LOW-LEVEL SELF-CONTAINED LIGHT SOURCES. (U)

D. J. GOGAN, H. W. CARHART

UNCLASSIFIED
NRL-NIR-4729

FEB 82
This report is a brief survey of the methods available for production of low-level continuous light by simple, trouble-free self-contained devices. Some order of magnitude calculations of efficiency are presented with a brief discussion of the practical advantages and disadvantages of several light generating schemes. The most promising of these schemes are solid-state devices.
CONTENTS

EXECUTIVE SUMMARY ................................................... 1
INTRODUCTION ............................................................. 2
DISCUSSION ............................................................... 2
Chemical Light Sources ................................................... 3
Fluorescence Excited by Radiation .................................. 4
Fluorescence ............................................................. 5
Photo-Induced Chemiluminescence .................................. 5
CONCLUSION ............................................................... 6
REFERENCES ............................................................... 7
APPENDIX A — SPECTRAL RESPONSE OF THE EYE ................. 8
APPENDIX B — NUMBER OF PHOTONS PER SECOND IN A FIREFLY FLASH ....... 9
APPENDIX C — CALCULATION OF AMOUNT OF MATERIAL NEEDED TO PRODUCE A STEADY STATE LIGHT SOURCE OF "FIREFLY" INTENSITY HAVING A ONE YEAR HALF LIFE .................................................... 11
APPENDIX D — COMMERCIAL LED FLASHER-OSCILLATOR CIRCUIT .......... 12
EXECUTIVE SUMMARY

This report is a brief survey of the methods available for production of low-level continuous light by simple, trouble-free self-contained devices. Some order of magnitude calculations of efficiency are presented with a brief discussion of the practical advantages and disadvantages of several light generating schemes. The schemes considered are:

1. Chemical reaction
2. Scintillation (fluorescence resulting from radioactive decay)
3. True Fluorescence (delayed emission of light from a fluorescent material previously illuminated by sunlight)
4. Solid-state devices (solar cell, rechargeable battery, light emitting diode)

The most promising of these schemes are solid-state devices. The proposed solid-state device has the following advantages over other schemes presented in this report.

1. The light intensity will not be degraded with time until the battery is nearly exhausted; this can be avoided with proper design.
2. It will not be degraded by ambient weather conditions.
3. It will not be bulky or demand sophisticated optics as might a chemical source.
4. It will not involve radioactivity.
5. It can be designed and scaled easily to fit the needed light level.
6. It can be made to produce a blinking display or patterned display for maximum recognition ability.
7. Rapid improvement in performance and reduction in cost continues to characterize the solid-state industry.

INTRODUCTION

Under emergency conditions it is important that members of damage control parties aboard ship be able to find and distinguish control devices quickly and unequivocally. As an example, fire-fighters should be able to find the controls for activating fire-fighting hose reels on the catwalks of aircraft carriers at night. Normally these are not illuminated in any way and if the system cannot be found and put into operation quickly, precious fire-fighting time is lost, causing greater fire involvement and growth which might lead to potential disaster. This report discusses a study of several self-contained sources of low level illumination that might be used to locate and identify vital equipment and controls in otherwise total darkness for possible application aboard Navy ships.

DISCUSSION

As a reference intensity standard, familiar from common experience, we use the light intensity of a firefly flash. A typical flash lasts about one second. The maximum requirement is for a continuous light source, so we base our calculations on the intensity level of one flash continued indefinitely. The dark adapted human eye can readily perceive a firefly at 100 feet. The response of the human eye is doubled for each increase of 2.5 in the intensity of the light source, that is, eye response is logarithmic to base 2.5. Therefore, if the light source requirement is for a perception level n times that of a firefly, the increase in light intensity needed is 2.5 raised to the (n-1) power. Thus, a five-fold increase in eye response requires a 40-fold increase in intensity and a 10-fold increase in eye response a 4000-fold increase in intensity. The light needed must be obtained from the controlled conversion of some form of energy, chemical, electrical, nuclear, etc. The eye response-intensity relation and the energy conversion efficiency place fundamental limits on the needed amount of energy.

The wavelength of the light will also affect the efficiency. The light adapted eye has maximum sensitivity to light of 555 nanometers (nm) wavelength, which appears yellow-green. Other wavelengths are less well seen. The dark adapted eye has maximum sensitivity at 507 nm. The spectral response curves of the eye are shown in Appendix A. Thus, green and yellow light sources of spectral distribution similar to the firefly will be the most energy efficient for the given application and red will be least efficient. It is also well known that the human eye is more sensitive to light just outside the focal point in the retina, advantage of which the Navy has used for years in wartime.
Instructing the watch to look just off the horizon at the beginning of dawn to spot enemy ships.

