand the amount of coloured material available under equilibrium conditions to produce a change in chrominance is proportional to the spacing between plates, hence to achieve a high degree of colouration larger spacing is preferred. If the spacing is reduced the rate of colouration must be increased to achieve the same level of colouration or chrominance. Further, decreasing the spacing between glass plates 16, 18 increases the current density by decreasing the resistance between the opposing column and row electrodes 26, 30 and simultaneously increases the resistance presented by the electrochromic fluid to spreading of the electrical energization of a cell to surrounding areas. Increasing the conductivity of electrochromic fluid improves the rate of increase of colouration, but also reduces the resistance to spreading of cell energisation. In general, it has been found that the spacing between the glass plates 16, 18 should be between 0.0127 mm (.0005 in.) and 0.127 mm (.005 in.) with a spacing of approximately 0.0381 mm (0.0015 in.) being optimum. The decay time constant of the electrochromic fluid is preferably between 0.1 and 0.4 second and the resistivity of the electrochromic fluid is preferable between 5000 and 50 ohm-centimeters.

In general, the electrochromic fluid disposed in the cavity 22 between the plates 16, 18 should consist of a redox couple which will react reversibly at the anode, a second redox couple which will react reversibly at the cathode, a salt which is electrochemically inert and provides the required electrical conductivity to the formulation, and a solvent for dissolving the other three components. One or both of the redox couples should provide a change in colouration upon oxidation or reduction to facilitate the display of desired information upon electrical energisation. For energisation in a coincident matrix address mode, the electrochromic fluid should also have a threshold voltage characteristic.

It should be realised that the electrochromic solution is in physical contact with a given row and column electrode for the entire length of these electrodes in the active display area of the panel, yet when a potential difference is applied across the electrodes by the drive circuitry to properly display the desired information, the current flow which produces the colouration should be localised to the area where the two electrodes overlap. This can be accomplished if the lateral resistance of the electrochromic solution is high compared to the resistance along an electrode. The current will thus be confined to the electrodes except when it must pass through the solution to cross between electrodes where they are most nearly in contact. To obtain the proper high resistance ratio of the solution to the electrodes it is desirable to use non-aqueous solvents, since salt solutions of these solvents in general are not as conductive as aqueous salt solutions. In general, electrochromic fluid formulations of the type described in U.S. Patent 3,451,741 are operative. It has been found that solutions which use pyrazoline material as the colour forming redox couple are particularly effective and some of these materials show an exceptionally high electrochromic efficiency.

One electrochromic fluid formulation which has been found to be particularly useful is 0.09 mole of 1-p-methoxyphenyl-3-p-diethylamino styryl-5-diethylamino phenyl-Δ^2-pyrazoline, 0.2 mole phenyl-p-benzoquinone, and 0.4 mole tetrabutylammonium fluoroborate in methylethyl ketone. A second formulation which has been found to be particularly suitable is 0.2 mole 1-p-methoxy-phenyl-3-p-dipropylamino styryl-5-dipropylamino phenyl-Δ^2-pyrazoline, 0.4 mole phenyl-p-benzoquinone, and 0.8 mole tetrabutyl-ammonium fluoroborate in methylethyl ketone.

Because the column and row electrodes 26, 30 are driven by low impedance sources, the individual energised electrochromic cells discharge through the electrodes. The cell decay is thus dependent upon the voltage across the electrodes and there is a tendency for the cells along a given column electrode for which a large number of the cells are energised for a particular display to experience a much greater average voltage potential and thus decay much more slowly than for example a cell along a column electrode for which only a single cell is energised for a given display. As a result, the cells along a column electrode having multiple energised cells would present an apparent increased chrominance compared to a cell energised along a column electrode for which only one cell is energised. For example, the uprights of an H pattern would display an increased chrominance relative to the crossbar.

The drive circuitry 14 eliminates this pattern sensitive chrominance intensity problem by driving the electrodes in a special mode such that the time average voltage applied to all display elements is identical. The display is refreshed at a rate of 30 refreshes per second which is sufficiently rapid that the human eye integrates the light emanating from the display and does not see the results of individual refreshes.

