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CHEMILUMINESCENCE AS A SIGNALLING DEVICE

J. Evraea Gischard

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FOREWORD

This report covers work performed as an in-house research effort concerning the investigation of the phenomenon of chemiluminescence for signalling purposes. The effort was conducted by the Air Force Flight Dynamics Laboratory of the Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The investigation was initiated for the Limited War effort under a special charge number 041A-7763. The chief investigator was J. Brennan Gisclard. The work commenced in September 1965 and was completed in December 1965. The manuscript was released by the author in March 1966 for publication as a technical report. Resumption of any additional exploratory work will be only upon request from an interested department or agency.

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Abstract

Reliable and unique signalling devices are a military necessity and the vagaries of nocturnal operations on land and sea engender a constant search for improvements and innovations. The phenomenon of chemiluminescence has been under study as a simple, reliable means of producing a unique light that might be adaptable as a signalling device. The chemical compound commonly known as luminol remains the best producer of “cold” light. Various attempts were made to oxidize the compound using reagents that would be safe to handle and easily available for field use but would be capable of producing a visible glow. It was found that the luminol can be oxidized with any ordinary chlorine-containing bleach to produce a greenish blue light that can be made to function as a flash or continuous glow that is visible from a considerable distance. Provided water is available, the method offers a means of signalling when electrical equipment of any kind is not available or has ceased to function. The phenomenon might also be used to create bizarre effects for psychological warfare.
INTRODUCTION

The chemical, 5-amino-2,3-dihydro-1,4
phthalazinedione, commonly known as luminol, exhibits the unique property of giving
off a greenish blue light when it is oxidized
in an alkaline solution. The light is short
lived, however, and the reaction is irre-
versible so that a continuous glow is emitted
only while an oxidizing agent is brought
in contact with unreacted luminol. The light
may therefore consist of a single flash that
deteriorates rapidly or a continuous glowing
stream depending upon the manner in which
the chemicals are mixed.

The luminescence of luminol was first
studied in detail and described by Albrecht
(Reference 1). The phenomenon gained the
attention of Langenbeck and Ruge (Refer-
ence 2) who performed additional experiments
featuring light production, and their work
was followed closely by Huntress, Stanley,
and Parker (Reference 3). Other publica-
tions have appeared on luminol but the authors
have concerned themselves primarily with
the study of the mechanism of the reaction
which is beyond the scope of this report.

The data that follows describes the various
ways in which luminol can be made to react
with an oxidizing agent to produce a strongly
visible luminescence. In selecting the test
procedures consideration was given to prob-
lems that arise from the use of chemicals by
nontechnical personnel. The difference
between field conditions versus laboratory,
the hazards involved, and the cost of the
chemicals employed in the reaction.

TEST PROCEDURE

Reference to the literature cited and that
of a recent publication (Reference 4) indicate
that the desirable alkalinity which optimizes
light production is furnished by solutions of
sodium hydroxide. Accordingly, the experi-
ments were performed in this reagent in
varying concentrations but other alkaline
materials were also investigated.

Basic considerations for the use of luminol
in the field are the following:

1. The compounds to be made into

solutions should preferably be solids for ease
of packaging and transporting.

2. They should be very soluble in water
and require no special mixing procedures.

3. To reduce cost and hazard to personnel
they should be capable of producing the de-
sired effect in very low concentrations.

In view of these considerations, a number
of preliminary experiments were performed.
These experiments consisted of: (a) Pre-
paring an alkaline solution and dissolving
the luminol in the solution, or first mixing
the solid reagent and luminol together, then
dissolving the mixture, and (b) Adding an
oxidizing agent to the prepared alkaline
solution of luminol in the dark to observe
the effects. The results are shown in Table I.

The results in Table I reveal that the
most desirable effects are produced when a
solution of luminol in NaOH is mixed with
a dilute solution of a bleaching compound.
Either 5 percent sodium hypochlorite or a
prepared solution of Du-chlor can be used.
The Du-chlor is preferred, however, be-
cause it is a pure white powder that is
easily handled and more stable in solution.
The attached photograph shows the chemi-
luminescent phenomenon as produced in the
laboratory. The brighter glow resulted from
the usual and well-known oxidation of luminol
with hydrogen peroxide and potassium fer-
ricyanide. Hydrogen peroxide is an unstable
liquid, however, and requires further inves-
tigation for field use. The glow of a deeper
blue was produced with solid chemicals that
can be easily adapted to field use.

