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DISPLAY DEVICES

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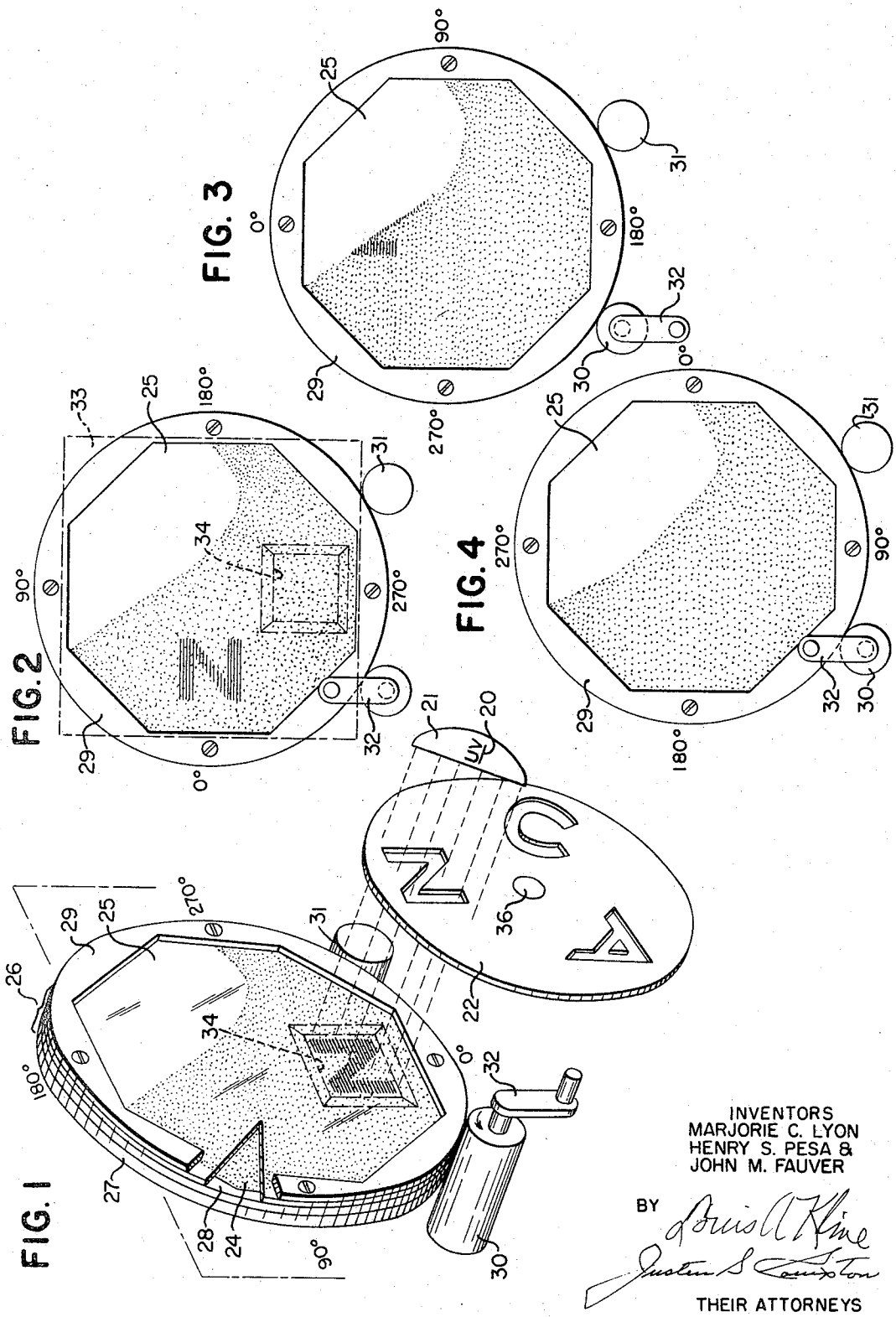


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# DISPLAY DEVICES

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This invention relates to a regenerating display screen on which data may be written by light and from which the data may be removed either by fading or by mechanical manipulation or by both.