The typical light intensity of a firefly is approximately 1/400 candle. The fundamental unit of light is the photon. In Appendix B, the conversion of 1/400 candle to photons is calculated. The result is that the "typical" firefly flash emits light at the rate of approximately $1.4 \times 10^{-4}$ photons per second. From this we can estimate the feasibility of using chemical and other light sources.

Chemical Light Sources

In a chemical reaction each molecule consumed will produce at most one photon. The most efficient known chemical light is the firefly which converts 90% of the available chemical free energy into light. A commercially available chemical light source, the Cyalume Light Stick made by American Cyanamid Co., Bound Brook, New Jersey, has an efficiency of about 20%. The light stick consists of a flexible polyethylene tube containing a solution of an oxalate ester, a fluorescent dye, and a glass capillary filled with hydrogen peroxide. When the stick is bent, the glass capillary is broken mixing the hydrogen peroxide with the solution, which activates the light emitting reaction. The light intensity is initially bright enough for reading and considerably brighter than one firefly. However, the intensity is halved in 8-10 hours after activation. One author (Denis J. Bogan) has verified that in approximately one week (18 half lives) the light is no longer perceptible. The half life is governed by the chemical reaction rate which, in turn, cannot be much affected without sacrifice of the desired chemiluminescent property.

It should be possible to construct a device, similar in principle to the light stick, in which the reactants are mixed by slow diffusion of the hydrogen peroxide through a semi-permeable membrane. The half life of the device would then be the half life for diffusion across the membrane separating the two reactants. The technology exists for making membranes of almost any desired permeability. One source of such membranes is Millipore Corp., Bedford, MA. With the half life thus established, the light intensity of the device would be a function of the amount of chemical reactant and of the chemical efficiency. The light stick is about the length of a pencil and twice as thick.

In Appendix C we have calculated the amount of chemical needed to produce a steady state light source of "firefly intensity" having a half life of one year. The amount is 10 to 100 times that of a light stick. The source would have to emit light
from a concentrated spot of the same size as a firefly tail. Dispersal of the light over a 10 times larger area would cause it to be perceived only 1/10 as well as a firefly. Therefore, the rather large amount of solution (1 to 10 ounces) of the chemical source would have to be contained in an efficient reflector cavity with a small fisheye lens.

A further disadvantage of the chemical source is that it would be degraded by exposure to sunlight and by heat. The fisheye lens could be made of glass which absorbs short wavelength light, however, it is still likely that significant photo and thermal degradation would occur in one year. In addition, freezing of the hydrogen peroxide, which occurs above the freezing point of water, would stop diffusion through the membrane. The half life of the device would then be decreased to the half life of the already mixed reactants, or 8-10 hours. It is obvious that a chemical light source of much greater brightness could only be obtained by decreasing the half life requirement, since the device described is already rather large.

In summary, a chemical light source appears to be only marginally capable of meeting the requirement. It also suffers from serious disadvantages of inability to withstand large changes in temperature and high ambient sunlight levels. The present efficiency of chemical light sources, about 20% of the theoretical limit, means that future improvements in technology will allow at most a factor of five improvement over our estimates.

Fluorescence Excited by Radiation

Excitation of fluorescent molecules by radioactive decay is a well-known phenomenon. It is most familiar as the light source for luminous wristwatch dials. Such dials were once made of fluorescent paints and doped with radium. Radium is now considered too dangerous, and at present the relatively innocuous β decay of tritium is used as the energy source. Fluorescence excited by radioactive decay is the basis of a widely used laboratory standard for absolute light intensity. Hastings and Weber measured the number of photons emitted by "scintillation cocktails" composed of the organic dyes 2,5-diphenyloxazole (PPO), 2,2'-p-phenylbis-(5-phenyloxazole) (POPOP) excited by carbon 14 and tritium decay. Under their conditions, the efficiency with carbon 14 was 793 photons per β decay and with tritium it was 80 photons per β decay. The half life of these light sources is the half life of the radioactive decay, 12.26 years for tritium and 5730 years for carbon 14.

Radioactive light sources have two significant advantages over chemical sources; they will withstand any terrestrial weather and sunlight without serious degradation, and their high photon
efficiency per radioactive decay allows them to be quite small. They have the disadvantage of including radioactivity sources with their concomitant undesirable properties and side effects in certain locations.