The drive circuitry 14 is shown in somewhat simplified form in Fig. 1 and includes a clock generator 38 and a divide-by-two counter 52 which generate a 540 hertz clock signal and a 270 hertz clock signal respectively, row select circuitry 54, 56 and 58 which sequentially select the row electrodes for energisation, in response to the 270 hertz clock signal, a display input source 42 which may be a microprocessor or any other source of characters to be displayed, a recirculating character display memory 44 which stores the characters which are to be displayed and sequentially presents them to a character generator 46, an Exclusive-OR gate 48 and a 28 bit shift and store circuit 50. The row select circuitry 40 includes a divide-by-two counter 52 which is responsive to the 540 hertz clock pulse, a divide-by-nine row counter 54 which is responsive to the 270 hertz output of divide-by-two counter 52, a one of nine decoder 56 which decodes the output of row counter 54, and row drivers 58 which drive the individual row electrodes of the display panel 12 in response to the outputs from decoder 56 and divide-by-two counter 52.

Because each row electrode communicates with 28 individual display elements or cells, each of which may produce a current load of 1 milliamp, the maximum current load is 28 milliamps. A larger 16 character display may produce a current load as high a 112 milliamps for the row driver 60.

A totem pole inverter circuit 60 shown in Fig. 2 is capable of handling this current load and providing the required low impedance output which is preferably less than 300 ohms to each of the row electrodes. The row drivers 58 thus might include nine of the inverter circuits 60 each being responsive to a different output from the decoder 56.

Decoder 56 is enabled during only a second half of each row period by the 50% duty cycle signal the divide-by-two counter 52. Thus during the first half of each row period all row electrodes 26 are coupled to ground and during a second half of each row period a selected one of the nine row electrodes is driven at a voltage of +1 volt while the other eight remain at ground potential.

The display input device 42 provides data information to the recirculating character display memory 44 which sequentially outputs the four display characters at a rate of 2160 characters per second. At this speed, all four display characters are output for each half of a row update period. Character generator 46 responds to the data characters indicated by memory 44 and to the row update information from row counter 54 to provide that pattern refresh data at a serial data rate of 15,120 display elements per second. This data rate enables the refresh dot display data for a given row position to be provided to shift and store circuit 50 during each half of a row refresh time period. Exclusive-OR gate 48 responds to the output of the divide-by-two counter 52 and to the serial data output of character generator 46 to pass to shift and store circuit 50 the required dot pattern update data during the first half of a row period and the complement of the dot pattern update data during the second half of the row period.

Shift and store circuit 50 is a combination 28 bit serial in parallel out shift register and 28 latches which receive and latch the parallel outputs of the shift register. It may be similar to a series combination of four RCA C-Mos CD 4094 8 bit shift and store integrated circuits. The shift and store circuit requires output drivers such as the C-Mos output driver 62 shown in Fig. 3 to maintain the column outputs at either +0.5 volts or -0.5 volts. Each output of driver 62 preferably has an impedance less than 300 ohms. During the first half of a row refresh period, the un-complemented dot display refresh pattern for a given row is shifted into shift and store circuit 50. At the end of the first half of the row refresh period the dot pattern information is loaded into the output latches to drive the column electrodes while the decoder 56 is enabled to cause a selected row electrode to be energised to provide a co-incident selection dot display element energisation for one row of display cells in the display panel 12. Also during the second half of the row refresh period the output of divide-by-two counter 52 drives Exclusive-OR gate 48 with a logic one input to cause the complement of the dot refresh pattern data for the next row refresh period to be loaded into shift and store circuit 50.

At the end of the second half of the row refresh period, the complement refresh dot pattern data for the next period is loaded into the latches of shift and store circuit 50 to drive the column electrodes with complement refresh data during the first half of the next row refresh period while uncomplemented dot refresh data corresponding thereto is serially shifted into shift and store circuit 50. Thus during the first half of each row refresh period the shift and store circuit drives the column electrodes with the complement of the dot refresh pattern data for the row re-fresh operation. However, because the row decoder 56 is not enabled during this first half of a row refresh period, the complement data does not exceed the threshold voltage at any column position in the display panel 12 and cannot cause the energisation of a display cell. Nevertheless each column electrode is necessarily driven alternately with

+V threshold for 1/2 row period and -V threshold for another 1/2 row period to provide a time average of 0 volts during the non-select time. Therefore, the discharge rate and hence apparent colouration of the cell is independent of the information being displayed.

A further understanding of the refreshing of a cell may be had from reference to Fig. 4 which shows the row voltage column voltage, and total voltage at a given cell for the four possible different voltage states corresponding to the row selected or non-selected and the column write or clear. Row energisation period states A represents a condition corresponding to full selection with the row selected and the write waveform of the column. During the first half of state A, a given selected cell receives a total voltage thereacross of 1.5 volts. This is three times the threshold voltage of 0.5 volts and causes the cell to rapidly recharge and display a chrominance differential from non-charged display cells. During the first half of state A the selected cell experiences a voltage thereacross of -0.5 volts.

