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16. Abstract

This study was undertaken to evaluate the feasibility of adapting a bio or chemiluminescent system for use in a highway marker for wet-night lane delineation. The study involved a literature survey, theoretical evaluation of systems reported in the literature, limited laboratory verification and investigation of the visibility problem. Recommendations for further research and development are presented based on this preliminary work.

The chemiluminescent reaction of siloxene derivatives is recommended because it is expected that this system can be placed in a solid matrix and activated in rainy weather by diffusion of water through a bed of solid oxidizer. The siloxene system is cheaper and more readily adaptable to use in a highway marker than several bio or chemiluminescent systems evaluated.

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INTRODUCTION

Basically, self-luminous systems are potentially high-yield switchable light sources useful as markers rather than sources of illumination. In this sense they are efficient energy transducers; being self contained and switchable light sources derived from self contained chemical energy. The drawbacks are of a technical rather than inherent nature. At present there is no proven solid matrix self-luminous marker and no self luminous system has been made to cycle or regenerate chemically. The intensity and duration of such systems is the prime technical problem, for these systems are not (though they can be theoretically) usually more than 25% efficient. An exception is the firefly bioluminescence which is about 90% efficient. Presently several systems have been improved in their efficiency by factors of 10 to 1000X by "molecular engineering". The major drawback of most systems is their need for a liquid (solvent) matrix. The system that we have found most promising, siloxene, is inherently a solid-type system, easily adapted both physically and in terms of its intensity-duration properties to a marker application. In addition it has the capability of serving a dual function - both chemiluminescence and fluorescence in the same marker system.

Self-luminous chemical systems, in concept, could be developed into low-profile highway markers. Self-luminous systems have already been developed as temporary emergency markers. The highway application is more demanding. First, the marker must have a solid configuration (although wet). Secondly, it must be bright enough long enough to be functional. Third, it must be compatible

with the road surface and resist the extremes of climate encountered on the road surface. An fourth, it must be cost effective and "environmentally sound". No system known at present meets all of these qualifications.

Such a system could exist within the theoretical limits of chemiluminescent* liquid reactions, given near-ideal conditions. If, however, the reaction could be carried out in the solid phase, both the concentration and yield might be increased orders of magnitude. This possibility--the potentials of a solid chemiluminescent marker--was developed previous to this contract at ATP Systems. These developments, presented in our contract proposal, provide an optimistic view of the "marker potential" of a solid-compatible system. For instance, the reaction might be diffusion-controlled and even "switched" on and off by the presence and absence of, for instance, water, and the light output even might be oriented to a degree. Further, if energy transfer can occur, the color of the light might be adjusted (true also of liquid systems). And finally, the fluorescent output of a solid (possibly oriented) energy-transfer system might provide a visible-light (headlight)-activated light source capable of extending the range of utility of such an active and passive marker. Some of the demanding aspects of a highway marker might be met if a known system could be developed-or one found--to fulfill some of these properties. Such a system would have "marker potential."

During World War II, the Japanese used the light generated from dried Cypridina (a small crustacean), activated by saliva, to read maps in the field. An effective self-illuminating, solid marking system derived from an appropriate chemi-(or bio-) luminescent reaction has been the goal of a considerable industrial research effort

* This and other technical terms are defined in the Glossary found in Appendix C.

in at least three major chemical companies as well as the Department of Defense for at least ten years. Researchers at American Cyanamid and at China Lake, California (Naval Ordinance Test Station) have succeeded in developing self-luminous markers (liquid-filled) from an oxalate ester derivative ("Oxalume" at A. C.) and tetrakis (dimethylamino) ethylene ("TMAE" at C. L.) chemiluminescence reaction systems. As yet, however, neither system has been adapted to a matrix "more solid" than a thixotropic mixture, applicable to temporary, emergency use. The output from these laboratories (reports, publications, etc.) proved to be knowledgeable, sophisticated, and thorough. Soon, therefore, considering the efforts that had been made, we were pessimistic about our chances for finding a chemi-(or bio-) luminescent reaction with sufficient brightness and durability for highway applications, especially since a highway marker must be a solid-in-place system. Our approach, then, was to carefully examine the available information on the well known systems for possible "flaws" or "loopholes" indicating the possibility of "marker potential." The information on less well known systems was gathered by extensive literature-search procedures and consultation with experts, then evaluated for potential marker system candidates (see Appendix A). Biological systems, being most familiar to ATP Systems - the principal investigator, received less strict attention than the chemical systems, which were vigorously pursued. Rough criteria, bearing on the intensity (brightness or quantum yield), color and physical characteristics (e.g., gaseous systems excluded) were drawn up and

used in screening systems for marker potential. The ATP Systems-developed solid marker system criteria were kept in mind in estimating marker potential. Some criteria were relaxed when a system showed potential to fulfill most other criteria, especially if the system had potential as being solid-compatible. New developments in the field were vigorously pursued. As the information became available the field of candiate systems narrowed. The limitations of each system became more defined. Eventually the siloxene derivatives system with the most potential was chosen and investigated in detail. Promising systems with less potential were kept in the study as back-ups. This report describes the feasibility of the use of self-luminous materials in an effective pavement marking system for rainy nighttime conditions. First the criteria used in evaluation of self-luminous reactions are discussed. Then a number of bioluminescent reactions are theoretically evaluated, followed by a full system definition and laboratory verification of the siloxene-derivative system. Appropriate references are cited and gathered in the bibliography (Appendix D). Five (5) detailed preliminary reports were submitted to the Technical Officer (NASA/GSFC) during the course of this investigation. These can be made available to authorized personnel.

PROGRAM APPROACH AND CRITERIA

In order to carry out this program, a system of criteria and decision steps were developed to process the information gathered by an extensive literature-search effort combined with interviews of research personnel in the fields of chemi-and bioluminescence. The criteria and decision steps are discussed below. The given technical guidelines--listed below--fall into two categories: visibility and durability.

Technical Guidelines

Visibility:	"On" condition:	Rain (water cover of 1/32 inch), Nighttime
	Distance:	Visible at 150 feet from auto, Non-distracting
	Size:	Strip 4" x 36"
	Duration:	Up to 10 hours continuous output
	Lifetime:	Two months, six months desired
	Color:	Yellow or white preferred, blue or green acceptable, and red unacceptable
Durability:	Temperature:	$-20^{o}F$ to $+140^{o}F$ (desired, 0^{o} lower limit will be considered)
	Highway Conditions:	High traffic flow patterns. Asphalt and/or concrete compatible. Snow, oil and sand tolerant, non-spreading
	Profile:	0.015 inch thickness-resistant to effects of snowplows

The "on" condition requires that the system be light-producing at night when it rains. It does not require that the system be "off" at other times, but this would be an advantage in saving the chemicals in the marker. There are two aspects to this criterion that might allow a control of the luminous output of the marker: rain (water) and night (no sunlight). A water-activated and dry-deactivated system is conceivable (as stated above) and a bright-light-inactivated system is not outside the realm of possibilities. Such properties, although not necessary, would certainly add to the "marker potential" of a reaction.

The visibility model developed by Fairchild in this program (see Appendix B) concludes that at 150 ft, the minimum light-output level from an effective (2" x 80") marker should be 0.2 to 0.5 foot Lamberts (fL). Other researchers conclude that a luminosity of 10 to 30 fL gives optimum visibility (1). Previous testing of highway markers for optimum luminance was subjective (using observers). A level of 1 fL was then somewhat arbitrarily chosen as an "order of magnitude" estimate of the minimum allowable output. With this as a goal, we set a quantum yield of 0.1% as a rough (and flexible) lower limit for the efficiency of a candidate reaction system.* The reaction efficiency is a property that has been improved in the better-known systems by orders of magnitude. Consequently, we would expect that such improvements might be made in using "rough" criteria--an estimate of the potential to improve a given aspect of the performance of a particular system.
These estimates are based on ATP System's experience with

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*The upper practical limit for the quantum yield of chemiluminescent quantum yields is 10-20% (0.1-0.2).

Reasoning by which a level of 1 fL was equated to a quantum yield of 0.1% is not given.

self-luminous systems as well as the considered opinions of the interviewed researchers in this field. The possibility of orienting the light output of the system (possibly by mechanical orientation as with polarizing films) has the potential of raising the efficiency a factor of 10-30.

The duration and lifetime (10 hours, 2-6 months) of the system are subject to even rougher lower limits in terms of a given reactions "marker potential." Neither quantity can be effectively tested without a prototype in hand. We felt that it is important to develop an almost constant-output device. Several factors contribute to the limits of a marker in this regard: efficiency and durability (especially to temperature). Using the 10^{-3} (0.1%) rough limit on light-producing efficiency we might impose a rough temperature criterion on potentially labile constituents of a marker system. This criterion almost immediately excludes biological systems to be discussed starting on page 10. The near-constant-output goal alone makes it difficult to use liquid systems whose output decays almost exponentially. We have suggested that limitation of the diffusion of an essential component in a solid matrix system would tend to make the rate of light output nearly constant--not dependent on the remaining concentrations of the reaction components. Even oxygen (were it a reaction component) might be diffusion-controlled. Ideally we envisioned a system dependent, in some way, on water diffusion. This instance might allow both switching (on/off) and near-constant-output by a control of the diffusion of water. It would greatly extend the lifetime of a marker system if the limiting reactants could be regenerated in place. No such systems are known, but the potential bears attention.

The color of the light output is of little concern since few luminescent reactions emit red light. The output color of some energy-transfer (E.T.) systems can even be "adjusted" by choosing an appro-

priate fluorescent compound (to receive the energy and emit it). Most luminescent reactions produce blue, green or yellow light.

As mentioned before, the temperature range (-20°F or 0°F to +140°F) excludes the use of most (if not all) biological systems. In addition to the potential deterioration of the reactants (probably less in a solid matrix) there is the problem of the reaction kinetics dependence on temperature. Most chemical reactions increase in rate at high temperatures. This is true of diffusion rates as well. Obviously, it is important to have a high enough rate at +40°F to be seen, while at 140°F the (probably higher) rate must not expend the material too rapidly.