Essentially, the device consists of a receptacle containing a mass of very minute light-colorable solid particles, the exposed particles of which mass in repose afford an apparently smooth surface on which exciting light may be played to depict data which persists after cessation of the light, said particles comprising material which changes from a normal state to a temporarily colored state when struck by ultraviolet light, the color disappearing (fading) gradually, over the course of several minutes, particle by particle, due to the action of the ambient heat of room temperature environment. The colored particles at the surface, which form the data, may be mechanically mixed in with the rest of the mass of particles to cause said data to disappear from view, while it is fading.

By "solid" is meant either a solid-walled capsule with liquid contents or a solid beadlet particle, as hereinafter described.

An essential portion of the device is a receptacle, or bin, for holding the mass of minute particles, said receptacle being provided with a window-like retaining wall through which exciting light may pass and through which the surface particles of the mass in repose may be seen, so that one may view what is written by the exciting light. Equipment auxiliary to the receptacle is means for tumbling it at will to mix the particles when the disappearance of the written matter is required. To write the data, there is provided a source of ultraviolet radiation, with appropriate light-control and directing means, whereby data may be written on the screen surface in the desired configuration.

The most desirable form of receptacle is a drum which is rotatable about its cylindrical axis, one end of the drum being a transparent retaining wall through which the ultraviolet writing light may pass and through which the written data may be seen. This drum form of receptacle is shown in the drawing, the drum being shallow from front to back and the tumbling axis of the drum being horizontal, so that it may be rotated to tumble the colorable particles within the enclosure. The drum is not quite full of the colorable particles, so that freedom of mixing by the tumbling action is assured. In this form of receptacle, the writing is done on the drum end through the transparent wall beneath the horizontal level of the axis, and the rotation turns what is written in a circular manner until it reaches the level at which gravity makes the particles flow in a slope and mix with the remainder of the uncolored particles within the mass. To this end, conformations are provided within the drum, on the inside cylindrical sruface, to aid in the tumbling action, as is common with the drum mixing devices.

As to the particles themselves, while there are many materials which are colorable by ultraviolet light, the materials which have proved most valuable in this respect, for this purpose, are minute capsules having walls of translucent or transparent polymeric material and a liquid content, which liquid contains in solution a photochromic dye. A photochromic dye in solution has a normally colorless state, which is turned to a brilliant color, temporarily, by the application of ultraviolet light, only to fade to its original color after the passage of time which may range from seconds, minutes, or hours to days and months. This coloration is provided by a distortion of configuration of the dye molecules, and does not involve a chemical reaction, so that the material, when returned to normal state, is again ready to assume a color. For display function, there is chosen a dye which in solution has a reversion time of several minutes at normal room temperature, so that capsule particles which have been written upon and made colored will fade to the colorless state in several minutes. By use of such materials, the written matter will persist on display for several minutes but will then disappear, so that the screen is ready for another writing operation automatically; or, on the other hand, the drum may be rotated to tumble the colored particles or capsules out of sight among the mass of capsules, which additionally brings a new writing surface, which has been on its way around the course of the tumbling station, so that, immediately, without any delay, a new record may be written on a new part of the screen surface that is presented at what will be called a "writing" station.

Although not necessary, in front of the drum between the screen face and a viewer's standpoint there may be placed an opaque screen having a viewing aperture which shows this "writing" station area. Through it, the writing light may be projected and the written data viewed.

Inasmuch as material which is colorable by the ultraviolet writing light is known, such will be described with reference to its best embodiment (that is, minute capsules containing a liquid), so that the rest of the device may be described with reference thereto. Attention is called to United States Patent No. 2,953,454, which issued on the application of Elliot Berman (Sept. 20, 1960), in which patent are shown encapsulated solutions of photochromic dyes of the benzo-indolinospiropyran type which are stable at room temperature for an appreciable time, which renders such capsules suitable for the purpose of writing data thereon with ultraviolet light at room temperature. Specifically, the particular compound 1,3,3-trimethyl-6'-nitrospiro (2'-H-1-benzopyran-2,2'-indoline) is a preferred one of these compounds because it has the relatively short room-temperature life necessary for the proper performance of the display device if it is to be used for both automatic and tumbling types of erasure. If more permanent types of dyes of this photochromic type are to be used, so that the tumbling alone is used for erasure and the recovery of the written capsules to normal takes place over a longer period than a few minutes, than other derivatives named in the said patent would be better; for instance, the 8' $NO_2$; the 6' $NO_2$—$OCH_3$; and the 5-$NO_2$, 8'$OCH_3$ derivatives would give such longer coloration persistence. These capsules are made by dispersing the dye, dissolved in the amount of several percent in an inert oil such as chlorinated diphenyl, as the inner phase of an emulsion in a solution of film-forming polymeric material as the outer phase. A coacervation step is performed wherein a polymer-rich liquid phase is caused to separate from the solution and deposit on the inner-phase particles to form liquid-walled minute capsules, which walls are later made rigid, as by gelling or hardening agents. Exact methods of producing such capsules are shown in United States Patent No. 2,800,457, which issued July 23, 1957, on the application of Barrett K. Green and Lowell Schleicher, and in United States Patent No. 3,041,289, which issued June 26, 1962, on the application of Bernard Katchen and Robert E. Miller. These capsules ordinarily are from five to fifteen microns in average largest dimension and,