Self-contained radioactive light sources called Betalights are sold by Sanders-Roe Developments Ltd in England. The Betalights are sealed glass capsules coated internally with a phosphor and filled with tritium gas. They are used principally in bioluminescence research.

Fluorescence

Fluorescence is the emission of light by excited molecules occurring a relatively long time after the excitation of those same molecules by light of photon energy at least equal to that of the emitted light. The excited molecules are prevented from fast radiative decay by one or more "selection rules." Such molecules are called "metastable" which we will define for the present purpose as having a lifetime of seconds to hours. These are practical layman's definitions which would be recognizable but not fully correct to physicists or chemists.

Long fluorescence half life is always associated with low fluorescence efficiency. This is because there are many ways, other than emission of a visible photon, in which an excited molecule can lose excitation. These all tend to liberate the excitation energy as heat rather than light.

Some commercial fluorescent tapes were evaluated in this Laboratory several years ago. Their intensity was quite weak, considerably below the firefly intensity and had a half life of approximately 10 minutes. A similar study including reflective tapes was made at DTNSRDC/A following the ORISKANY, FORRESTAL AND ENTERPRISE fires, and published in 1968-9.

Photo-Induced Chemiluminescence

A phenomenon closely related to fluorescence is creation of free radicals by incident light followed by the slow chemiluminescent recombination of the free radicals. In this case, the energy is stored as chemical potential energy rather than electronic excitation energy. Bright chemiluminescences of one hour or longer half life have been observed following illumination of cryogenic solid matrices doped with certain molecules. These results have been accomplished in fairly demanding research laboratory situations which require liquid nitrogen or liquid helium coolants. As such, they would not be practical for present shipboard use because of the constant need for cooling.
CONCLUSION

We consider fluorescence and chemiluminescence to be the least promising of the low-level light source schemes treated in this paper.

We believe that the most promising scheme should take advantage of solid-state devices in the form of a battery-powered light source. These could be made on a single chip or on a small card and would contain a silicon photocell, battery, and a light-producing electronic device such as a light emitting diode (LED). Wrist watches based upon this scheme have been sold commercially for several years. The watches seen by the authors had liquid crystal displays which use much less power than LED's. However, a modest increase in size of the silicon cell and/or battery should permit such a device to operate an LED. A blinking LED could also be used and this would decrease power consumption by the ratio of the time off:time on. The most efficient color for maximum eye sensitivity would be yellow-green. Most LED's emit red. However, red is perceived by the dark adapted eye only about 1/20 as well as yellow-green (see Appendix A). Thus, the choice of a red LED would be feasible if its electrical efficiency were 20 times higher than a yellow-green LED. Appendix D describes an LED flasher-oscillator chip made by National Semiconductor, Santa Clara, CA.

The proposed solid-state device has the following advantages over other schemes presented in this report:

1. The light intensity will not be degraded with time until the battery is near exhaustion; this can be avoided with proper design.
2. It will not be degraded by ambient conditions.
3. It will not be bulky or demand sophisticated optics as might a chemical source.
4. It will not involve radioactivity.
5. It can be designed and scaled easily to fit the needed light level.
6. It can be made to produce a blinking display or patterned display for maximum recognition ability.
7. Rapid improvement in performance and reduction in cost continues to characterize the solid-state industry.
REFERENCES

1. Taken from the stellar magnitude scale used in astronomy; J. Strong, "Procedures in Experimental Physics," Prentice-Hall, N.Y., 1945. The number 2.5 is not exact, it varies with the color temperature of the star. Physiological researchers confirm the logarithmic dependence of eye response to photon intensity; however, various numbers from 2.3 to 2.85 have been measured as the logarithmic base; J. P. C. Southall, editor, Helmholtz's Treatise on Physiological Optics, Vol. II, 3rd ed., Optical Society of America, 1924.


APPENDIX A

SPECTRAL RESPONSE OF THE EYE.

Daylight vision is described by the curve labelled "photopic vision (cones)". Night vision is described by the curve labelled "scotopic vision (rods)". Note that: nm = µ x 1000, e.g. 0.507µ = 507 nm.

APPENDIX B

NUMBER OF PHOTONS PER SECOND IN A FIREFLY FLASH

Firefly flash typically 1/400 candle

1 standard candle emits $4\pi$ lumens equally in all directions

At 555 nm 1 lumen = 1/620 watt

(Firefly light has the peak of its spectral distribution very near 555 nm. The human eye sensitivity is maximum at 555 nm).