Resistance to traffic, etc., must be tested with a prototype, but it is indicated (along with the "snowplowable" criterion) that the marker must be solid and durable. The choice of reaction and solid matrix must be such that these criteria are met. Spreading and oil/salt resistance should not be problems once all the other criteria are met, since spreading would indicate undesired loss of material and oil/salt sensitivity should be (but might not be) taken care of by the solid matrix. The same argument can be made for the asphalt/cement compatibility, since these elements are probably not going to influence the state of a solid marker.

We have therefore developed a set of "desirable" properties for the candidate reaction indicating, to a degree, its "marker potential". potential":

1. Solid "matrix" compatible.
2. Diffusion controllable - water activated.
3. Efficiency greater than about 0.1%.
4. Temperature stable (both components and reaction rates).

5. Color-blue to yellow-possibly adjusted in energy transfer systems.
6. Orientation of output and regeneration of essential components.
7. Cost effective (difficult to assess except in some cases).

THEORETICAL EVALUATIONS

Although a great number of reaction systems were given serious consideration, only three or four are considered to be promising enough for brief theoretical evaluation. In addition one system was chosen for full system definition and laboratory verification. These reactions - cypridina bioluminescence, and the chemiluminescence of hydrazides (luminol and derivatives), oxalate esters ("oxalume" of American Cyanamid) and TMAE (tetrakis-dimethylamino-ethylene and derivatives) will be treated individually with respect to the properties pertinent to their potential use in marking systems.

BIOLUMINESCENCE

The low probability of success in applying bioluminescent reactions to a marker system results from rather elementary considerations of the nature of these systems. The first consideration is the doubtful availability of large enough quantities of the raw materials. Except in the case of bacteria, animals must be harvested from natural sources and cannot be grown. Secondly the cost of these materials is prohibitive (see Table 1). Additional expenses would be incurred by the processing of these materials. Only in the case of bacterial bioluminescence can we foresee a significant cost reduction with high production. However, with bacteria (as with other biological systems) none of the biological enzymes have been shown to act as true catalysts - they become product inhibited. In most systems this occurs when the enzyme has reacted only once. In addition, the enzymes are very heat sensitive with respect to both their stability and activity. Only the firefly enzyme can be made to withstand temperatures greater than about $120^{o}F$ for even short periods

TABLE 1

BIOLUMINESCENCE: COST ESTIMATE TABLE FOR THREE SELECTED SYSTEMS

(Due to the high costs of the basic material there is no estimate of the complete system costs).

Reaction System	Component	Cost Estimate Per Pound
Bacterial (A. fischeri)	Enzyme partly purified*	$75K
Cypridiana purified	Synthetic (substrate)**	$50-100K
	Enzyme**	$500K-1000K
	Dried whole**	$5-10K
Firefly (P. pyralis)	Synthetic substrate*	$400-1500K
	Purified enzyme*	$2M-4M

* Based on current per gram market prices (Sigma Chem Co.)

** Based on current cost in research program, not commercially available.

of time (minutes), and in all cases the enzymes are essentially inactive below 40^{o}F and above 100^{o}F. Further technical considerations are even more discouraging. Among these are availability, cost, and heat sensitivity of the substrates and the complex chemistry of these reactions, especially in the case of bacteria where at least two "substrates" are necessary in addition to an enzyme and oxygen.

CHEMILUMINESCENCE

Although chemiluminescent systems are less expensive and more stable, some factors remain as problems. For instance most derivatives of organic molecules that are not commercially available are relatively expensive to synthesize. Cost for those available is usally $10 to $100 per pound. Although high production levels should lower these costs somewhat they remain high and do not reflect possible complications in the synthesis. Stability is not an easy matter either. Most large organic molecules are heat sensitive. Additionally they are labile to attack by sunlight and oxygen-especially the combination at higher temperatures. It is unlikely that, for the above reasons alone, an organic chemiluminescent system would be stable enough or cost-effective. Additionally, there is the problem of yield in liquid systems. The yield can be very high at low concentrations of reactant due to self-quenching. In a solid system this may not be a problem. Also something may be done to reduce costs and increase stability. With this pessimistic introduction we will briefly sketch the three systems to be considered here on a theoretical basis.

HYDRAZIDES (Luminol and Derivatives)

One of the oldest known and most efficient chemiluminescent reactions, this reaction has been studied widely, but recently particularly in the laboratories of E. H. White (2) , and K. D. Gundermann (3). This

reaction was studied by the British Army and at American Cyanamid in the late 1930's and early 40's for marker potential-unsuccessfully. These compounds are derivatives of 3 - aminophthalhydrazide (Figure 1a). The highest yields are obtained when the molecule is substituted at the 5-position by groups that can release electrons by resonance (4). Blue light is normally produced (aminophthalate dianion). Sensitized chemiluminescence is also possible by energy transfer to a fluorescent molecule such as rubrene which increases the yield to 50%. Two sets of conditions produce light: in aqueous alkali (ca 0.1N), H_2O_2 (3%). Oxidation is catalyzed by haemin (10^{-5}M), in dimethyl sulfoxide (anhydrous);only base (ca 1.0N) and oxygen are required. Luminol is not particularly efficient in light production, the quantum yield being slightly over 1%. Yields of 7-26% have been reported. The major problems with this system are:

(1) High cost of producing high yield reactants
(2) Lability of luminol and derivatives to heat
(3) Self-quenching of system at high concentrations
(4) Difficulty in incorporating high base concentrations and/or hydrogen peroxide into solid matrix and
(5) Control of the reaction rate

OXALATE ESTERS AND DERIVATIVES

Since 1961 research aimed at the eventual marketing of a luminous source (marker) has been carried out at American Cyanamid under the direction of M. Rauhut. An excellent review of this work has appeared (5). They concluded, in the process of searching for a suitable reaction for development as a marker that luminol would not suffice due to its low yield. In fact it was poor (less than 0.1% of expected need) and other systems were not better. Thus,they set about to "discover" a

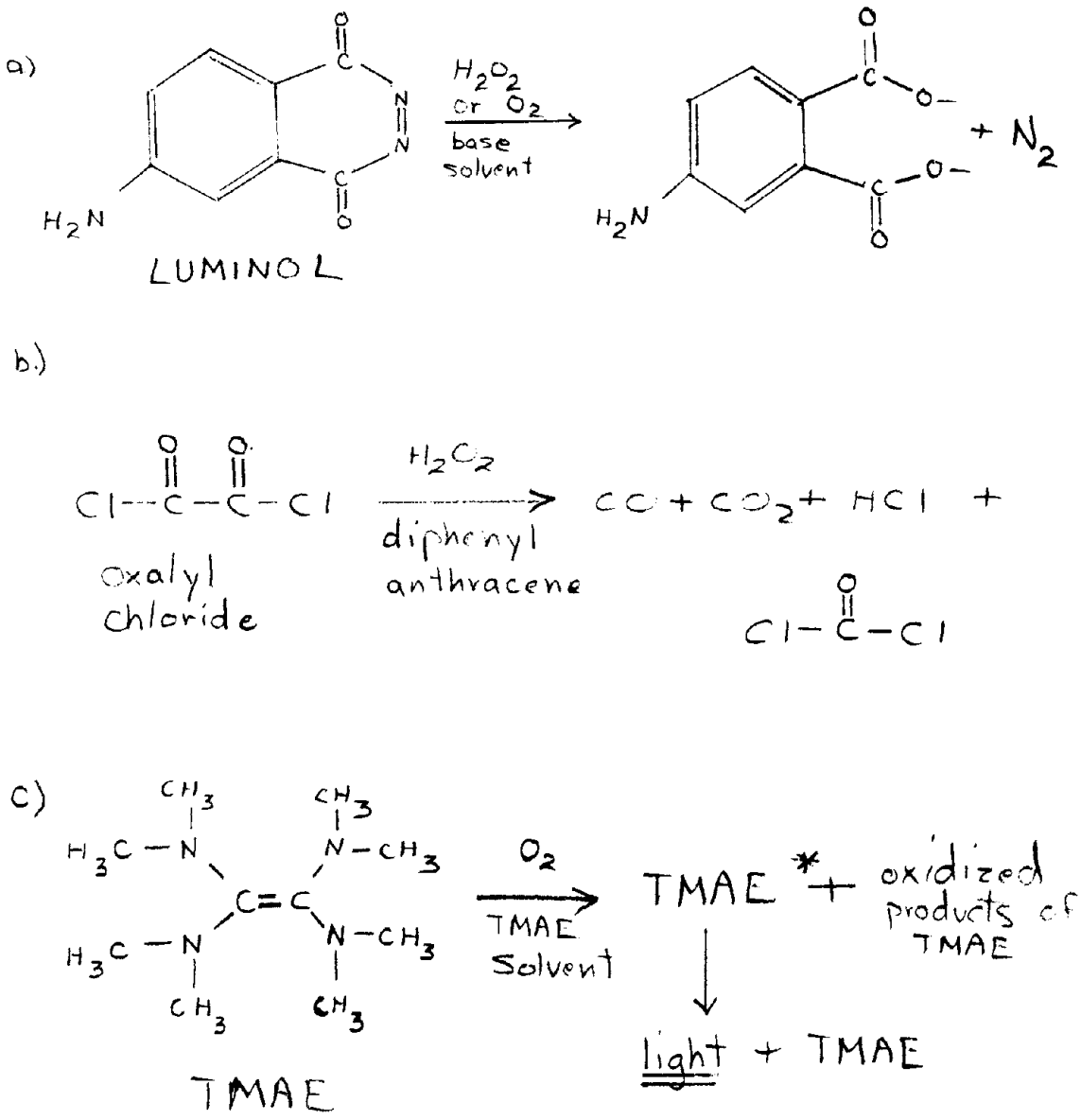


FIGURE. 1 REACTIONS

new system and the oxalate ester series began. This system requires an oxalate ester derivative (Figure 1b), a fluorescent energy transfer acceptor, H_2O_2, and a catalyst. This reaction provides yields as high as 28% and has been successfully encapsulated in a commercially available liquid light "wand." Efforts to provide a solid matrix support have failed, however, the best approximation being a thixotropic mix which can be "painted" on vertical surfaces but does not dry. The color can be varied and the lifetime lengthened but this is still a liquid system (non-aqueous). Without going into great detail it should suffice to observe that the failure of such a large and capable effort in adapting this system to a solid support indicates that its "marker potential" is poor in this case. It is still a two component liquid system utilizing a strong peroxide in every case.

