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## **3,015,747** Patented Jan. 2, 1962

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## 3,015,747 FLUORESCENT SCREEN Barnett Rosenberg, New York, N.Y., assignor to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania Filed June 19, 1959, Ser. No. 821,510 6 Claims. (Cl. 313-108)

This invention relates to a fluorescent screen, and more particularly to a fluorescent screen for the production of 10 color images.

It has been known for some time that certain materials will exhibit fluorescence in aqueous solutions over a limited range of pH values (i.e. hydrogen ion concentration), when excited by electromagnetic radiation such as 15 ultra violet. These materials are presently being used as indicators to determine the pH of solutions and also in chemical analysis procedures to adjust the pH of a solution to a desired value. In these procedures a small 20 quantity of such an indicator is added to a solution, the pH of which is to be adjusted. The indicator added is generally in a fluorescent state at the pH desired and in a non-fluorescent state at all other pH values. The solution is positioned so that electromagnetic radiation such as ultra violet is incident thereon and either an acid or 25 a base is slowly added until the solution fluoresces. At this point the pH is that at which the indicator is known to change from the non-fluorescent to the fluorescent These materials are especially adapted to be used state. in imaging display devices because of the quantum efficiency of fluorescence. That is, the energy output comes close to the energy input. Further by a proper choice of the indicator any desired fluorescent color can be obtained.

For use as an imaging device it is necessary to alter 35 the pH of the solution independently over elementary areas of the solution. This can be accomplished by providing a grid like structure of conductors on either side of the solution. By impressing an electric field gradient across the solution a charge migration will result and a large concentration of negative ions will surround the positive electrode and a large concentration of positive ions will surround the negative electrode, thus changing the pH over an elemental area. The indicator chosen will be such that it is in the non-fluorescent state when a field is applied and in the fluorescent state when a field is applied across the solution.

By the use of an electrode system that will provide a plurality of continuing paths through the solution, a cell member containing such a solution may be utilized as an 50 imaging display device.

It is, therefore, an object of this invention to provide an improved image display device.

Another object is to provide a colored imaging display device.

A further object is to provide an improved imaging display device that may be viewed in ordinary light.

An auxiliary object is to provide an improved imaging display device utilizing a material which exhibits a body color change upon a change in hydrogen ion concentration.

An additional object is to provide an improved imaging display device having good definition and brightness characteristics.

A supplementary object is to provide an improved **65** imaging display device utilizing fluorescent indicators.

These and other objects of this invention will be apparent from the following description taken in accordance with the accompanying drawing throughout which, like reference characters indicate like parts, which drawing forms a part of this application in which:

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FIGURE 1 is a cutaway perspective view of a mono-

2

color image display device in accordance with this invention,

FIG. 2 is a cross-sectional view of a tricolor image display device in accordance with this invention, and;

FIG. 3 is an exploded perspective view of the embodiment shown in FIG. 2, together with associated circuitry.

In FIG. 1, there is illustrated a cutaway perspective view of a monocolor image display device comprising a single cell member 11. The cell member includes a first support member 13 transmissive to electromagnetic radiation, such as glass. The support member 13 is provided with a first grid member 15 comprising a plurality of electrically conducting members 17 which are arranged in a parallel fashion. Adjacent the conducting member 15 is disposed a voltage controllable fluorescent solution 19. That is a solution which will change from a non-fluorescent state to a fluorescent state upon the application of a voltage across the solution. It is to be understood that in this application including the claims the term "solution" includes, but is not limited to liquid solutions, solid solutions, colloids, sols, suspensions, gels, suspended particles in a generally wide range of sizes and materials impregnated with a synthetic resin.

An example of such a solution may be made by dissolving a suitable fluorescent indicator such as brilliant diazo yellow, chromotropic acid, Cleve's acid, coumaric acid, dichlorofluorescein, eosin, eosin yellow, eosin BN porphyrin and other materials which will exhibit fluorescence upon a change in the hydrogen ion concentration 30 in a water, alcohol or glycerine solvent. To this solution is added a small quantity of a highly ionized salt, such as potassium chloride, sodium chloride, sodium fluoride, sodium sulfate and other such salts of this class. Those salts are to be used which have no quenching effect on the solution fluorescence. The solvent chosen to dissolve the organic dye should be miscible with water to guarantee the complete solution of the water soluble indicator and salts. If it is desirable gelatin may be added to form a gel of the solution. The pH of the solution is then adjusted to that value at which the indicator will be in the non-fluorescent state.

