

United States Patent

Ogawa et al.

[15] 3,679,976

[45] July 25, 1972

[54] **ELAPSED TIME INDICATOR HAVING
COLOR INDICATION**

3,045,179 7/1962 Maer.....324/94 X

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[22] Filed: **March 23, 1971**

[21] Appl. No.: **127,193**

[57] **ABSTRACT**

The anode electrode of an elapsed time indicator includes an elapsed time measuring metallic element superposed on a coloring metallic element, the normal electrode potential of the coloring element being higher than that of the elapsed time measuring element, and lower than the electrolyzing potential of the electrolytic solution, so that electrolysis of the elapsed time measuring element precedes that of the coloring element. The electrolytic solution contains a substance which reacts with the coloring element on electrolysis thereof to change the color of the electrolytic solution, thereby indicating the elapsed time.

[30] **Foreign Application Priority Data**

March 31, 1970 Japan.....45/27557
Nov. 9, 1970 Japan.....45/98543

[52] U.S. Cl.....**324/182, 317/230, 324/94**

[51] Int. Cl.....**G04f 9/00, G01r 11/44**

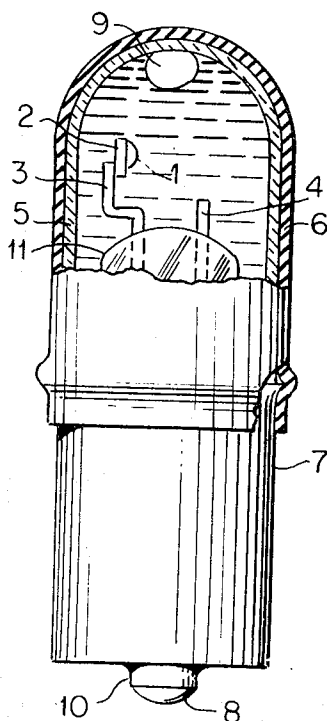
[58] Field of Search.....**324/182, 181 A, 94; 317/230**

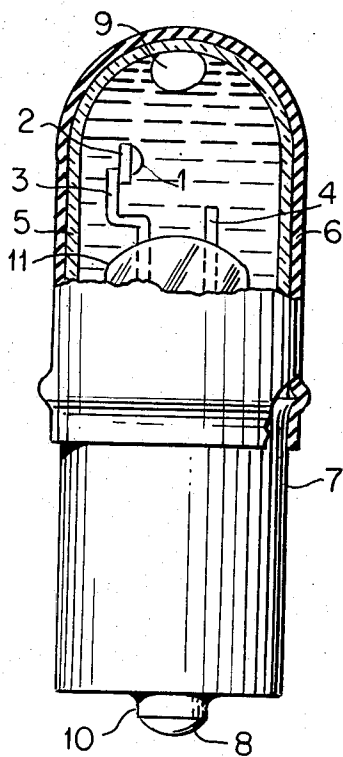
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13 Claims, 1 Drawing Figure





ELAPSED TIME INDICATOR HAVING COLOR INDICATION

The present invention relates to elapsed time indicators, and more particularly, to an electrolytic color indicating elapsed time indicator.

Elapsed time indicators of the electrolytic type employing the principle of electroplating in accordance with Faraday's law are well known in the art as comprising an anode, a cathode and an electrolytic solution housed in a sealed transparent envelope, the main constituent of the electrolytic solution being a salt of the same metal as the anode metal. A reduction of the anode length and an extension of the cathode length is effected by applying a direct current between the electrodes and the elapsed time during which the current is flowing can be determined as a function of the reduction in length of the anode or the increase in length of the cathode by means of a scale on the envelope.

Such prior art indicators have difficulties in that the type of electrolytic solution is restricted because it is necessary that the electrolysis and electrodeposition of metal take place uniform and flatly on the opposite surfaces of the anode and the cathode. Further, the use of such indicators in recumbent positions is prohibited since they will not properly function.