The reaction parameters in the oxalate reaction require the use of materials and conditions that make it difficult to conceive how a solid or encapsulated system could be designed-even in concept. The necessity of an energy transfer acceptor dictates that the oxalate and acceptor be closely associated spatially. In solution this condition is obtained by the random distribution of high concentrations of fluorescent acceptors in the liquid phase, but in a solid phase the necessary juxtaposition would have to be engineered into the molecular design of the marker. Solvation plays an important role in this system and a non-aqueous medium is necessary. It is difficult to imagine how the system could be water activated in principal. The requirement of a strong peroxide in the reaction makes control and stability an even more prohibitive task. The "light wand" achieves the task of fulfilling these requirements by using a two component liquid system with the peroxide contained in a fragile glass ampule which is broken to initiate the reaction. The development of this "light wand" required an eleven year effort with as many as six full time professional personnel working on the project at once.

TETRAKIS (DIMETHYLANIMO) ETHYLENE (TMAE) AND DERIVATIVES

Work on this system began at DuPont and has continued at China Lake USN Weapons Center, China Lake, California (6). This is an interesting, if not curious, reaction system based on the "auto-oxidation" of TMAE (Figure 1c) in the presence of oxygen and a long chain alcohol. The system requires energy transfer, either to unoxidized TMAE or an added fluorescer. Essentially the addition of air (0_2) to an acidic solution of the components produces light. But the system requires the presence of a solvent, and again the possibility of a solid-type marker has been thoroughly investigated. In this and the oxalate cases the primary reactants are relatively inexpensive but the systems require a fluorescer to be efficient. Several additional properties make this system of doubtful potential:

(1) Extremely rapid reaction rate
(2) Lability to light and air
(3) Difficult control (oxygen)
(4) Product Inhibited
(5) Relatively low quantum yields (ca . 1%)
(6) Apparent absolute requirement of liquid phase

Again the difficulties stem from the liquid phase requirements, self quenching at high concentrations, possible cost-ineffectiveness, and the apparent failure to produce a solid matrix compatible system by a number of capable investigators who are anxious to do so.

FULL SYSTEM DEFINITION SILOXENE DERIVATIVES

The system chosen for full system definition and laboratory verification is derived from a silicon compound, siloxene (Figure 2a). This system was discovered in 1921 by H. Kautsky and his coworkers (7) who published only a few articles (in German) relating their experiments on the bright chemiluminescence resulting from the interaction of the inorganic "hydroxy siloxene" with an inorganic oxidant in acidic aqueous media. The light produced can range from green to orange, depending on the conditions. The outstanding feature of this system is that siloxene and its derivatives are solids. In addition to the work done by Kautsky, some contractual studies were performed by a group at TRW Systems (8) supported by the military (U. S. Army at Picatinny Arsenal, N. J.). This system has been somewhat obscure and has gone largely unnoticed. There has been little published work (none in English) and the system is inorganic. It has escaped the attention of almost all reviewers.

Siloxene and its derivatives are high polymer, dense, insoluble lamellar, crystalline solid compounds of silica having the monomeric structure $Si_6O_3H_6$. Siloxene and some of its hydroxy (-OH) substituted derivatives (and possibly others) are inorganic reactants for a bright chemiluminescent reaction seen in the acid-medium oxidation by any one of a number of inorganic oxidants, such as ceric ammonium sulfate. The synthesis of siloxene is carried out by the addition of any of a number of strong halogen containing acids to $CaSi_2$ in at least a partially aqueous solution (9). Calcium silicide ($CaSi_2$) is a hard crystal melt formed directly at about 1000° from its elements (a very inexpensive

process). Siloxene itself is a spontaneously combustible compound when dry, thus its hydroxy derivatives, which are stable, are used as reactants. It seems that either the mono or di-substituted compounds are most efficient light producers.

Hydroxy derivatives of siloxene are formed by hydrolyzing siloxene (in the reaction mix) following its formation from $CaSi_2$. The syntheses of these compounds, other than siloxene itself, are not well understood, and, in fact, there are differences in the product depending on the acid used. The structure of siloxene is shown as partial polymer (a) and the lamellar structure maintained in the synthesis (b).

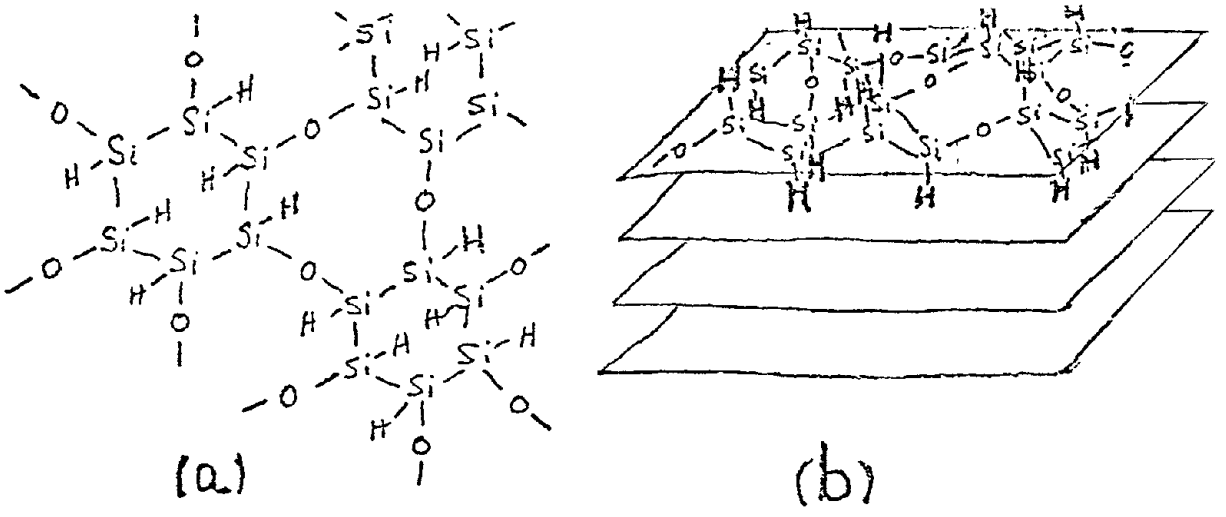


Figure 2. Siloxene Structure

This sheet-like crystal structure is maintained in the chemiluminescent reaction and may, in some cases, swell slightly. Hydroxy derivatives are formed by displacement of a hydrogen (-H) on the silicon ring.

Siloxene and its derivatives have a high affinity for fluorescent dyes, which are absorbed in between the lamellar sheets. These dyes can act as energy acceptors in the chemiluminescence. The hydroxy derivatives are neither impact sensitive nor tend to ignite. These compounds show little decrease in activity when stored at $-65^{o}F$ to $140^{o}F$ under nitrogen in the absence of light. They have been made in a silica gel form which is also stable in the absence of oxygen. They are compatible with a number of plastic materials containing acid and water. Dyes can be absorbed prior to initiating the reaction. The resulting emission color is then the color of the fluorescence of the emitting dye. This is a simple reaction, possibly not involving oxygen. The eventual product is thought to be silica (SiO_2, sand). The mechanism of the reaction is not understood.

The color of the emission ranges from green (siloxene) yellow (-OH siloxene) to red (4 or 5-OH substituted siloxene) depending on the reactant. There also appears to be a color dependence on the acid used. The derivatives (hydroxy) formed in the presence of HF gives blue-green light, with HCl gives yellow light, with HBr an orange light. These results are not consistent with any simple chemiluminescence mechanism and suggest that either the emitter in the reaction is an impurity or some halogen substitution of the reactant compound is necessary.

The quantum yield has not been determined, but the crude reaction can be seen (as a flash) in room light and reaches a peak intensity of 10-300 candelas (maximum intensity 500 candles) and sustains 0.1 candela for over an hour.

Work at TRW Systems, under contract to the Army, although largely a duplication of the work of Kautsky (1921-56), indicate some properties in addition to the obviously good potential of the system favorable to marker construction, including restricting diffusion (reaction rate) by gel encapsulation.

The marker potential of this system is good. The system is very inexpensive to produce and is a solid-oxidant two component system. It is capable of high, although unsustained light emission levels. There is evidence that by diffusion control (in a gel) the duration can be lengthened. This same property allows for water-activation of the system. If the siloxene-derivative is put in one gel layer and the oxidant is put in another gel layer chemiluminescence results when the addition of water allows the movement of oxidant from one gel (layer) to the other. Drying the system results in the cessation of light emission, which can then be restored by addition of water. Further increases in intensity and duration might be achieved by the use of absorbed fluorescent dye and by orienting the lamellae of the "crystals".

The reactant is quite stable (as is the oxidizer) and the light producing reaction is visible from at least 40^{o} to 90^{o}F. The luminescent reaction is relatively insensitive to high concentrations of calcium chloride. The reactants are stable over a wide range of temperature (-65^{o}F to 140^{o}F) when stored separately in the dark in the absence of oxygen (air). The siloxene derivative used was non-toxic. Most of these results (largely taken from the tests by TRW Systems) indicate an inherently stable system, but since there is no chemical identification of the most efficient reactant it is difficult to take them as anything but preliminary. On the surface, however, this system seems to fulfill all the requirements of the ideal reaction for use in a pavement marker with the exception of the intensity-duration properties. As stated previously, the yield is one area where one can expect improvement.