State B represents a partial selection condition in which a given cell is row selected but is not column selected. During the second half of state B the given cell experiences a total voltage of +0.5 volts. This is equal to the voltage threshold of the cell and is insufficient to charge the cell. The cell thus remains in its uncharged nonchrominant state. During the first half of state B the electrodes are energised with -0.5 volts on the column electrodes and 0 volts on the row electrode to provide a total voltage across the cell of +0.5 volts. Thus, even though the select waveform is applied to the row electrode, the crosspoint voltage does not exceed the threshold at any time during the period and no colouration occurs.

In a similar manner the crosspoint voltages corresponding to time period C, row non-selected and column write, and D, row non-selected and column clear, can be obtained. Since the row non-selected waveform is always zero the crosspoint voltage is simply the inverse of the column waveform and never exceeds the threshold value of 0.5 volts.

During eight out of nine of the row refresh periods a cell will remain unselected by the row electrode with either the write waveform on the column electrode as shown for state C or with the clear waveform on the column electrode as shown for state D. Regardless of which column selection condition exists, the given cell experiences either + or -0.5 volts during the first half of the row refresh period and the complement - or +0.5 volts during the second half of the row refresh period. The cell thus experiences a time average 0 volts during eight out of nine of the row refresh periods without regard to the data information being displayed. As long as the non-selected row waveform is zero, this condition only depends on using symmetrical column waveforms and is independent of the ratio of the row to column voltages. During the non-selected row refresh periods the display decay rate and hence chrominance for energised cells is thus independent of the particular display pattern and the chrominance remains uniform and constant for all energised cells.

CLAIMS

1. An electrochromic display device comprising a pair of dielectric plates, at least one of which is transparent, sealed together to enclose an electrochromic redox composition, electrodes disposed on the inner faces of the plates so as to define display sites at each of which current may flow from an electrode on one face to an electrode on the other face, and drive means arranged to supply drive voltages selectively to individual electrodes, characterised in that the inner faces of the dielectric plates are flat and each carry a set of display electrodes, the respective sets defining a matrix of display sites, the drive means is such as to supply to the display electrodes a voltage signal such that the potential difference between the electrodes at selected display sites only is at a level in excess of a given threshold, dependent on the electrochromic composition, and the drive means is of such low impedance and the electrodes of such low resistance that the voltage levels at displays sites are independent of whether or not a display is being effected at a display site.

2. A device as claimed in claim 1, characterised in that the electrochromic composition is such that the display effect at a display site fades in the absence of a potential difference exceeding the given potential, and the drive means is arranged to supply cyclic pulse signals to selected display electrodes such that the display effect is regularly regenerated.

3. A device as claimed in claim 2, characterised in that the drive means is arranged to supply voltage signals to electrodes such that the time average of the potential difference across unselected display sites is zero.

4. A device as claimed in claim 2 or claim 3, characterised in that the electrochromic composition includes a pyrazoline.

5. A device as claimed in claim 2 or claim 3, characterised in that the electrochromic composition consists of

methyl ethyl ketone solvent containing

0.09 mole 1-p-methoxyphenyl-3-p-diethylamino styryl-5-diethylamino phenyl-Δ^2-pyrazoline,

0.02 mole phenyl-p-benzoquinine, and

0.4 mole tetrabutyl ammonium fluoroborate.

6. A device as claimed in claim 2 or claim 3, characterised in that the electrochromic composition consists of

methyl ethyl ketone solvent containing

0.2 mole 1-p-methoxyphenyl-3-p-dipropylamino styryl-5-dipropylamino phenyl-Δ^2-pyrazoline,

0.4 mole phenyl-p-benzoquinine, and

0.8 mole tetrabutyl ammonium fluoroborate.

7. A device as claimed in any one of the preceding claims, wherein the inner faces of the dielectric plates are spaced apart a distance in the range 0.0127 mm to 0.127 mm.