if dried, are of a powdery nature. It is probably better for the use of these capsules in a display device to have them larger, so that the tumbling of them and the intermixing of them are easier, and for that purpose larger capsules of the order of two hundred to five hundred microns may be used. These capsules are made in a liquid vehicle, as has been described, in which the polymeric material is dissolved in a solvent into which dissolved dye-in-oil particles are introduced. The difference in the process of making large capsules is that the oil is not emulsified in the solution of polymeric material but is kept as large droplets by being introduced into the solution through a pipette and being knocked off of the end of the pipette by a fan-type mixing apparatus. A special technique developed by Carl Brynko and Joseph A. Scarpelli and disclosed in application for United States Letters Patent Serial No. 784,020, filed Dec. 31, 1958, shows how to make these capsules of a size approaching one quarter-inch in largest dimension. As such large capsules are preferred for use in this display device, the disclosure as set out in said patent application will be repeated here, inasmuch as said application has not yet issued into a patent. The capsule core material is a toluene solution of the dye and is dispersed as minute droplets in water in which there has previously been dissolved a mixture of gelatin (preferably having an isoelectric point of about pH 8), acacia, and a polyethylenemaleic anhydride copolymer, as capsular wall material. The process, in the beginning, is carried on in an open-top vessel, with the ingredients at about thirty-five degrees centigrade, that temperature being selected so that the encapsulating raw material ingredients will all be in liquid form during the process. Coacervation is induced to cause the wall material to deposit on the oil particles as a rich liquid solution. With the particular material used for the walls of the capsules, the temperature may be lowered after the liquid capsule walls are deposited, to gel and thus solidify the deposit thereof around each core entity, thus to form solid capsules with liquid cores. A further step to the process, as described so far, may be performed, in which the solidified wall material, now encapsulating each core entity, is hardened with cross-linking agents such as formaldehyde, glutaraldehyde, or equivalents. Coming, now to quantities of materials used, 1500 cc. of water maintained at 35 degrees centigrade, and agitated from the beginning and throughout the addition of the materials which are added thereto, has dissolved therein 150 grams of an 11%, by weight, aqueous gelatin sol, of the mentioned isoelectric value, and, thereafter, the so-formed solution is adjusted to pH 9 or has been so adjusted by the pH of the added materials. Next is added 150 grams of an 11%, by weight, aqueous sol of acacia, also adjusted to pH 9. As a third capsular wall ingredient is added 40 grams of a 2%, by weight, aqueous solution of polyethylenemaleic anhydride copolymer having a molecular weight af approximately 1000–2000 as determined by its viscosity as 1% solution in dimethylformamide, at 25 degrees centigrade, according to the "Ostwald method (B)," the latter solution also being adjusted to pH 9 if not at that point. This water solution of the initial wall-forming materials, kept at 35 degrees centigrade, is stirred, so that the liquid rotates about a vertical central axis, and then the core material, which in this example is toluene with the selected photochromic dye in solution, is introduced, or exuded, into the moving liquid, under its surface, by a burette or other orificed emitter, at a drop-forming station, drop by drop, so that the drops will shear off and be carried away by the rotation of dispersion—the burette, or emitter, being so controlled that the drops enter the liquid dispersion in such timing relative to the rotational speed of dispersion liquid past the end of the burette that drops of the desired size are formed. In this preferred example, the drops are so regulated as to size that the finished capsules, including the core material and