To reiterate the list of properties desirable in a potential self-luminous marking system reaction fulfilled by this system:

1. Solid matrix compatible
2. Diffusion controllable - water activated
3. Efficiency greater than about 0.1%
4. Temperature stable (both components and reaction rate)
5. Color - blue to yellow - possibly adjustable in energy transfer systems
6. Orientation of output (and regeneration of essential components)
7. Cost effective (difficult to thoroughly assess at this moment)

As a result of the above analysis the requested laboratory tests were performed on this system. The results are summarized below.

LABORATORY VERIFICATION

Hydroxy siloxene derivatives were provided by ATP Systems, Inc., by a modification of the methods of Kautsky (7). A developmental research program is underway sponsored by ATP Systems to improve the output of the siloxene-derivative system. Results of the laboratory verification tests show that a peak output intensity of at least 300 fL is obtainable (see Figures 3 and 4). The decay of the intensity and the total light depend on the preparation (impure starting material gives a greater amount of light than pure) and the medium (gel-solid-like systems peak at lower intensities and decay much more slowly - Figures 3 and 4). The emission maximum varies from 540 nm to 560 nm depending on the initial conditions and the time after initiation when the spectrum is measured (it becomes more red with time without an added dye). Unfortunately there is little consistency in the results here, presumably due to the known variability in the starting material (which is undefined in structure) and the dependence of emission color on this material. Although the effective life of the solid support (matrix) systems is relatively short, these experiments were performed under the conditions previously defined. It is encouraging that the use of gels increases both the length of time for decay (almost 30 min at 0.1 fL) and the total light that the reaction emits. The reaction conditions (except for the use of agar and silica gels) were standardized as follows:

Starting material (siloxene hydroxide)	0.5 g per 10 ml
Final Concentration of Acid	0.2 M H_2SO_4
Concentration of Oxidant	0.2 - 0.5M

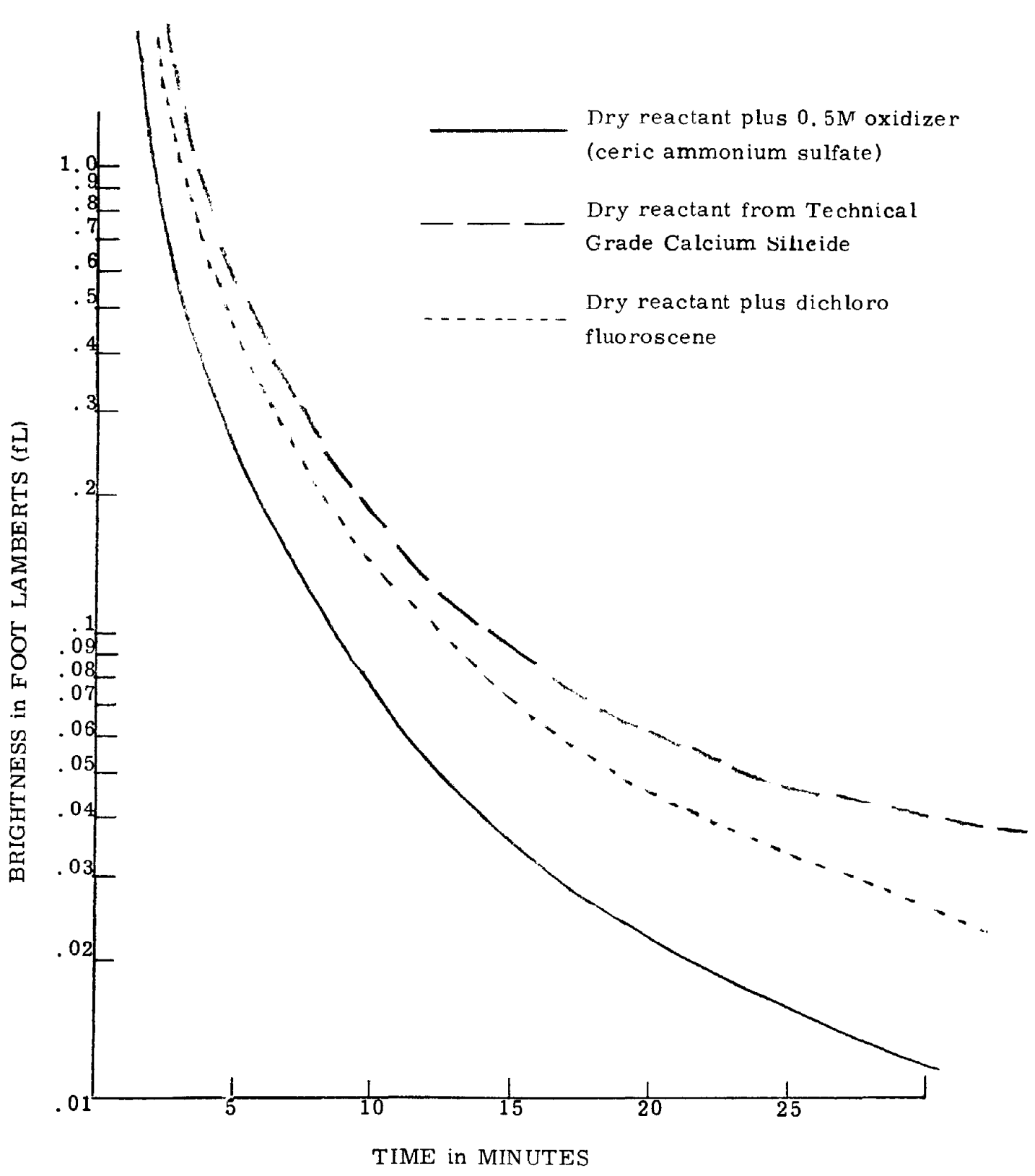


Figure 3. Chemiluminescence of Siloxene Derivatives

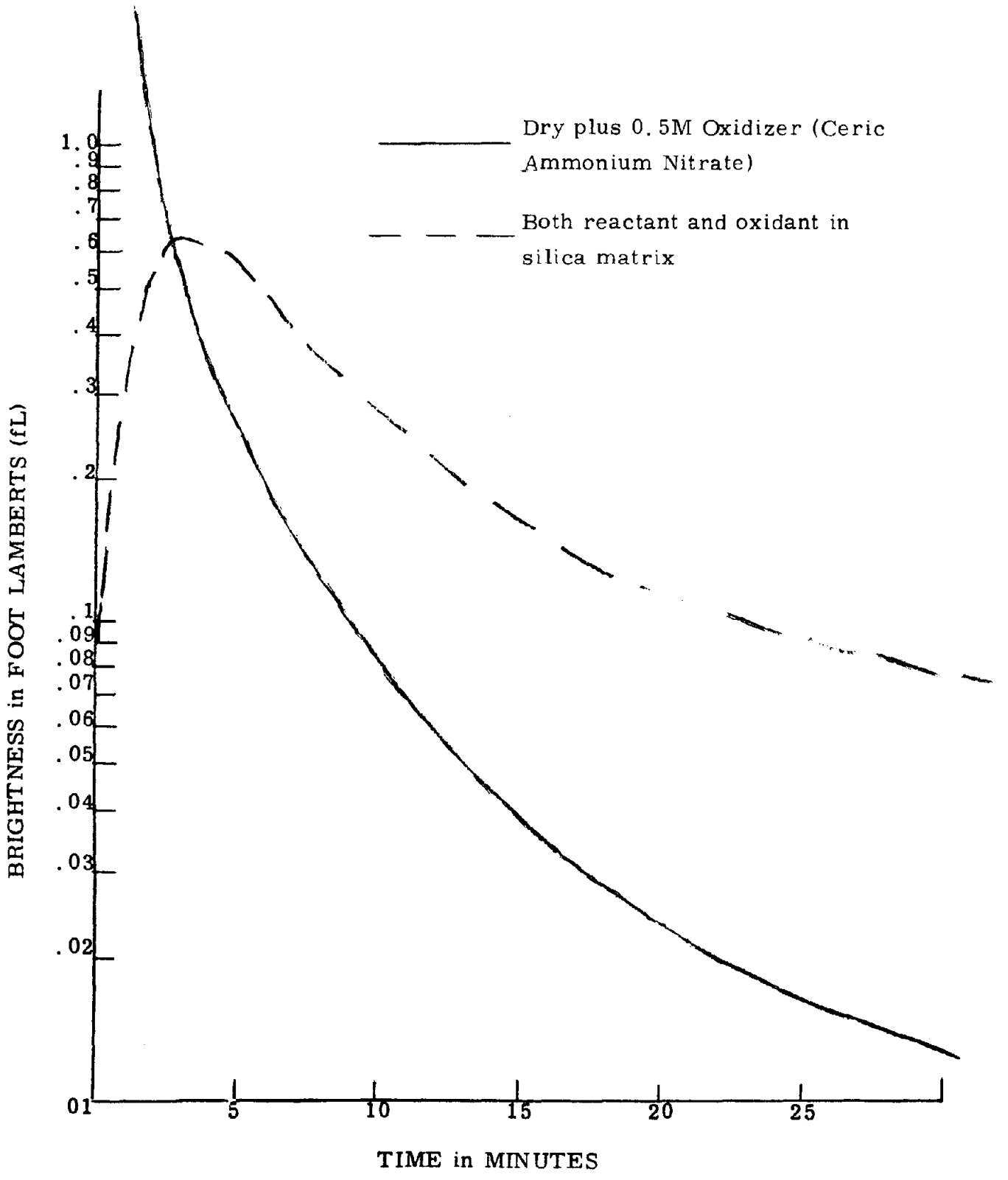


Figure 4. Chemiluminescence of Siloxene Derivative

The addition of fluorescent energy exchange acceptors increased the yield 50-200% and the light output color was the characteristic fluorescence emission color for the added dye (dichlorofluoreoscenie added produced a color characteristic of its fluorescent emission). The pH of the exterior surface does not affect the output of the system but the reaction "pH" even in the gel must be near 1. The silica gel matrixes do not seem to be temperature sensitive while the agar gels deteriorate both with high temperatures and during the course of the reaction (de - graded by the low pH - acidic medium). Thus there seems to be little chance of there being a problem with road surface compatability, since an encapsulation of the system is envisioned (see Model section below).