On the opposing side of the solution 19, with respect to the first support member 13, is disposed a second support member 21 having a second grid member 23 of parallel conductors 25. Conductors 25 are disposed at an angle with respect to the conductors 17 on the first support member 13, so that projections of both grid members 15 and 23 form an intersecting pattern. It is preferable that the conductors 17 on the first support member 13 be at right angles with the conductors 25 on the second support member 21 but any angle will operate satisfactorily. A source of electromagnetic radiation 27, such as ultra violet light, may be positioned around the cell structure 11 or may be spaced from the cell structure 11 in such a manner that the rad ation is 55 incident upon the voltage controlled fluorescent solution 19.

The conductors 17 and 25 may also be covered with an insulating layer (not shown) to prevent electrolytic 60 action at the electrodes. Of course, if the voltage controlled fluorescent solution 19 is a liquid, the volume between the support members should be made liquid tight by sealing the support members together around their periphery by a suitable insulating material, such as g'ass.

In operation, a video signal would be impressed on one of the conductors 17 and 25 of each grid member in accordance with the incoming information bearing signal. At the point where the two conductors cross the ions in the voltage controlled fluorescent solution 19 will migrate toward the conductors 17 and 25 causing a change in the hydrogen ion concentration of the solution over a small elemental area of the entire cell member 11. Upon the incidence of ultra violet radiation, this point will be the only point to emit visible light since the remainder of the solution in the cell 11 has not been altered from its non-fluorescent state. In this manner, an image could be produced by applying a time 5 sequential information bearing signal to the conductors 17 and 25. The associated circuitry shown is one means by which an information bearing signal could be distributed so as to form a visible image.

As shown in FIG. 1, the video signal is derived from 10 a video signal source 10 which may be a video information bearing signal from the video amplifier of a conventional television receiver circuit. Synchronizing information is derived from the video signal in the sync separator 12. The sync signal is resolved into X and 15 Y components in the X scan generator 14 and the Y scan generator 16 and applied to the X distributor 18 and the Y distributor 20 respectively. The distributors 18 and 20 have a plurality of output circuits 22 and 24 for sequential application of the switching pulses to the 20 conductors 17 and 25 respectively. The distributors 18 and 20 may comprise pulse delay lines constructed in accordance with practices well known in the art and there may be other types as described in copending application Serial No. 747,799 entitled "Signal Distribu- 25 tion System," by Francis T. Thompson, filed July 10, 1958, and assigned to the same assignee.

The inelligence signal from the video source 10 is fed directly to the X distributor 18 and through a phase inverter 26, to reverse the polarity, to the Y distributor 30 20. These information bearing signals are applied sequentially in accordance with the scanning rate to produce an image on cell member 11.

The conductors 17 and 25 may be made by evaporating metallic materials onto a glass plate and then rul- 35 ing away a portion to form parallel conductors. Another method would be to evaporate a metallic material through a masking pattern. The conductors 17 and 25, if made of a metallic material, should be a thin laver which would not render the conductors opaque. Metal- 40 lic materials that may be used for the conductors 17 and 25 include: aluminum, cadmium, platinum, nickel and silver. The conductors 17 and 25 also may be a coating of tin oxide. Conductors of tin oxide may be made by spraying a solution of stannic chloride onto the glass 45 support members 13 and 21 which have been heated to a temperature of approximately 600° C. To prevent electrolytic action at the conductors 17 and 25, they may be coated with a thin layer of insulating material such 50 as polyethylene or nylon.

A specific example of the solution used in the cell member 11 may be made by dissolving one gram of dichlorofluorescein in alcohol, such as a methyl, ethyl, butyl type of alcohol or any other alcohol which is 55 miscible with water. This solution of the dichlorofluorescein in alcohol is then admixed with one liter of water. To this solution is added 50 to 100 grams of sodium chloride. The solution is then adjusted to a pH value of below 4. In this condition, the solution is in the non-fluorescent state. When the pH is changed by any means to the range of 4 to 6, the solution is rendered florescent and will emit light in the green region of the spectrum upon the incidence of ultra violet light. For optimum light output the cell member should be approximately .004 inch thick but for varied uses it may 65 be between .0005 inch and .008 inch.