surrounding capsular walls, may average 500 microns in largest dimension. After dispersion of the core material droplets into the liquid solution of capsular-wall-forming materials, the wall-forming materials are caused to make a first deposit onto the droplets by lowering of the pH of the aqueous liquid medium to about 4.8, which may be done by the introduction of a 10%, by weight, aqueous solution of acetic acid. With the concentration of the initial ingredients proposed in this specific example, the deposition of the initial wall-forming ingredients which have so far been provided results in a wall thickness of about 5 microns, whereupon such deposition stops, although some remnants of the wall-forming ingredients in the formed coacervate droplets are left, in the dispersion, undeposited. It is to be understood that this first deposition of wall-forming material, at this stage, is in the liquid state. Next, the aqueous medium, which contains a remnant of the original encapsulating wall material in complex coacervate form, which is not deposited on the liquid droplets, is raised for a short period of time to a pH of about 6.8 by use of a 10%, by weight, aqueous solution of sodium hydroxide, which causes such remnants of encapsulating wall material to return to their original uncomplexed state before substantially disturbing the deposited liquid complex material which has already been deposited on the droplet core entities. Continued agitation of the dispersion mixture containing the partially completed capsules will keep them as separate entities which will not coalesce. Next, before the partially formed capsules have been substantially affected by decoacervation, there is introduced into the aqueous medium, containing the partially formed capsules and the decomplexed remnants of first encapsulating ingredients, a 2%, by weight, aqueous solution of 40 grams of polyethylenemaleic anhydride copolymer having a substantially higher molecular weight than that used in the initial ingredients, preferably polyethylenemaleic anhydride copolymer having a molecular weight of about 60,000–70,000, as determined by the viscosity method mentioned before. A separate preliminary step of adjusting the pH of the dispersion, before the second polymeric material is added, may be eliminated if the added polymeric material is of high enough pH naturally, or has been made so, which prevents spontaneous coacervation when added to the solution. After thorough mixing of the newly-added polyethylenemaleic anhydride copolymer, the pH of the liquid dispersion mixture is lowered to approximately 4.6, before the partially formed capsule walls have been substantially affected by decoacervation, by the addition of 10%, by weight, solution of the acetic acid, which causes deposition of said newly-added polyethylenemaleic anhydride copolymer and the remnants of the first-added film-forming material, in complex units, around each of the partially-completed capsules, individually, as a second liquid deposit coherent to the first deposit, thus completing a composite wall around each of the droplets of core material, the composite wall then totalling approximately 100 microns in thickness when the second deposition ceases. The capsules now are completed, as far as the deposition of the encapsulating wall-forming material is concerned, but the encapsulating walls at this point are still in liquid form. It is desired to have the colloid capsular walls in a rigid and solid gel state and, in addition, hardened by cross-linkage, and, therefore, in this preferred embodiment, the temperature of the aqueous dispersion of the liquid-walled capsules is lowered as rapidly as feasible to about 13 degrees centigrade to make the solidification of the capsule walls proceed rapidly. The capsule walls, then rigid and solid, are still in a temperature-reversible state and revert to the liquid state upon being heated. To render the capsule walls irreversible in this sense, by being heated, the capsular wall material is cross-linked by treatment with formaldehyde, glutaraldehyde, or equivalent similar material such as alpha-hydroxy-adipaldehyde. For instance, if formalde-