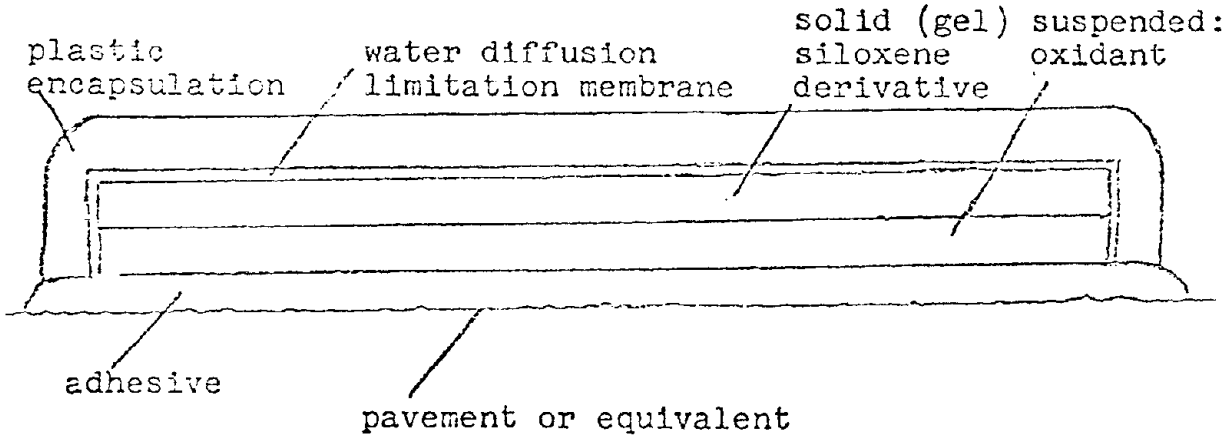
Further experiments designed to develop this system for marker use are underway, as stated above, and are outside the scope of this study. The properties of this system, except for the notable lack of sufficient intensity, seem to be tailor-made for a solid type marker. A suggested mode of use for this system is an encapsulated two-phase marker strip, described in the following section.

MARKER MODEL

The proceding five sections present work done during this study and this section presents a concept of how a marker might be arrayed.

To be explicit about the form and structure of the marker we are conceiving we refer first to the comments in our proposal and the reports following concerning various aspects of this model.

An encapsulated two or three layer strip is envisioned. Two adjacent layers contain acidic hydroxy-siloxene (or other derivative) plus absorbed dye (if necessary), possibly arranged so that the lamellar structure is oriented - so that output is beamed at the proper angle. The oxidizer (diffusible) is in the second layer. Diffusion of water into the layers is achieved by proper choice of encapsulating material or by using an inner selective diffusion membrane. The rate of diffusion of oxidizer into the siloxene derivative containing layer is controlled by the rate of water diffusion into the layers and through the oxidizer layer. This rate will be adjusted so that the light intensity remains contant - at a much lower level than if water were freely circulating. This device, pictured below, would take a period of time, possibly minutes, to establish equilibrium and "turn on". It would be applied by adhesive, possibly even as a paint applied in layers.



SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The feasibility of utilizing bioluminescent concepts and materials for an effective pavement marking system for wet nighttime conditions has been investigated by processing and evaluating information gained through literature searches, interviews of research personnel, laboratory experiments, and the extensive past experience in the field of the principal investigator. This application of chemical luminescence, in terms of intensity, duration and durability is most demanding. An analysis of these technical demands led us to conclude that the system must be compatable with a solid matrix and should be water-activatable. Other properties would increase the usefulness of the system, such as energy-transfer capabilities and low production costs. One chemical reaction system, involving solid derivatives of the low-cost inorganic solid silicon compound "siloxene" being oxidized by a water-diffusible inorganic oxidizer, promises to fulfill most of the requirements of this application. Biological systems, possibly of use as self-luminous markers elsewhere, are too unstable and expensive for this application. Some other chemiluminescent systems (organic) have been developed as (liquid) markers, but are as yet incompatible with a solid support and water activation. In addition, these systems appear to be less cost effective and more likely to deteriorate under highway surface conditions.

The siloxene-chemiluminescent system has been the subject of very little research effort since the 1930's. Little, if anything, is understood of the chemistry, let alone mechanism, of this reaction. It is, therefore, difficult to assess the prospects for the success of the application of this system without using arguments based on analogies. This

system has, as a most obvious drawback, too low a light yield for this application. There is a good probability, based on our experience with other systems, that modern concepts and techniques will allow the improvement of this property possibly by orders of magnitude. The inherent properties of this system make it very attractive for this application in terms of it being solid, water activated, stable, low-cost and generally versatile.

We suggest that with the siloxene derivative system there is a good possibility that a development effort directed toward:

1. Understanding the chemistry
2. Improving the light yield and
3. Design of a diffusion-controlled matrix

would yield a prototype marker capable of being tested for application as a self luminous roadway marker, visible under rain nighttime conditions. A simultaneous effort, aimed toward finding conditions for the use of the presently more efficient (organic) chemiluminescent reactions in a solid and water activated matrix, would increase the prospects of success for attaining the desired product. Such a program would best be carried out in stages, with close supervision and control, such that continued support would be dependent on progress.

Insofar as evaluation of a marker prototype is concerned, consistent minimum perceptibility measurements are difficult to perform due to the following factors influencing the results.

1. State of adaptation of the eye
2. The average luminance level in the visual field
3. The uniformity of the luminance
4. The size of the source
5. The location of the source in a visual field

6. The duration of the light emittance
7. The effort and concentration of the observer

We will attempt to take these factors into account during future development of our marker model.

In conclusion, visibility enhancement on the roadway at all distances is valuable both near and far; it is hoped that this study will lead to enhanced roadway visibility and all the positive ramifications thereof.

APPENDIX A

EXPERTS CONSULTED

During the course of the "search" phase, early in the study, we contacted in person a number of professional personnel currently involved in research in chemiluminescent and bioluminescent systems. These professionals and/or their research support staff (students and postdoctorals) were asked to suggest potential candidates for a marker reaction system. In addition they were asked to critically assess the direction and tentative conclusions of the search phase. Additionally Prof. E. H. White at John Hopkins University in Baltimore was consulted regularly regarding the progress of the study. Additional professional advice was obtained by telephone. The directors of research personnel contacted in person are listed below with an indication of the general area of their expertise: bioluminescense, B, chemiluminescense, C, instrumentation, I.

Dr. John B. Buck, Marine Biological Laboratories, Woods Hole, Mass. and N.I.H., Bethesda, Md. (B)

Prof. James Case, MBL, Woods Hole, Mass. and University of California (U. Cal.) Santa Barbara, California (B)

Prof. Milton J. Cormier, University of Georgia, Athens, Georgia (B, C)

Prof. Frank H. Hanson, University of Maryland, Baltimore County, Md. (B)

Prof. J. Woodland Hastings, MBL and Harvard University, Cambridge Mass. (B, C)

Prof. David M. Hercules, University of Georgia, Athens, Georgia (C)

Prof. John Lee, University of Georgia, Athens, Georgia (B, C, I)

Prof. James Morin, MBL and U. Cal at Los Angeles, California (B)

Prof. George Reynolds, MBL and Princeton Univ., Princeton, N.J. (B, I)

Prof. David F. Roswell, Loyola College, Baltimore, Md. (C)

Prof. Ruth Weiner, Univ. of So. Florida, Miami, Florida (C)

Prof. Emil H. White, Johns Hopkins University, Baltimore, Md. (C, B)

LITERATURE SEARCHES

A number of literature search procedures were used to obtain sources of information relevant to this study. Both published literature and reports of government supported research projects were surveyed. The general areas of chemiluminescence and bioluminescence were covered until it became obvious that few if any of the bioluminescent systems would be practical. Additionally the specific areas of siloxene (triepoxy cyclohexylsilane), oxalate esters, tetrakis dimethyl aminoethylene (TMAE) and luminol were searched in Chemical Abstracts. Following is a list of the search sources:

1. RECON/NASA - computerized keyword and abstracts for government supported research and general literature references. Over 500 subjects retrieved. Source Goddard Space Flight Center
2. DDC/DOD - Mostly defense related government supported research reports. Over 300 subjects retrieved. Source Department of Defense
3. SIE/NTIS - largely literature survey. Output limited to 125 subjects. Source Smithsonian Institution National Technology Information service
4. Chemical Abstracts - Searched manually by professional library personnel. Over 100 selected subjects retrieved and reviewed.

APPENDIX B

VISIBILITY MODEL

The highway marking problem can be expressed in terms of the light reaching the motorist's eye (illuminance in foot-candles or candelas/distance^2) and the intensity or brightness of the delineator (in candelas for point sources and in foot lamberts for lines). This is an oversimplification because visibility of a marking system on a highway depends not only upon its intensity or brightness, but also on its size, its shape, time available for seeing the marker (speed dependent), the viewing angle, adaptation of the eye(recent exposure of the eyes), luminance contrast (with background), glare, light dissipation by surface water or airborne particles such as fog, haze, and rain and other factors. (See Figure B-1, "The Driving Task" for an impression of the complexities involved.)

The above-cited variables will be amplified upon.