Another type of known elapsed time indicator which is improved relative to the aforementioned prior art indicator comprises an electrolytic solution enclosed in a narrow tube, both ends of which are sealed with mercury. However, this indicator has the disadvantage that it is fragile against mechanical vibrations and that the cost thereof is very high.

Another type of known elapsed time indicator includes an anode which comprises an electrolyzable metallic element and a non-electrolyzable metallic element. In this type of elapsed time indicator the internal resistance of the indicator increases substantially at the ending stage when the entire electrolyzable element has been completely electrolyzed, so that the voltage between the anode and the cathode is rapidly increased, which can be indicated by means of a meter or an alarm in an external circuit. Thus, the warning of the predetermined lapse of time is available. However, the cost increases due to the necessity of providing an external indicating circuit. Further, at the ending stage of electrolysis, an overvoltage can be applied to the elapsed time indicator so that the pressure within the envelope increases due to the bubbles generated by the electrolysis in the electrolytic solution. This can cause unexpected damage such as breakage of the envelope or leakage of the electrolytic solution from the envelope.

Further, the conventional elapsed time indicators described above have a common disadvantage in that the elapsed time can be observed or determined only by viewing the indicator from the outside.

The main object of the present invention is to provide an elapsed time indicator which avoids the disadvantages and the difficulties of the prior art indicators as discussed above. The present invention is directed to an elapsed time indicator wherein when electrolysis has proceeded until a predetermined time has elapsed, the electrolytic solution is caused to color, or discolor, so that it may be readily determined when a predetermined period of time has elapsed.

SUMMARY OF THE INVENTION

According to the present invention, an elapsed time indicator includes an envelope containing an electrolytic solution, an anode electrode and a cathode electrode housed therein. The anode electrode comprises an elapsed time measuring metallic element and a coloring metallic element superposed on one another, the normal electrode potential of the coloring metallic element being higher than that of the elapsed time measuring metallic element, and lower than the electrolyzing potential of the electrolytic solution, so that electrolysis of the elapsed time measuring metallic element preceeds that of the coloring metallic element. The electrolytic solution contained in the envelope includes a substance which reacts with the

coloring metallic element on electrolysis thereof, so that electrolysis of the coloring metallic element cause the color of the electrolytic solution to change. Thus, after a predetermined period of time has elapsed, which corresponds to the amount of time required to transfer the elapsed time measuring metallic element material to the cathode electrode, the electrolytic solution is caused to change color to thereby indicate the elapsed period of time.

Generally, in electrolytic elapsed time indicators, it has been well known that the anode electrode may comprise two kinds of metallic elements whose normal electrode potentials relative to the electrolytic solution are different. It is also known to use the first metallic anode element to measure the elapsed time, and to use the second metallic element as the supporting element for the first metallic element. The second metallic element used only as the supporting element and is not to be electrolyzed. Therefore, it has been preferable that the normal electrode potential of the first metallic anode element relative to the electrolytic solution is selected to be lower than the electrolyzing potential of the water in the electrolytic solution, while that of the second metallic element is selected to be higher than the electrolyzing potential of the water.

In the present invention, on the contrary, electrolysis of the first and second metallic elements in accordance with Faraday's law takes place successively by selecting the normal electrode potential of the second metallic element relative to the electrolytic solution to be higher than that of the first metallic element and to be lower than the electrolyzing potential of the water in the electrolytic solution. That is, the first metallic element is first electrolyzed so as to serve as an elapsed time measuring element, while the second metallic element is then electrolyzed as a discoloring element after the elapsed time measuring element has been electrolyzed. Electrolyzing of the second metallic element causes discoloring or coloring of the electrolytic solution.

The composition of the electrolytic solution must be such that it is not discolored nor colored by the electrolysis of the first elapsed time measuring metallic element. The electrolytic solution of the color indicating timer according to one embodiment of the present invention includes a ligand, in the form of a salt with the elapsed time measuring metal ions, which can produce a deep color complex by coordinating with the discoloring metal ions which are produced in the electrolytic solution at the time of electrolysis of the second coloring metallic element.