hyde is used, for the amount of material under process, .19 milliliter of a 37%, by weight, aqueous solution of formaldehyde per gram of gelatin is stirred in. If glutaraldehyde is used, .5 milliliter of a 25%, by weight, aqueous solution per gram of gelatin is used. Amounts of other cross-linking agents may be found by trial-and-error methods. In the event that the formaldehyde solution is used, the aqueous dispersion of capsules should have its pH raised to between 7 and 9, to render it fully effective, and the pH may be left there until the capsules are ready for use. Where a solution of glutaraldehyde is used, no raising of the pH is necessary. The capsules may be recovered from the aqueous medium by filtration, by centrifuging, or by spraying the dispersed capsules in a (preferably hot) gas medium, and, when dry, the capsules may be used as the particulate material for the purposes of the invention.

The toluene may have dissolved in it the selected amount of the photochromic material taken from those specified. Other room-temperature-operable photochromic materials may be selected from the disclosure of United States Patent No. 3,100,778, which issued Aug. 13, 1963, on the application of the beforementioned Elliot Berman.

Not only may such photochromic materials be used as coloring agents in the liquid contents of minute capsules, but the materials may be incorporated as a solute in a solid solution of it and polymeric material, in the necessary amounts to give the degree of coloration desired, but the solid state of the materials will give a slower fading time than the capsule-type of particle of liquid content. These solid solutions may be of the water-soluble wall polymeric material type such as the gelatin which is used in forming the capsules, or such solutions may be any one of the film-forming polymeric materials which are commonly used for forming beadlets for various uses, such beadlets either being made in a liquid manufacturing bath or being comminuted from a slab of rigidly-set polymeric material solution containing the dye. These are matters of selection for the ultimate user to decide for himself through trial and error as to what makes the best display appearance.

Inasmuch as ultraviolet light radiation is impeded by some transparent window materials, the thinner the window material through which the particles in the drum are to be seen, the more efficient will be the penetration of the incident ultraviolet light. There are a number of film materials which are more transparent to ultraviolet light than are ordinary forms of window glass, and it is known also to use quartz or quartz-like rigid transparent or translucent materials for ultraviolet-light-passing aperture covers.

In the drawing:

FIGURE 1 is a perspective view of both the device and a stencil showing a letter displayed on the device by means of a beam of ultraviolet light issuing through the stencil and impinging upon the device.

FIGURE 2 is a front elevational view of the display device rotated clockwise ninety degrees from its position in FIGURE 1. An opaque shield having an aperture is shown in phantom.

FIGURE 3 is a front elevational view of the display device rotated clockwise an additional ninety degrees illustrating partial erasure of the letter shown in FIGURES 1 and 2.

FIGURE 4 is again a front elevational view of the display device rotated clockwise still another ninety degrees showing complete erasure of the letter.

Referring to FIGURE 1, the ultraviolet light source **20** (FIG. 1) has been shown as being situated inside of a concave projecting mirror **21** to issue a beam of light controlled through a cut-out stencil **22** to "write" the letter N on the particles **24** behind the transparent end window disc **25** of the drum **26**.

In the embodiment of the invention disclosed in the drawing, the parts are shown, where possible, in diagrammatic form to render the combination of elements of the invention portrayed in a functional sense. The drum **26** consists of a back plate **27**, a separator rim **28**, which has a circular outer perimeter and an octagonal inner perimeter, the transparent window disc **25**, and the cover plate, screwed together to form the shallow drum-like receptacle, or bin. This drum is filled above the halfway mark with the particulate color-responsive material **24** described, and is mounted on a set of rollers **30** and **31**, the roller **30** being equipped with a turning handle **32** to illustrate a method by which the drum-like receptacle may be rotated on its cylindrical axis. In phantom is shown the optional opaque shield **33** (FIG. 2) with an aperture **34**, by which the screen may be viewed and through which the "writing" light may be projected. It is not necessary to have this shield **33** for a display fixture, as the rotation of the drum and the disappearance of the written letters as the drum contents mix are themselves an attraction. Successive ninety-degree rotational positions of the drum are indicated by the degrees of rotation indicated adjacent the circumference of the front face thereon, shown respectively in FIGURES 2, 3, and 4 in which the reference numerals refer to the same parts, respectively, as described in FIGURE 1, and such portrayal aids in an understanding of what is taking place within the drum in a complete clockwise rotation. It is to be understood that the tumbling action of the particles, as shown, is but one means by which the displayed data is made to disappear, the fading of the colored particles, even though the drum is not rotated, being a second method by which the written data disappears.

It will be apparent that the drum may be rotated in steps or continuously to make a complete circle and that at a certain number of degrees of movement which carries the written matter beyond the aperture a new area of screen is presented, on which other data may be written and which in turn will be carried beyond the writing station as the drum is rotated or will remain in place if the drum is not rotated. If the drum is rotated reversely, the written material that has passed from the writing station in one direction will be returned to be viewable again if it is still in existence because sufficient time has not elapsed for it to have disappeared by fading.

It will be understood that, without the presence of the shield **33**, whatever is written on the screen and rotated clockwise one quarter of a turn from the writing station will be seen as shown in FIG. 2 by the written letter N, which has assumed a ninety-degree turn in position from the position which it had when written. Not only may letters be printed, but the writing may be in the form of a continuous line such as graph, which will gradually disappear as the drum is rotated.