Luminance/Illuminance Relationship

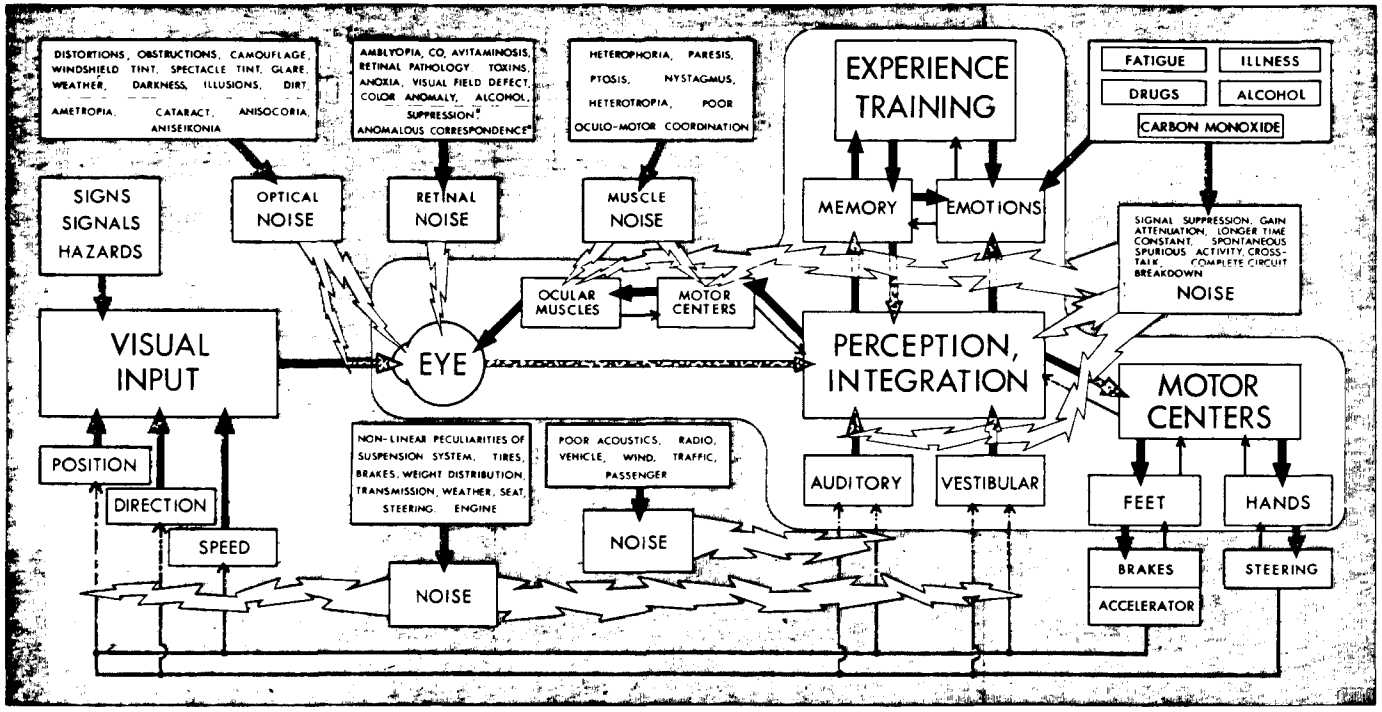
The following relationships are of interest in correlating the luminance of a marker to the illuminance at the human eye:

The intensity of the marker (I_m) is the luminance of the marker (L) times the area of the marker (A) or written as an equation:

$$I_m(\text{candelas}) = L_m \left(\frac{1}{\pi} \text{ Ft Lamberts}\right) \times A \ (\text{ft}^2)$$

The illuminance (in clear air) at the eye ($E_{(eye)}$) then depends on the distance (D) from the marker as follows:

$$E_{(eye)} \ (\text{foot candles}) = \frac{I_m \ (\text{candelas})}{D^2 \ (\text{ft}^2)}$$



A schematic diagram of the driving task. The visual input into the eye is the beginning of a closed loop which proceeds via the perception-integration and motor control centers of the brain through the hands and feet, the vehicle, the position on the road, and finally back to the visual input. The lightning streaks represent potential or real interferences which operate to reduce the efficiency of the driver. The main arrows show interference (noise) by being drawn as spotty. Note that the brain is able to sort out the noise and obtain surprisingly accurate information. Because of the brain's ability, few realize how much impairment occurs in everyday driving that may become serious if the brain's ability is compromised by fatigue, illness, lack of training, or overloading.

Figure B1: The Driving Task

(Source: Merrill J. Allen, Vision & Highway Safety Chilton Book Co., c 1970 p. 6)

Combining and simplifying these two equations gives us the following relationship between luminance of a marker and the resultant illuminance of the eye.

$$L_m\ (fL) \cdot A\ (ft^2) = E_{eye}\ (fc) \cdot D^2(ft^2) \cdot \pi \quad *$$

Given this relationship and the threshold value 10^{-7} fc illuminance at the eye in Table B-1, for instance, it is found that marker luminance might reasonably be 7.068×10^{-3} fL over one square foot of area.

Luminance Contrast

If the chromaticity of an object and its background is the same, the object must be darker or lighter than the background to be seen. Luminance contrast is the relationship between the luminances of an object and its immediate background. The contrast between the two adjoining areas is defined as:

$$C = \frac{L_{bg} - L_{ob}}{L_{bg}}$$

where L_{bg} and L_{ob} are the luminances of the background and object respectively. The contrast can also be computed from:

$$C = \frac{L_{ob} - L_{bg}}{L_{bg}}$$

If contrast values are presented, it should be stated which equation was use used for the computations.

$$C = \frac{L_{bg} - L_{ob}}{L_{bg}} = \frac{\Delta L}{L_{bg}}$$

* Equation derived from equations given in Reference 1 , page 220.

Table B1. Threshold Values

Visibility (the ability of an average observer to detect the presence of a marker) is assumed if the illuminance at the eye is above some threshold value.

Threshold varies for individual observers because of visual capabilities; what, where, and if the observer expects to see something.

IDEAL	REASONABLE	CONSERVATIVE
		(attention attracting)
.5 mile-candle .5 cd/mi^2 .5 cd/$(5280)^2$ 1.8×10^{-8} fc	10^{-7}fc	10^{-5} fc

(source: National Cooperative Highway Research Program Report #130 p. 221)

where ΔL represents the numerical luminance difference. The equation can be used whether L_{bg} or L_{ob} is the larger value, although it is essential to specify in the results whether the higher or lower luminance value was used in the denominator. In most instances the larger of the two areas constitutes the background, but in some cases where the two contrasting areas are nearly the same size, it is necessary to define arbitrarily which represents the background and which the object, (see Table B2).

The luminance of a light source has to exceed a minimum limit to be seen. For a completely dark-adapted eye, the lower limit or the threshold of luminance of the visual field (background intensity) is approximately 10^{-6} footlamberts. At this level only the rods respond to light. Since the cones are not functioning, sharp vision is impossible and colors cannot be seen. Increasing the luminance to 10^{-2} footlamberts activates the cones, making it possible to distinguish colors. However, the rods continue to operate, but above 1 footlambert level the vision is dominated by the cones. The visual range of the human eye is:

Rod vision (scotopic), (Black-white): 10^{-6} footlamberts - 10^{2} footlamberts

Rod-cone vision: 10^{-2} -1 footlamberts

Cone vision (photopic), (color): above 1 footlambert (see Table B-1.

The following table was derived from the information in Figure B-2, Table B-2 and cranking these data through the contrast equation to find L_{ob}.

Background Intensity Situation	L_{bg}	Figure B2 Contrast Req'd for L_{bg}	L_{ob}
Overcast Moon (Raining)	.001 fL	200	.2 fL
Clear Moonlit Nite	.01 fL	27	.28 fL
Gray Concrete Road Under Low Beams Ref(2),Page 3	.05 (fL).	9	.5 fL

Computed Object Luminances

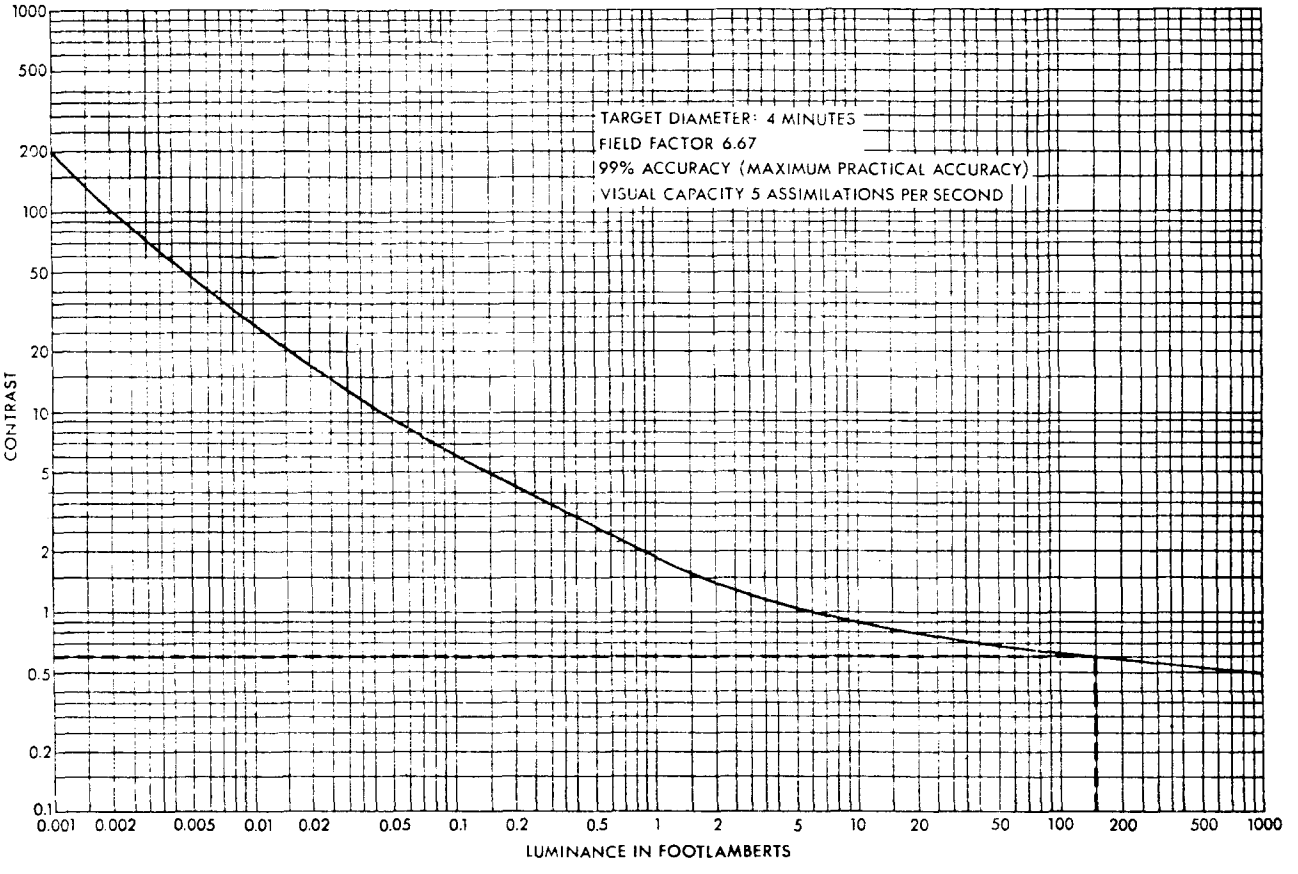


Figure B 2. Contrast Required for Various Backgrounds

(Source: IES Lighting Handbook, 4th Edition, p. 2-16.)