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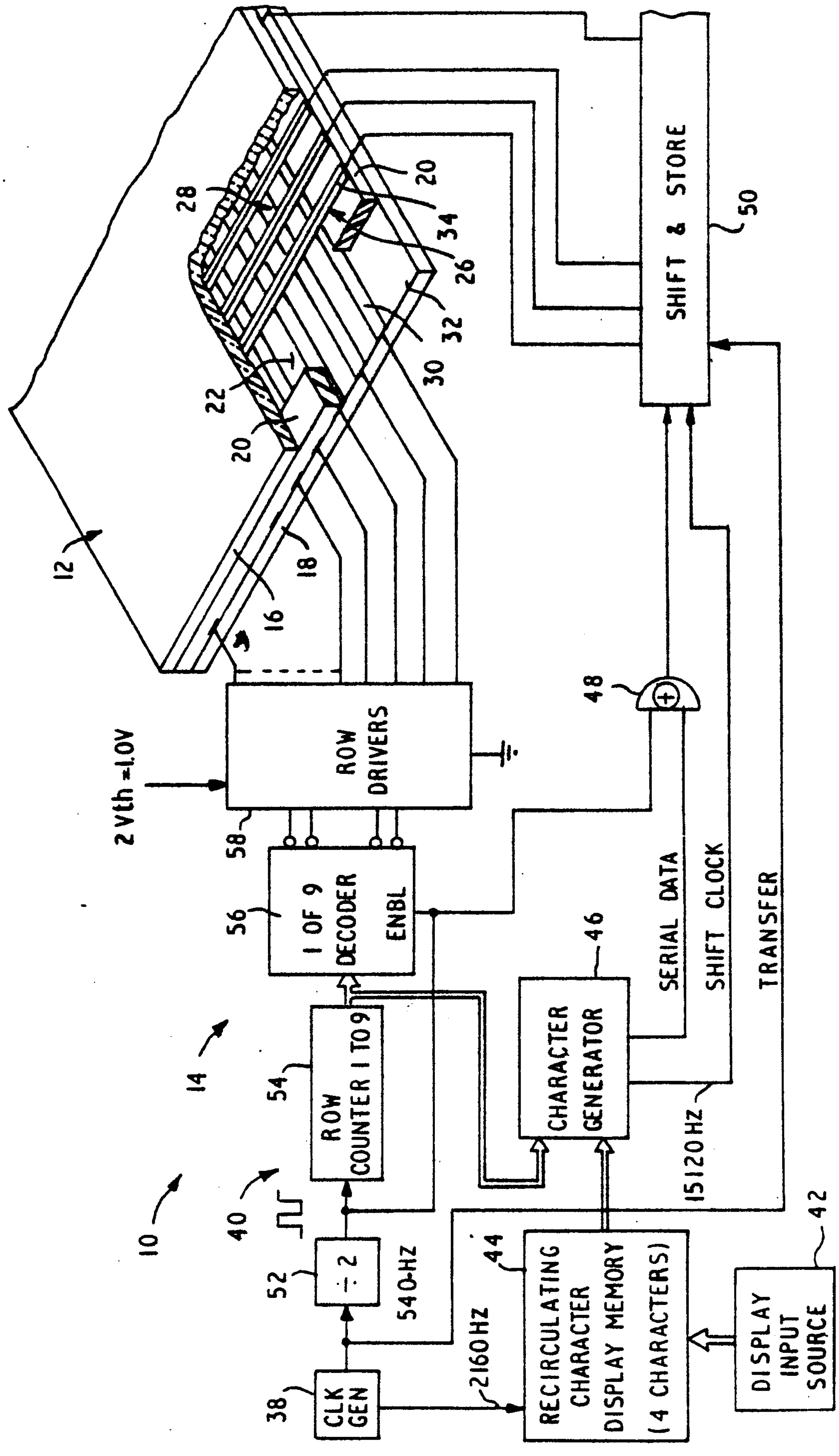

12
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34
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SHIFT & STORE
50
48
ROW DRIVERS
2 Vth ≈ 1.0V
58
1 OF 9 DECODER
ENBL
56
CHARACTER GENERATOR
46
SERIAL DATA
SHIFT CLOCK
TRANSFER
14
ROW COUNTER 1 TO 9
54
10
40
÷ 2
52
540-HZ
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DISPLAY INPUT SOURCE
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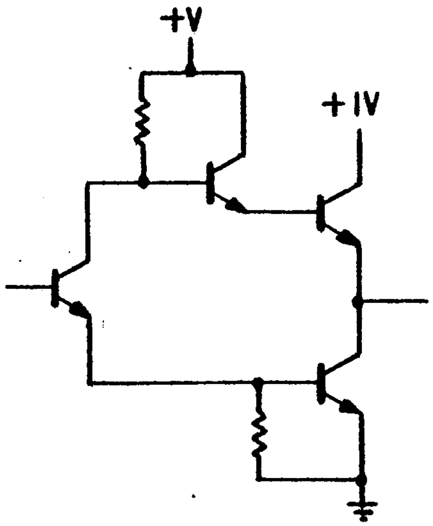
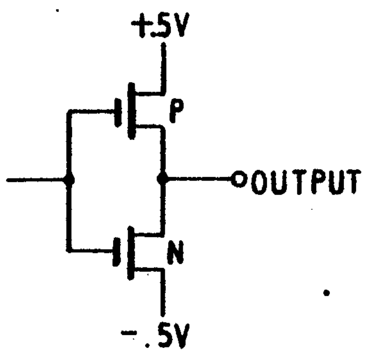
15120Hz