The time required for the complete electrolysis of the first elapsed time measuring metallic element, that is, the predetermined elapsed time, can be chosen by selecting the mass of the elapsed time measuring metallic element in accordance with the magnitude of the direct current in accordance with Faraday's laws.

When the electrolysis of the second coloring or discoloring metallic element proceeds until the electrolytic solution is saturated with the coloring metal complex ions, the metallic surface of the anode is saturated with the coloring metal complex ions(anions) so that the current flowing is automatically reduced. As a result, electrolysis ceases. This prevents the internal pressure within the envelope of the timer to dangerously increase due to the bubbles produced in the electrolytic solution by unnecessary electrolysis.

In another embodiment of the present invention, no ligand is contained in the electrolytic solution. In this alternate embodiment, the plating solution for the elapsed time measuring metal of which the main constituent is a salt of said elapsed time measuring metal is used as the electrolytic solution. A coloring agent is added to the solution beforehand and the coloring metal ions react with the coloring agent at the time when the coloring metal (i.e., the second metallic element) is electrolyzed. The reaction results in discoloring or coloring of the electrolytic solution.

However, differently from the first-mentioned embodiment employing the complex formation, the second embodiment

employing the color agent does not have the advantage that the current flow is automatically reduced by the action of the complex ions in the electrolytic solution after the electrolytic solution has been colored. Further, the first-mentioned embodiment has a higher sensitivity in coloring and exhibits less fading of the color than the second embodiment.

The present invention will be described in detail with reference to the accompanying drawing, in which the single FIGURE illustrates an embodiment of an electrolytic color indicating elapsed time indicator in accordance with the present invention.

DESCRIPTION OF PREFERRED EMBODIMENT

Referring to the single FIGURE, the elapsed time indicator of the present invention includes an envelope 5 containing an anode which comprises an elapsed time measuring metallic element (first metal) 1 superposed on a coloring metallic element (second metal) 2. Elements 1 and 2 may be secured together by welding, bonding, or the like. The entire anode is supported by an anode supporting metallic element 3 welded or otherwise secured to a surface of the coloring metallic element 2, which surface is not welded with the elapsed time measuring metallic element 1. Further included is a cathode element 4, the surface of which is exposed to the electrolytic solution preferably being coated with, for example, silver to improve the electrodeposition of the elapsed time measuring metal 1 on the cathode 4. The anode support element 3 and the cathode 4 are preferably supported in the envelope 5 by means of an insulating member 11. The envelope 5 comprises a transparent or semi-transparent material such as, for example, glass or an organic macro-molecular material such as polyethylene, polyester or epoxide resin. The external surface of the envelope 5 can be provided with a transparent or semi-transparent protective film 6 made of, for example, a rubber material such as silicone rubber. The protective film is used to protect the envelope 5 against mechanical shocks. Even if the envelope is broken, the leakage of the electrolytic solution from within the envelope can be inhibited by the film 6.

A base 7 is connected to the envelope 5 and is electrically connected to the cathode 4. The protective film 6 can be so formed that the external surface of the envelope 5 and the marginal part of the base 7 adjacent the envelope 5 are coated with liquid silicone rubber by spraying and drying, for example. In this manner, the upper marginal part of the base 7 and the lower marginal part of the envelope 5 are air-tightly sealed to each other. The anode support element 3 is electrically connected to a contact 8 at the end of base 7. Contact 8 is insulated from base 7 by an insulator 10.

A bubble 9 (or foamed styrene) is contained together with the electrolytic solution in the envelope 5 to inhibit the increase of internal pressure. If there was no bubble 9 contained in the envelope 5, an intensive internal pressure from the inside of the envelope, which can be produced by the expansion of the electrolytic solution or its change to the gaseous state due to increase in temperature in the atmosphere outside the envelope, could cause the envelope 5 to explode. The contained bubble 9 is useful to avoid such dangerous accidents. Even if the temperature in the atmosphere outside the envelope increases up to 130° C, the temperature of the electrolytic solution in the envelope will not increase to such a degree that will cause the electrolytic solution to evaporate. This is because the bubble 9 inhibits an excessive increase of internal pressure.