Table B2. Luminance Values of Various Backgrounds

Luminance Values of Various Backgrounds Against Which Luminous Signals Are Viewed

Background	Background Luminance (footlamberts)
Horizon sky	
Overcast, no moon	0.00001
Clear, no moon	.0001
Overcast, moon	
Clear, moonlight	.01
Deep twilight	.1
Twilight	1
Very dark day	10
Overcast day	100
Clear day	1000
Clouds, sun-lighted	10000
Daylight fog	
Dull	100–300
Typical	300–1000
Bright	1000–5000
Ground	
On sunny day	100
On overcast day	10–30
Snow, full sunlight	5000

Sources: IES Lighting Handbook, 4th Edition, P. 2-27.

It becomes readily apparent that a marker of .007 fL would not be useful for our application due to contrast considerations.

Glare is the sensation produced by brightnesses within the visual field that are sufficiently greater than the luminance to which the eyes are adapted. It causes annoyance, discomfort, or loss in visual performance and visibility. The magnitude of the sensation of glare depends upon such factors as the size, position, and luminance of a source, the number of sources, and the luminance to which the eyes are adapted. Thus, lights from cars traveling in the opposite direction may cause a very detrimental affect on marker visibility.

Size

The visual size of any marker that needs to be seen is a function of its physical size and its distance from the observer. By combining these two dimensions, one can express the size as a visual angle which usually is measured in minutes of arc. The visual angle is the angle which an object subtends at the optical center of the eye. (see Table B3, Marker Size.)

For large light sources, the lower luminance threshold is proportional to the luminance of the source and independent of the angle size of the source. For example, if the luminance of two light sources, 12 inches square and six inches square, is slowly increased at the same rate from zero, the two sources will be seen simultaneously if observed from a short distance, e.g., two feet.

For small sources the luminance threshold is proportional to the luminous flux reaching the eye, which in turn is proportional to the lumen output of the source. The above mentioned two light sources, with gradually increasing intensity and viewed from afar will not appear simultaneously but the larger light source will be noticed first.

MARKER SIZE

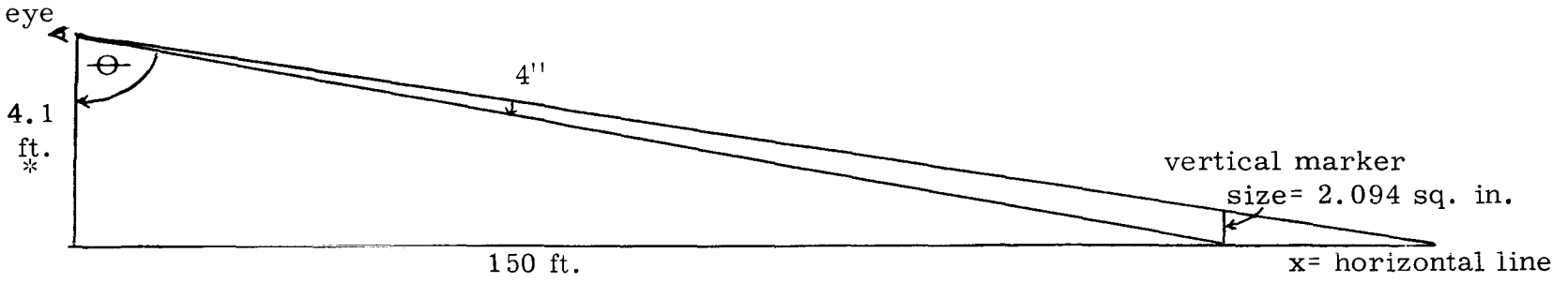
"Under road lighting conditions, the visual threshold (for size), which is approximately 1 min. of arc in the laboratory, will increase to 3 to 4 min of arc at best."*

Table B3
Target Size for Various Distances
and Angular Size Thresholds

ANGLE (min) α \ DIST (ft)	50	100	150	200
3	.523"	1.047"	1.570"	2.094"
4	.698"	1.396"	2.094"	2.790"
5	.873"	1.745"	2.618"	3.490"
6	1.047"	2.094"	3.142"	4.189"

(Thus, for example, we find through simple trigonometry that a marker 2.094" across subtends an angle of 4' at 150 ft.)

* Allen, M.J., "Vision & Driving," Traffic Safety, Vol. 69, No. 9, (Sept. 1969) p. 8.



$\tan \angle \Theta = \frac{150}{4.1} = 36.58536585$

arc tan 36.58---= 88.4340522° = Θ

$\Theta + 4'' = 88.50097189°$

$\tan \Theta + 4'' = \frac{150 + x}{4.1} = 38.21322982$

$x = 6.6742423$ ft.

thus, a horizontal line must be approx. 2 in. wide and $6\frac{2}{3}$ ft. long to be equivalent to a vertical marker 2.094 inches square under this set of circumstances.

* 4.1 ft. is the average height of the average persons eye above the roadway surface in an American automobile

Figure B3. Line Size Equivalent Computation

In physiological optics a point source is defined as a source that is perceived by the eye as a point. The image of such light sources as formed on the retina is so small that it occupies only one of the light-sensitive elements of the retina. A reduction in the size of the source, or an increase in the distance from which it is observed, does not therefore alter the apparent size of the (point) source. When the size of the source is increased, or the distance reduced, the point as seen by the eye only becomes larger when the image on the retina covers more than one of the light-sensitive elements.

Small Sources

The threshold luminance of a small source ($\alpha < 20$ minutes) depends only upon the light output of the source.* Therefore, the threshold luminance, L_o, and the threshold luminous flux, ϕ_o, are:

$$L_o = \frac{\text{constant}}{A}, \text{ where A = the projected area of the marker}$$

The smaller the source, the higher luminance it must have to be seen. We can express the threshold luminous flux also in respect to the illumination on the eye, E_o:

$$E_o = \frac{\Phi_o}{P} = \text{constant}$$

where P represents the area of the pupil. Since the illumination is in turn proportional to the luminous intensity (luminance) of the source, we can state that in case of a small light source the sensation of light is proportional to the luminous intensity of the source in the direction of the eye.

Intermediate Sources

For sources of intermediate size the threshold is influenced by luminance and also by lumen output. The following approximation can be applied to intermediate sources:

The threshold luminance of intermediate size (10 degrees $>\alpha>$ 20 minutes) depends upon the size of the source and also on its luminance.

Therefore, the threshold luminance and the threshold luminous flux are:

$$L_o = \frac{\text{constant}}{\sqrt{A}}$$

$$\Phi_o = \text{constant} \quad \sqrt{A}$$

* The statement is somewhat oversimplified, since other factors, such as brightness of the background as we noted earlier may considerably influence the threshold. α = the angle subtended by the observers eye.

For sources of extended size the sensation of light or subjective brightness* is produced by luminance: whereas, for a point source the sensation of light is proportional to the illumination on the eye, which in turn is proportional to the lumen output of the source in the direction at the eye. The border values (α = 10 degrees and α = 20 minutes) are valid only for threshold levels of light emittance and should be used prudently. The limits will change with an increase of luminance above the threshold level. The angular size of a source at average luminance level must be under 1 minute before it will appear as a point source. For example, a 2-inch diameter completely diffuse source of 100 fL will not appear as a point source at 29 feet (α = 20 minutes) but will certainly at 600 feet (α < 1 minute).

The luminance levels at which we are working are so low that the angular size can be much greater than one minute of arc and appear as a point source.

(The lower threshold of eye response to weak point sources can also be expressed with respect to the illumination the source produces upon the eye. This threshold is around 2×10^{-4} footcandles. **)

* Subjective brightness: An attribute of visual sensation by which a body is judged to emit a greater or smaller proportion of light.

** Source: Light and Color of Small Lamps c 1971 G.E. by Boris Merik. page 65. (Note difference between this and Table B-1; with this kind of variation in data given by experts it is apparent that actual testing is required.)

At low illumination levels the pupil size is maximum with a diameter of 8 - 9 millimeters. Increasing the light levels decreases the pupil. The size of the pupil and the sensation of light depends not only on the intensity of the light source but also on the direction the light beam reaches the eye in respect to the line of sight. (Stiles - Crawford effect).

Thus, the size threshold of a roadway marker is dependent upon the phenomena luminance and distance. A roadway marker will act as a point (small source), intermediate, and extended source as a vehicle approaches it and passes. Thus, a luminescent marker can be useful in delineation of distances from far to near.

Time

In addition to the intensity and size of the light source, the lower visual threshold depends upon the time the eye is exposed to the light. If the exposure time decreases, the light source intensity must increase. The relationship between luminance and exposure time is expressed by the Blondel-Rey equation:

$$L_t \cdot t = L_o (0.21 + t)$$

where L_o represents the luminance threshold for unlimited exposure time and L_t represents the threshold at exposure time t. The following simplified relationship can be applied to exposure time under 0.05 second duration:

$$L_t \cdot t = \text{constant}$$

The dependence of visual sensitivity upon the duration of observation is shown by Exner's sensitivity curve, Figure B-4. The curve is valid for medium luminance levels which exceed the threshold. The maximum visual sensitivity is reached between 0.2 and 0.3 seconds of observation time. After that the sensitivity of the eye decreases due

to saturation. Discontinuing the excitation does not stop the visual sensation immediately: rather it fades gradually because of the after-image. Due to this, the flicker of lamps operated on alternating current of adequately high frequency, such as 60 Hz, is normally not noticed.