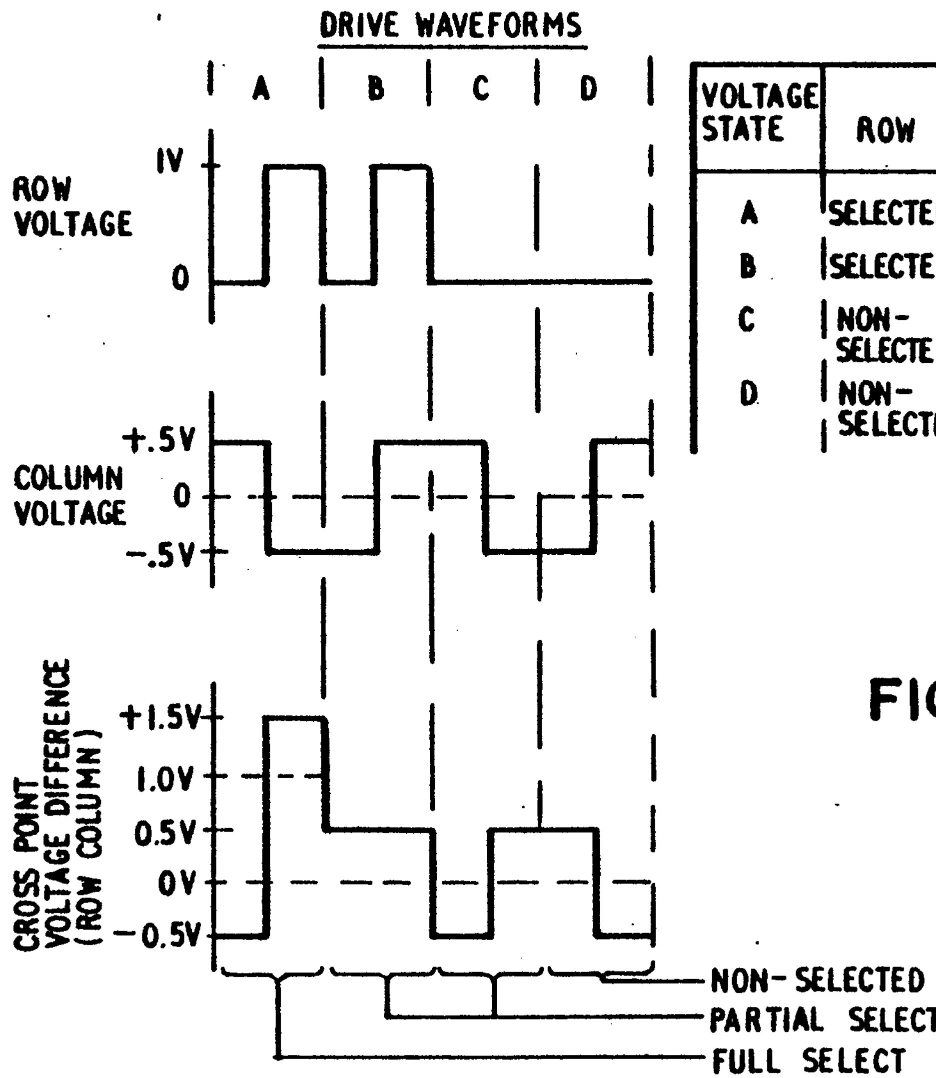
ROW DRIVER 60.

FIG. 2



COLUMN DRIVER 62

FIG. 3



VOLTAGE STATE	ROW	COL. WAVE-FORM	CROSS POINT VOLTAGE (ROW COLUMN)
A	SELECTED	WRITE	-.5 / 1.5V
B	SELECTED	CLEAR	.5/ .5V
C	NON-SELECTED	WRITE	-.5/+.5V
D	NON-SELECTED	CLEAR	+.5/-.5V

FIG. 4

European Patent Office

EUROPEAN SEARCH REPORT

0000616

Application number

EP 78 30 0063

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CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

G 02 F 1/17

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

G 02 F 1/17
G 06 F 3/14
G 04 C 17/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search | Date of completion of the search | Examiner

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EUROPEAN SEARCH REPORT

0000616

Application number
EP 78 30 0063.5
-2-

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
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