FIG. 2 shows an arrangement wherein a series of three cells 35, 37 and 39, as described in FIG. 1, are arranged in a parallel adjacent relationship. By this arrangement, each cell may contain a different voltage 70 controlled fluorescent solution which emits in the red, green and blue regions of the visible spectrum, to obtain a colored imaging device. A material which will undergo a change from the non-fluorescent state to a fluorescent state in the red region of the spectrum is 75 material which undergoes a color change from colorless

porphyrin. This material is non-fluorescent in alkali solution and fluorescent in acid solution. A solution which will undergo a change from the non-florescent state to a fluorescent state in the blue region of the spectrum is chromotropic acid. This acid will be fluorescent at a pH of 3.5 to 4.5 and non-florescent at other pH's. A solution which will undergo a change from the nonfluorescent state to a fluorescent state in the green region of the spectrum is coumaric acid or dichlorofluorescein. Coumaric acid undergoes a change from non-fluorescent to the fluorescent state when a change in the pH occurs to 6 to 8, while dichlorofluorescein undergoes a change from the non-fluorescent to the fluorescent state by a change in pH to 4 to 6. The conductors of each of the cell members are in registry so that by color addition any elemental area may appear to the eye to have any color of the visible spectrum.

Each cell member 35, 37 and 39 is identical with the exception that each cell contains a different solution. For example cell 35 may contain porphyrin which will fluoresce in the red. Cell 37 may contain chromotropic acid which will fluoresce in the blue and cell 39 may contain coumaric acid which will fluoresce in the green.

As shown in FIG. 2, cell member 35 includes support member 36 having conductors 38 disposed thereon, a voltage controlled solution 41 and support member 43 having conductors 45 disposed thereon. Cell member 37 includes support member 43, which is common to both cell members 35 and 37, and has disposed thereon conductors 47 on the side opposed to that on which conductors 45 are located. The cell member 37 also includes a voltage controlled solution 49 and a second support member 51 having conductors 53 disposed thereon. Cell member 39 includes support member 51, which is common to both cell members 37 and 39. Conductors 55 are disposed on the surface of support member 51 opposed to the surface on which conductors 53 are located. The cell member 39 also includes a voltage controlled solution 57 and a second support member 59 having disposed thereon conductors 61. The solutions are contained within each of the cell members 35, 37 and **39** by the envelope **63** which makes a liquid tight joint with support members 36, 43, 51 and 59 around their periphery. The adjacent cell members may have common support members as shown in FIG. 2, or they may be a series of stacked individual cells arranged in parallel adjacent relationship.

In FIG. 3 there is shown an exploded view of a series of cell members 35, 37 and 39 arranged for color rendition. The cells may be as shown in FIG. 2 or they may be a series of individual cells, each containing a different solution and arranged in a stacked relationship.

The circuit for the application of intelligence signals to the cells is substantially the same as that shown in FIG. 1 with the exception that a synchronous demodulation means 40 is included between the video source 10 and the phase inverter 26 to separate the red, green and blue color signals. The phase inverters and X and Y distributors for the green and blue signals have been omitted for the purpose of simplicity but this portion of each circuit may be identical with that shown for the red signal with the exception that the output circuits of the distributors would be connected to cells 37 and 39. As can be seen in FIGS. 2 and 3 the conductors of each cell are in registry, therefore by applying time sequential signals to each cell simultaneously, the image produced will appear to the viewer to be a colored replica of the scene being reproduced.

In some instances, it may be desirable to utilize materials which undergo a body change in color, instead of a change from a non-fluorescent to a fluorescent state. In such an example, the color of an elemental area would be arrived at by the subtractive method. In such an instance, the solution of each cell would contain a

5

to red, blue and yellow. Table I lists examples of materials that exhibit these properties together with the pH range and the color of each in the colored and colorless state.

Indicator	Acid Color	pH Tran- sition Range	Basic Color	
Quinaldine Red 2,4-Dinitro Phenol 2,5-Dinitro Phenol Heptamethoxy Red p-Nitro-Phenol Quinoline Blue Ethylbis - 2,4 - Dinitro - phenol- acetate, O-Cresolphthalein Thymolphthalein.	Red	6.6-8.6	Red. Yellow. Colorl:ss. Yellow. Blue. Blue. Red. Blue.	10 15

In such an embodiment as this, the ultra violet source 27 would be removed and a source of white light would be placed on the side of the cell structure opposite to the viewing side. This may take the form of a white emitting electroluminescent plate.

The dyes should have narrow absorption bands in the spectral regions. The color the dye takes when activated must be that of white light minus the region it absorbs. Thus for a black point on the picture, all three layers must be activated by a voltage pulse. For a white point on the picture no layers are activated. For a red signal the two layers that transmit red but absorb the blue and 30 yellow are activated.