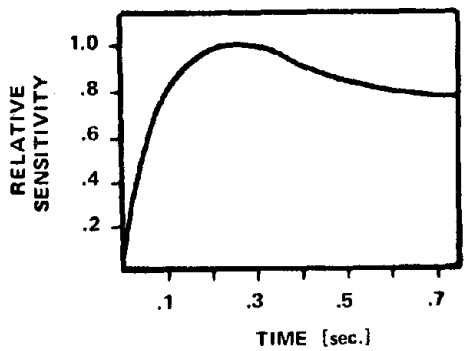


Figure B4 Visual Sensitivity as a Function of Time

Adaptation

Adaptation is the response of the eye to a changing luminance in the field of view. The eye adjusted to the dark will swiftly become light-adapted, if exposed to a higher level of luminance. However, the reverse process, adaptation from light to dark, is much slower and can be measured by the lower threshold level L_o, seen at a given state of adaptation. The degree of adaptation can also be expressed through the sensitivity S:

$$S = \frac{1}{L_o}$$

The course of adaptation from light to dark is shown by a typical curve in Figure B-5. The process of becoming dark-adapted is slow and exposure to light has to be avoided for at least an hour before the eye becomes completely dark-adapted. The rods recover from light adaptation notably slower than the cones.

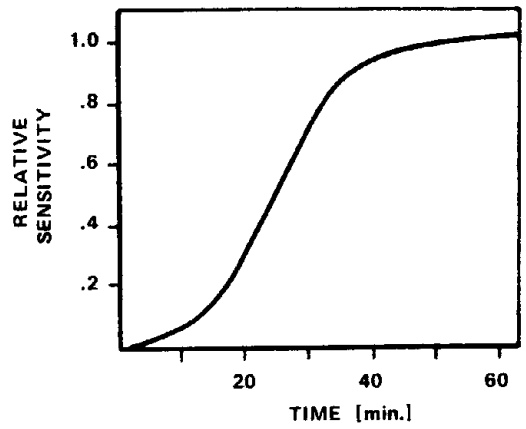


Figure B5. Time Required for Dark-Adaptation

Based upon the foregoing factors and other factors it is felt that an adequate luminescent delineator will have the following:

MARKER CHARACTERISTICS

2.094" Wide
6.67' Long
1/8" thick
Oriented (Optional)
.2 - .5 fL (contrast dependent)
Green-Yellow Color

With some feel for what our marker characteristics should be let us examine the siloxene reaction to get an approximation of the luminance output and potential useful lifetime of a marker containing this reaction chemistry.

The theoretical limits of brightness (luminance) and duration for a chemiluminescent reaction based lane marker depend on several factors; 1) the amount of chemical reactant that can be contained in a single 2" x 6' x 1/8" marker, 2) the efficiency of light production by the chemical reaction, 3) the color of the light produced, 4) the degree of control of the reaction by water-initiation and dry-shutoff, and 5) some special factors such as orientation and regeneration possibilities.

In making the following computations we have attempted to make simplifying assumptions in such manner as to be on the conservative side at all times.

Assuming a 100% efficiency* for the light reaction as a starting point for the light producing reaction, we can calculate the theoretical limits for a non-oriented, non-regenerable chemiluminescent. system which emits a yellow-green color such as the siloxene derivative system produces.

Marker Content - A marker with dimensions 2" x 80" x 1/8" has a volume of 20 cu. in. or more than 300 cu. cm. Assuming a density of 2 gm/cu. cm. (average density for silicon compounds is 2-4 gm/cu. cm.), a molecular weight of 200 (silical hydroxide = 248), and assuming the reaction occupies one third (1/3) of the marker total volume; the marker will contain one gram molecular weight of reactant or about 6×10^{23} molecules (Avogadro's number).

*100% efficiency assumes that every molecule of the reaction emits one photon or quantum of light.

Quantum Yield - A major simplification in the calculation equating quanta (photons)/sec emitted to the more commonly used luminance units of foot lamberts (fL) or foot-candles (fc) is that the yellow green colored emission (maximum at about 550 nm) nearly overlaps the spectrum of maximum eye sensitivity. Conservatively the overall bandwidth spectrum of our reaction emission is assumed to be half as efficient at producing eye-stimulating quanta as if all the emission occured at the 550 nm maximum.

The photometric equivalent of one lumen ($1/4\,\pi$ candelas) of emission at this wavelength is approximately 4×10^{15} photons/sec. *

Thus, the result of a yellow-green emitting reaction emitting a level of 1.0 candelas (cd) luminous intensity (candlepower) is 1.0 (cd) x 2 (efficiency loss) x $4\,\pi$ (conversion factor) (4×10^{15}) photons/sec $= 10^{17}$ quanta/sec. Therefore, the luminance or photometric brightness equivalent to footlamberts is $1\ fL = \frac{1\ cd}{\pi\ ft^2} = \frac{10^{17}}{\pi\ ft^2}$ photons/sec $= 3.18 \times 10^{16}$ photons/sec/ft^2.

$.5\ fL = 1.59 \times 10^{16}$ photons/sec/ft^2

The projected area of our marker model is .37 ft^2 (2.094 in^2), therefore our marker must put out 4.35×10^{16} photons/sec to equal 0.5 fL.

Efficiency/Time

Thus, assuming 100% reaction efficiency and assuming the initial presence of an Avagadro's number of molecules (each of which can emit a photon) we find that the reaction might be expected to last (total "on"

* H. H. Seliger and W. D. McElroy, Light: Physical and Biological Action, Academy Press, 1965, pp. 1-22

time) of

$$\frac{6 \times 10^{23} \text{ photons}}{4.35\ 10^{16} \text{ photons/sec}} = 1.38 \times 10^{7} \text{ seconds or } 3833 \text{ hrs.}$$

More realistically:

10% efficiency gives 6×10^{6} sec or 383 hrs.
1% efficiency gives 6×10^{5} sec or 38 hrs.
.1% efficiency gives 6×10^{4} sec or 4 hrs.

Though .1% efficiency appears inadequate 1% efficiency or more might be useful since an average of 1 hr/day "on time" might be available for over one month.

In addition to the aforementioned factors that were taken into account to predict the approximate theoretical output at 100% efficiency there are at least two additional factors that would enhance the lifetime of a marker system, particularly with the properties that the siloxene derivatives demonstrate. These factors are regeneration and orientation. As yet there is no indication that reactants in the siloxene system will be able to be regenerated from the products. And no approximation can be made to indicate the effect of such a property. Orientation of the light output on the other hand, is a real possibility. Consequently, the effect of this factor was calculated. Depending on the degree of orientation (the solid angle that includes the light output versus the total solid angle of a sphere) the intensity could be raised from 10 to 50 times based on conservative estimates of the degree of orientation practically obtainable. This would set the total theoretical limit of the marker output (if orientation is possible) at 3.8×10^{4} to 19×10^{4} hours for a 100% efficient light output.

APPENDIX C

GLOSSARY

The following terms are defined for ease of understanding and consistency throughout this work.

Bioluminescence: Chemiluminescence when catalyzed by an enzyme. The reactant in this case is called a "substrate".

Chemiluminescence: The luminescence of "product" excited-state molecules which have been produced as the direct result of a chemical reaction, usually involving the oxidation of the initial "reactant".

Compound: A chemical compound, reactant, or molecule.

Duration: The length of time that a light source emits an intensity greater or equal to a given value.

Energy-Transfer: Process whereby the energy from the excited state product (produced in a reaction) is transferred to an "acceptor molecule" which is usually fluorescent.

Fluorescence: The luminescence of excited-state molecules produced by light absorption.

Intensity: The rate of light production or photon flux at any one time. Measured as photons per second (photocurrent) and reported here as candelas. Units of illuminance and brightness will be referred to in terms of lumens (one lumen is the luminous flux emitted through a unit solid angle from a one candela point source, one footlambert is the brightness measured in candelas per square foot).

Luminescence: The phenomenon of light emission from a chemical (electronically excited-state molecules) which can be produced through a number of processes.

Luminol: 3-amino-phthalhydrazide, a chemiluminescence reactant requiring peroxide and base.

Matrix: The immediate environment of the system in the marker. In a liquid system this would be the solvent.

Oxalume: Oxalic acid ester derivatives, chemiluminescence reactants (requires a peroxide and solvent). American Cyanamide developed product.

Phosphorescence: The luminescence of excited-state molecules which have been produced by light absorption and which have undergone a process called "crossover" while in their excited state. Thus in phosphorescence there is a significant delay after light absorption before light is emitted, whereas fluorescence emission is immediate (10^{-9} sec delay).

Quantum Efficiency: The yield of emitted photons per unit input- for fluorescence, per photon absorbed; for chemiluminescence, per used reactant molecule - the product of the efficiency of production of excited-state product molecule in the given environment.

Reaction: This term, when unmodified, refers to the light-producing reaction in chemiluminescence.

Regeneration: Refers to the reformation of reactant or other compound which is in limiting concentration in the system - usually accomplished by a chemical reaction.

Sensitized Chemiluminescence: Luminescence resulting from a fluorescent "acceptor" excited state produced through energy transfer.

STELLER: Code name for siloxene derivatives as reactants in chemiluminescence (requires inorganic oxidant, water).

System: This term, when unmodified, refers to the collection of reactions and conditions necessary for light production in the chemiluminescence of a compound or class of compounds.

TMAE: Tetrakis - (dimethyl amino) - ethylene, an "auto-oxidizable" chemiluminescence reactant (requires oxygen and solvent).

APPENDIX D

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