Thus, the radiant power of one flash is

$$P = \left(\frac{4\pi}{400}\right) \left(\frac{1}{620}\right) = 5.1 \times 10^{-5} \text{ W}$$

The flash duration is ca. one sec.

1 watt sec. = 1 Volt amp. sec.

Therefore, the equivalent electric current = $5.1 \times 10^{-5}$ amp at 1 volt flowing for 1 sec.

555 nm light has a frequency of $18018 \text{ cm}^{-1} = 2.23 \text{ eV}$

Thus, at 555 nm (2.23 eV) the equivalent current is

$$\frac{5.1 \times 10^{-5}}{2.23} = 2.3 \times 10^{-5} \text{ amp at 2.23 V for 1 sec.}$$

1 amp. = $\frac{1}{1}$ coulomb/sec. Thus, the equivalent charge is $2.3 \times 10^{-5}$ coulomb at 2.23 V. The electronic charge is

$$1.6 \times 10^{-19} \text{ coulombs per electron}$$

Thus, we have

$$\frac{2.3 \times 10^{-5}}{1.6 \times 10^{-19}}\text{ coul} = 1.4 \times 10^{14} \text{ electrons at 2.23 eV}$$
This is equivalent to $1.4 \times 10^{14}$ photons at 555 nm.

Alternatively:

1 mole of electrons = 1 Farad
1 Farad = 96500 coulombs

Thus,

\[
\frac{2.3 \times 10^{-5} \text{ coul}}{96500 \text{ coul/mole}} = 2.4 \times 10^{-10} \text{ moles}
\]

1 mole = $6.023 \times 10^{23}$ = Avogadro number

\[
2.4 \times 10^{-10} \times 6 \times 10^{23} = 1.4 \times 10^{14} \text{ photons at 555 nm}
\]

There are several sources of uncertainty in this number.

The most important are

a) Variability in firefly flash intensity.

b) Both firefly light and human eye sensitivity have spectral distribution curves. They do overlap quite closely.

CONCLUSION: The "typical" firefly flash has an intensity of $1.4 \times 10^{14}$ photons/sec.

This number is uncertain. Its probable range at one $\sigma$ (68% confidence) is estimated as

$1.4 \times 10^{13}$ to $1.4 \times 10^{15}$
APPENDIX C

CALCULATION OF AMOUNT OF MATERIAL NEEDED TO PRODUCE

A STEADY STATE LIGHT SOURCE OF "FIREFLY"

INTENSITY HAVING A ONE YEAR HALF LIFE

Given:  1. "Firefly" intensity = \(1.4 \times 10^{14}\) photons/sec.

2. Efficiency of 20% in conversion of chemical free
   energy into light. (This is the approximate
   efficiency of the American Cyanamid Cyalume™ Light
   Stick.)

The number of molecules needed is ca,

\[
2 \times \frac{1.4 \times 10^{14} \text{ photons/sec}}{0.2 \text{ photon/molec}} \times \frac{3 \times 10^{7} \text{ sec/yr}}{6 \times 10^{23} \text{ molec/mole}} = 4.2 \times 10^{22} \text{ molecules}
\]

This is, \(4.2 \times 10^{22} \text{ molec} / 6 \times 10^{23} \text{ molec/mole} = 0.07 \text{ moles}\)

For a reactant having a molecular formula weight of \(200 \text{ grams/mole}\)

This is, \(200 \times 0.07 = 14 \text{ grams}\)

\(= 1/2 \text{ ounce pure material}\)

If the same solvent system and dilution were used as are used
in the Cyalume Light Stick, this device would have to be 10 to
100 times larger than a Cyalume Light Stick.
COMMERCIAL LED FLASHER-Oscillator CIRCUIT

Industrial/Automotive/Functional Blocks

LM3909 LED flasher/oscillator

general description
The LM3909 is a monolithic oscillator specifically designed to flash Light Emitting Diodes. By using the timing capacitor for voltage boost, it delivers pulses of 2 or more volts to the LED while operating on a supply of 1.5V or less. The circuit is inherently self-starting, and requires addition of only a battery and capacitor to function as a LED flasher.

Packaged in an 8-lead plastic mini-DIP, the LM3909 will operate over the extended consumer temperature range of -25°C to +70°C. It has been optimized for low power drain and operation from weak batteries so that continuous operation life exceeds that expected from battery rating.

Application is made simple by inclusion of internal timing resistors and an internal LED current limit resistor. As shown in the first two application circuits, the timing resistors supplied are optimized for nominal flashing rates and minimum power drain at 1.5V and 3V.