The stencil **22** is shown as having the letters C and A, which are positionable, by rotation on the axis **36**, to intercept the ultraviolet light.

It is within the scope of the invention to provide more than one writing means for projecting data onto the display device, and to that end purpose the ultraviolet light may be projected either as a cone or as a beam that is controlled by a light mask, such as the stencil shown, or as a beam controlled by directional control means such as those well known in the art.

While the invention has been disclosed in the drawing with a relation to a drum type of receptacle, it is apparent that such is not a controlling feature of the invention, as the invention resides in the provision of a mass of colorable particles held in a receptacle, which particles may be tumbled from a screen surface area, after being colored, to be "lost" among the particles which are not colored, which effect is aided by the automatic fading of the particles in the course of time. The mixing of the particles so that those at the screen surface will be carried into the interior of the mass may be accomplished, in another modification of the invention, by a stirring means while

the receptacle is maintained in fixed position. Another method by which such a mass of particles may be positioned to be "written" upon is by holding them in an endless belt which has an interior pocket running its length and covered by translucent material. This belt may be carried over rollers past a writing station and beyond, to be tumbled on a change in direction of vertical travel. In this form of the invention, the mixing occurs as the belt reaches the top and starts downward, the particles falling by gravity to become mixed. It is also within the scope of the invention to provide an open box, with the opening facing upwardly, which box is supplied with particles and a mixer. The "writing" may be done on the top surface of the particles held within the box by gravity.

As a variation of the more or less planar screen described so far, there can be provided a system in which particles are allowed to drift down on a slanting surface or drift down as a curtain, and written on as they drift down past a station where ultraviolet light is projected thereon in order to color them as they fall, one such method being to put capsules, or other particles, in an hour-glass type of container and cause them to be subjected to ultraviolet light at the neck of the hour-glass as they are falling into the bottom half and being colored as they make their passage. By the time all the particles have fallen through, the hour-glass may be turned over, and, if enough time has elapsed between the coloration and the turning of the hour-glass, the particles will again be in the uncolored condition. In a way, the coloration and decoloration of the particles evidence the passage of time, and the time required to decolor the particles, on the average, may be used to advantage in further promoting the visual effect upon the viewer for any purposes in which the time element is involved. In this latter respect, the device may act as an indicator of the passage of time.

It is well known in the photochromic art that the temperature is a critical factor in the rate of the fading of these particles and that an increase in temperature causes the fading to occur at a faster rate. In that respect, both heat and the passage of time are controllable factors for erasing whatever data has been recorded in the device.

What is claimed is:

1. A display device including, in combination,

(a) a receptacle;

(b) a mass of minute ultraviolet-light-colorable solid particles comprising minute liquid-containing capsules retained in the receptacle, said particles in repose in response to the force of gravity providing a surface of particles on which ultraviolet light may be projected to color the surface particles; and



(c) means within the receptacle to intersperse the particles as the receptacle is rotated, to move particles from the surface, whereby any particles that may be colored are lost from view if the receptacle is rotated.

2. The device of claim 1 in which the liquid of the capsules is colorable by the ultraviolet light.

3. The device of claim 2 in which the receptacle is a drum with a viewing window in one end through which the capsules may be seen, which window provides a planar surface against which the capsules in repose rest to form a screen, and through which window ultraviolet light may be projected onto the capsules reposing next to the window.

4. The device of claim 3 provided with means to rotate the drum on a horizontal axis.

5. The device of claim 3 in which means is provided by which a data-representing shaft of ultraviolet light may be projected through the window.

6. The display device of claim 1 in which the receptacle is a drum mounted on a horizontal axis.

7. The display device of claim 6 in which means is provided to rotate the drum on its axis.

8. The display device of claim 7 in which means is provided to project a shaft of ultraviolet light through an end of the drum to write on the capsules reposing against said end.

9. The display device of claim 8 in which the said drum end is transparent to ultraviolet and visible light.

10. A display device consisting of a tumbling receptacle partly filled with a mass of solid particles that are colorable by ultraviolet light, said receptacle having a window against which the particles in repose rest by the force of gravity, and means to project ultraviolet light through the window in data-representing configuration which is reflected for view through the window as a colored pattern, the so-colored pattern being lost as the receptacle is tumbled and the particles are moved and mixed so that a new set of particles of the mass appear at the window.

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