In order to make the bubble 9 perform more effectively, the size of the bubble can preferably be selected to be more than 2 percent in volume relative to the volume of the electrolytic solution contained in envelope 5. Thus, the diameter of the bubble 9 can be about 4mm for a normal sized envelope. Generally, a bubble of 1 atm. air is contained in the envelope. A bubble including a gas without oxygen, such as, for example, nitrogen, can also be used with a favorable effect.

The details of coloring or discoloring of the electrolyte solution in the envelope 5 caused by the mutual reaction between the coloring metallic anode element 2 and the electrolytic solution will be described below in conjunction with a typical arrangement of a first embodiment of the invention.

The coloring metallic anode element 2 and the elapsed time measuring metallic element are secured together by welding in the gaseous current of hydrogen in an electric furnace or by supersonic welding to form an alloy junction region of ca. 20°A. thick at the contact surfaces thereof. This junction region prevents the contact surfaces between elements 1 and 2 from being electrolyzed before the elapsed time measuring metallic element 1 is completely electrolyzed, so that the accuracy in elapsed time measurement can be maintained.

In the electrolytic solution, a ligand, such as, for example, thiocyanate ions, cyanate ions, hydroxide ions, ammonium ions, chlorine ions, nitrate ions or thiosulfate ions, is contained which comprises a complex providing deep color in the electrolytic solution in reaction with the ions of the coloring metallic element 2, such as, for example, iron, nickel, cobalt, chromium, manganese or copper. Thus, the composition of the electrolytic solution for coloring or discoloring is relatively simple. The requirements for the cathode electrode 4 in electrodepositing the elapsed time measuring metallic anode element 1 can be relaxed, so that the electrolyzing current density can be selected in a very wide range of 0.01 to 1.0 amps/dm². The advantages that can be obtained by using such a complex in the electrolyte solution have been described above.

The components comprising the first embodiment of the elapsed time indicator according to the present invention are given below:

i. Anode metallic elements:

Elapsed time measuring element 1: cadmium

Coloring element 2: cobalt

Anode supporting element 3: silver-plated nickel wire

ii. Cathode metallic element 4: Silver-plated nickel wire.

iii. Electrolytic solution

Ammonium thiocyanate	5kg
Cadmium oxide	1kg
Water	1 ltr
Glazing agent (gelatin):	proper
Auxochromic agent (acetone):	proper

iv. Envelope 5: Glass bulb and stem for a midget lamp

v. External film 6: Silicone rubber

vi. Base 7: Commercial type base for a midget lamp

vii. Current density: 0.02–1 amps/dm²

In this first embodiment, iron, nickel, copper zinc or tin can be used for the elapsed time measuring metallic element 1. The auxochromic agent serves to promote the coloring by the complex and in place of acetone an organic compound with a small molecular weight, such as methanol or ethanol, can be used. The addition of the auxochromic agent gives a subsidiary action in that it improves the electrolytic effect in the electrolytic solution at a low temperature, because the freezing point of the electrolytic solution can be reduced by addition thereto of the auxochromic agent. The result is that the actual working temperature range for the electrolytic solution can be extended.

A second embodiment of the elapsed time indicator according to the present invention which employs the addition of a discoloring agent will now be described.

It is preferable that the coloring metallic element 2 comprises copper, silver, cobalt or iron and it is most favorable that the discoloring agent in the electrolytic solution is salicylic acid or nitroso-R-salt. For the elapsed time measuring metallic element 1, zinc, tin or cadmium is preferable, considering that the conditions for the normal electrode potential relative to the electrolytic solution and for the discoloring due to the reaction of the elapsed time measuring metal with the discoloring agent must be taken into account.