A specific embodiment of a single cell structure would have a total thickness of approximately 0.25 inch the thickness of the conductors would be 0.245 inch and the thickness of the voltage controlled solution would be  $_{35}$ 0.005 inch.

Such a system as described herein would find application in devices such as panel TV, plotting boards and panel displaying systems. In all of these systems, the desideratum is to control the light output, that is, intensity or color from an element of area of a broad area surface in proportion to some electrical or optical signal on that area. By the use of the voltage controlled fluorescent solutions as described herein, it is believed that many of the disadvantages which are found in the current devices, such as a need to reduce the ambient light surrounding the particular device, are eliminated.

While the present invention has been shown in several forms only, it will be obvious to those skilled in the art that it is not so limited, but is susceptible of various 50 changes and modifications without departing from the spirit and scope thereof.

I claim as my invention:

1. A color imaging screen comprising a plurality of cell members arranged in parallel relationship, each of said cell members including a solution capable of being transformed from a non-fluorescent to a fluorescent state upon a change of the hydrogen ion concentration of said solution, each of said cells having a different characteristic emission wavelength, a source of electromagnetic radiation positioned so as to irradiate said plurality of cells and a means for changing the hydrogen ion concentration of discrete elemental areas of said cell members.

2. A color imaging screen comprising a plurality of cell members arranged in parallel relationship, each of said cell members including a solution capable of being transformed from a non-fluorescent to a fluorescent state upon a change of the hydrogen ion concentration of said solution, each of said cells having a different characteristic emission wavelength, a source of electromagnetic radi-70 ation positioned so as to irradiate said plurality of cells

and a means for changing the hydrogen ion concentration of discrete elemental areas of said cell members, said means including a series of conductors on either side of each cell member so that projections of each form an intersecting pattern.

3. A color imaging screen comprising, a plurality of cell members arranged in parallel relationship, each of said cell members including a solution capable of being transformed from a non-fluorescent to a fluorescent state upon a change of the hydrogen ion concentration of said solution, each of said cells having a different characteristic emission wavelength, a source of electromagnetic radiation positioned so as to irradiate said plurality of cells and a means for changing the hydrogen ion concentration of discrete elemental areas of said cell members, said means including a pair of grid members associated with each of said cell members, said pair of grid members including a first grid member and a second grid member, said first grid member of each pair being disposed on one side of said associated cell member and including a plurality of parallel spaced conductors, the second grid member of each pair being disposed on the opposing side of said associated cell member and including a plurality of parallel spaced conductors being substantially at right angles to said conductors of said first grid member so that 25 projections of both grid members form an intersecting pattern.

4. An imaging screen comprising a cell member including a solution capable of being transformed from a nonfluorescent to a fluorescent state upon a change of the hydrogen ion concentration of said solution, said solution comprising a solvent. a readily ionizable salt and a material selected from the group consisting of diazo yellow, chromotropic acid, Cleve's acid, coumaric acid, dichlorofluorescein, eosin, eosin yellow and eosin BN porphyrin, a source of electromagnetic radiation positioned so as to irradiate said cell and means for changing the hydrogen ion concentration of discrete elemental areas of said cell.

5. An imaging screen comprising a cell member including a solution capable of being transformed from a nonfluorescent to a fluorescent state upon a change of the hydrogen ion concentration of said solution, said solution consisting essentially of a quantity of dichlorofluorescein, a quantity of water-miscible alcohol sufficient to dissolve said dichlorofluorescein and, for each gram of said dichlorofluorescein, 50 to 100 grams of sodium chloride and one liter of water, a source of ultraviolet light positioned so as to irradiate said cell member and a means for changing the hydrogen ion concentration of discrete elemental areas of said cell member.

6. A color imaging screen comprising three cell members arranged in parallel relationship, each of said cell members including a solution capable of being transformed from a non-fluorescent to a fluorescent state upon a change of the hydrogen ion concentration of said solution, a first of said cell members having a quantity of porphyrin in the solution therein, a second of said cell members having a quantity of chromotropic acid in the solution therein and a third of said cell members having a quantity of a material selected from the group consisting of coumaric acid and dichlorofluorescein, a source of electromagnetic radiation positioned so as to irradiate said plurality of cell members and means for changing the hydrogen ion concentration of discrete elemental areas of said cell members.

## References Cited in the file of this patent

Proceedings of the I.R.E., vol. 43, No. 12, December 1955, pages 1911 to 1940.

Electronic Industries and Tele-Tech, February 1957, pages 51 to 53.

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