VISIBLE EFFECTS FOR FIELD USE

Regardless of the degree of luminescence
produced by laboratory experiments, to be
useful, the effect must be demonstrated
under conditions approaching actual field
operations. In this respect, visibility must
be achieved and persist for a length of time
commensurate with the function of the signal-
ling device and its location. An arrangement
was set up in which a solution of 0.1 percent
luminol in 0.1 N NaOH was fed from a 500 ml
bottle at a controlled rate and merged in
a Y tube with a similarly contained 0.5 percent
TABLE 1

<table>
<thead>
<tr>
<th>ALKALINE REAGENT</th>
<th>OXIDISER USED</th>
<th>LIGHT EFFECTS</th>
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</thead>
<tbody>
<tr>
<td>1% Luminol in 1% K₂CO₃</td>
<td>Potassium Ferricyanide 1%</td>
<td>Barely visible</td>
</tr>
<tr>
<td>1% Luminol in 1% K₂CO₃</td>
<td>Sodium Hypochlorite 5%</td>
<td>Increased luminescence</td>
</tr>
<tr>
<td>1% Luminol in 1N NaOH</td>
<td>Sodium Hypochlorite 5%</td>
<td>Intense Green Light</td>
</tr>
<tr>
<td>1% Luminol in 0.1N NaOH</td>
<td>0.5% Sodium Hypochlorite in 0.1N NaOH</td>
<td>Bright Blue Glow</td>
</tr>
<tr>
<td>1% Luminol in 0.1N NaOH</td>
<td>Dilute Hydrogen Peroxide and Crystals of Potassium Ferricyanide</td>
<td>Bright Green Glow</td>
</tr>
<tr>
<td>1% Luminol in 1%K₂CO₃</td>
<td>Du-chlor (Sodium dichlorocyanurate) 1%</td>
<td>Poor Light</td>
</tr>
<tr>
<td>1% Luminol in 1N NaOH</td>
<td>Du-chlor, 1%</td>
<td>Bright Blue Glow</td>
</tr>
<tr>
<td>0.1% Luminol in 0.1N NaOH</td>
<td>Du-chlor 0.1%</td>
<td>Bright Blue Glow</td>
</tr>
<tr>
<td>0.1% Luminol in 1% Na₃PO₄</td>
<td>Du-chlor 0.1%</td>
<td>Good Luminescence</td>
</tr>
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</table>

solution of sodium hypochlorite. The merging mixture flowed by gravity through a section of 1/4 inch OD clear, plastic tubing. The device was positioned on a table three feet above the floor at one end of a tunnel used for experiments in lighting effects. As the two reagents flowed together they produced a blue glow in about three feet of the tubing. It was observed that the glow was visible at a distance of 300 feet. By changing the flow rate of the luminol solution a pulsing glow was produced which was also visible at this distance.

DISCUSSION

The oxidation of luminol in an alkaline solution in the dark produces an intense blue glow that is visible at 200 feet. It would probably be visible at greater distances provided the quantities used were proportional to those used in laboratory experiments. All the reagents required to produce the glow are very soluble in water.

The chemical reaction is unique and suggests the following possibilities for application to the limited war effort:

1. As a unique signalling device for night operations.
2. As a locating device for rescue operations when a fire or flare would be hazardous to use.
3. As a locating device for rescue at sea.
4. As an emergency landing light on air strips.
5. As a psychological weapon by virtue of the weird and bizarre effects that can be produced.

In any area of use additional tests would have to be made depending upon the intended application, the manner in which the reagents are to be handled, and the best means of packaging and transporting the reagents for field use.
REFERENCES


Reliable and unique signalling devices are a military necessity and the vagaries of nocturnal operations on land and sea engender a constant search for improvements and innovations. The phenomenon of chemiluminescence has been under study as a simple, reliable means of producing a unique light that might be adaptable as a signalling device. The chemical compound commonly known as luminol remains the best producer of "cold" light. Various attempts were made to oxidize the compound using reagents that would be safe to handle and easily available for field use but would be capable of producing a visible glow. It was found that the luminol can be oxidized with any ordinary chlorine-containing bleach to produce a greenish blue light that can be made to function as a flash or continuous glow that is visible from a considerable distance. Provided water is available, the method offers a means of signalling when electrical equipment of any kind is not available or has ceased to function. The phenomenon might also be used to create bizarre effects for psychological warfare.
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