By virtue of the addition of the discoloring agent, the color of the electrolytic solution is changed from gold to red by electrolyzing of the coloring metallic element 2.

The components of the second embodiment of the present invention are given below:

i. Anode metallic elements

Elapsed time measuring element 1: zinc

Coloring element 2: cobalt

Anode supporting element 3: gold-plated Dumet wire

ii. Cathode metallic element 4: nickel

iii. Electrolytic solution

Zinc sulfate	250g
Magnesium sulfate	20g
Aluminum sulfate	30g
Boric acid	20g
Water	1 ltr

iv. Discoloring agent: nitroso-R-salt

According to the present invention, as described above, a predetermined lapse of time can be recognized with ease only by viewing directly the discolored electrolytic solution in the envelope without any restrictions on the position of the timer in use and with no need of any additional external means such as an external indicator instrument or a display. The manufacturing cost is very low. Therefore, the elapsed time indicator of the present invention is suited for easy use in large numbers to recognize predetermined elapsed times, for example, the maintenance times of electric and/or electronic equipment.

Further, remote supervision of the automatic warning in discoloring or coloring can be realized if the present invention is used in connection with external means.

It should be clear that other modifications and alterations can be made within the scope of the present invention as set forth in the accompanying claims.

We claim:

1. In an elapsed time indicator including an envelope, an electrolytic solution, an anode electrode and a cathode electrode housed in said envelope, the improvement wherein: said anode electrode comprises an elapsed time measuring metallic element (1) and a coloring metallic element (2) superposed on one another, the normal electrode potential of said coloring metallic element (2) being higher than that of said elapsed time measuring metallic element (1), and lower than the electrolyzing potential of said electrolytic solution, so that electrolysis of said elapsed time measuring metallic element (1) preceeds that of said coloring metallic element (2); and said electrolytic solution contains a substance which reacts with said coloring metallic element (2) on electrolysis

thereof, so that electrolysis of said coloring metallic element (2) causes the color of said electrolytic solution to change.

2. The indicator of claim 1, wherein said envelope contains at least one bubble in said electrolytic solution to inhibit the increase of internal pressure in said envelope.

3. The indicator of claim 1, wherein said envelope comprises at least one mass of foamed material in said electrolytic solution to inhibit the increase of internal pressure in said envelope.

4. The indicator of claim 1, comprising a rubber-like material, which is at least semi-transparent, coating the outer surface of said envelope.

5. The indicator of claim 1, wherein an alloy junction region with a thickness of about 20 Å. is formed between the contact surfaces of said elapsed time measuring element and the coloring metallic element, said first and second anode metallic elements being electrolyzed selectively at different times with an electrolyzing current density of 0.01 to 1.0 A/dm².

6. The indicator of claim 1, wherein said electrolytic solution contains a ligand forming a deep-colored complex in reaction with the coloring metal ions produced by electrolyzing said coloring metallic element.

7. The indicator of claim 6 wherein said electrolytic solution contains an organic compound having a small molecular weight selected from the group consisting of acetone, methanol, ethanol, and ether, as an auxochromic agent.

8. The indicator of claim 6, wherein said coloring metallic anode element is at least one element selected from the group consisting of iron, nickel, cobalt, chromium, manganese and copper.

9. The indicator of claim 6, wherein said elapsed time measuring metallic anode element is at least one element selected from the group consisting of iron, nickel, copper, zinc, cadmium and tin.

10. The indicator of claim 1, wherein said electrolytic solution includes a discoloring agent to discolor or color said electrolytic solution in reaction with the coloring metal ions produced by electrolyzing said coloring metallic element.

11. The indicator of claim 10, wherein said coloring metallic anode element is at least one element selected from the group consisting of copper, silver, cobalt and iron.

12. The indicator of claim 10, wherein said elapsed time measuring metallic anode element is at least one element selected from the group consisting of zinc, tin and cadmium.

13. The indicator of claim 10, wherein said discoloring agent comprises at least one material selected from the group consisting of salicylic acid or nitroso-R-salt.

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