Timing capacitors will generally be of the electrolytic type, and a small 3V tantalum part will be suitable for any LED flasher using a supply up to 8V. However, when picking flash rates, it should be remembered that some electrolytics have very broad capacitance tolerances, for example -20% to +100%.

features
- Operation over one year from one C size flashlight cell
- Bright, high current LED pulse
- Minimum external parts
- Low cost
- Low voltage operation, from just over 1V to 5V
- Low current drain, averages under 0.5 mA during battery life
- Powerful; as an oscillator directly drives an 8Ω speaker
- Wide temperature range

applications
- Flashing flashlights in the dark, or locating boat mooring floats
- Sales and advertising gimmicks
- Emergency locators, for instance on fire extinguishers
- Toys and novelties
- Electronic applications such as trigger and sawtooth generators
- Siren for toy fire engine, (combined oscillator, speaker driver)
- Warning indicators powered by 1.4 to 200V

schematic diagram

circuit diagram

Typical 1.5V Flasher

connection diagram

Typical application

(See applications notes on page 2.)

Source: National Semiconductor, Santa Clara, CA
APPENDIX D (continued)

Absolute maximum ratings

- Power Dissipation: 500 mW
- Voltage: 6.4V
- Operating Temperature Range: -25°C to +70°C

**Electrical characteristics**

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>CONDITIONS</th>
<th>MIN</th>
<th>TVP</th>
<th>MAX</th>
<th>UNITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supply Voltage</td>
<td>(In Oscillation)</td>
<td>1.15</td>
<td>0.55</td>
<td>6.0</td>
<td>V</td>
</tr>
<tr>
<td>Operating Current</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mA</td>
</tr>
<tr>
<td>Flash Frequency</td>
<td>300μF, 5% Capacitor</td>
<td>0.65</td>
<td>1.0</td>
<td>1.3</td>
<td>Hz</td>
</tr>
<tr>
<td>High Flash Frequency</td>
<td>0.3μF, 5% Capacitor</td>
<td></td>
<td></td>
<td>1.1</td>
<td>kHz</td>
</tr>
<tr>
<td>Compatible LED Forward Drop</td>
<td>1 mA Forward Current</td>
<td>1.35</td>
<td></td>
<td>2.1</td>
<td>V</td>
</tr>
<tr>
<td>Peak LED Current</td>
<td>350μF Capacitor</td>
<td></td>
<td></td>
<td>45</td>
<td>mA</td>
</tr>
<tr>
<td>Tube Width</td>
<td>350μF Capacitors at 1/2</td>
<td></td>
<td></td>
<td>6.0</td>
<td>ms</td>
</tr>
</tbody>
</table>

**Additional typical applications** (See applications notes below.)

**Warning Flasher**

High Voltage Powered

**Typical Operating Conditions**

<table>
<thead>
<tr>
<th>Vp</th>
<th>NOMINAL FLASH Hz</th>
<th>Cr</th>
<th>Rs</th>
<th>Rs</th>
<th>V RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6V</td>
<td>2</td>
<td>470μF</td>
<td>1k</td>
<td>1k</td>
<td>5–26V</td>
</tr>
<tr>
<td>15V</td>
<td>2</td>
<td>1μF</td>
<td>2.5k</td>
<td>1k</td>
<td>13–50V</td>
</tr>
<tr>
<td>100V</td>
<td>1.7</td>
<td>180μF</td>
<td>43k</td>
<td>1k</td>
<td>85–200V</td>
</tr>
</tbody>
</table>

**1.5V Flasher**

**Estimated Battery Life**

(Continuous 1.5V Flasher Operation)

<table>
<thead>
<tr>
<th>SIZE CELL</th>
<th>TYPE</th>
<th>STANDARD</th>
<th>ALKALINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td></td>
<td>3 months</td>
<td>6 months</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>7 months</td>
<td>6 months</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>1.3 years</td>
<td>2.6 years</td>
</tr>
</tbody>
</table>

**Applications Notes**

Note 1: All capacitors shown are electrolytic unless marked otherwise.

Note 2: Flash rates and frequencies assume ±5% capacitor tolerance. Electrolytics may vary ±20% to ±100% of their stated value.

Note 3: Unless noted, measurements above are made with a 1.5V supply, a 25°C ambient temperature, and a LED with a forward drop of 1.5V at 1 mA forward current.

Note 4: Occasionally a flasher circuit will fail to oscillate due to a LED defect that may be masked because it only reduces light output 10% or so. Such LEDs can be identified by a large increase in conduction between 0.9V and 1.2V.