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Infochemistry

Long-Duration Transmission of Information with Infofuses**

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This paper describes a new system for non-electronic communication that can transmit alphanumeric information encoded as pulses of light, over intervals of hours. The objective of this research was to design "infofuses" that improved the previously described systems[1] in three ways: 1) they could transmit information for hours instead of seconds, 2) they could transmit long messages, and 3) they resisted accidental extinction. These characteristics improve the functionality and potential for practical use of infofuses, and make them more convenient to use as a test bed for a new approach to fusing chemistry and information—"infochemistry".

We consider the elements of a system for manipulating information that comprises seven steps: 1) generating the message (either by writing it, or by collecting it from a sensor), 2) encoding the information in a form that a device can transmit, 3) transmitting the information, 4) receiving the information, 5) decoding the information, 6) interpreting the decoded information, 7) acting on this information. Here, we focus on steps (2) and (3). To simplify the problem, we assume that reception and decoding will be accomplished optically and electronically, and that there are no constraints (that we must consider) on the complexity, cost, or performance of the systems that accomplish these functions. We also assume that generating the message involves a separate set of issues which may or may not be primarily chemical.

Systems based on infochemistry combine the storage and transmission of encoded information with four attractive features of chemistry: 1) high energy density; 2) autonomous generation of power that can be used for both sensing and for transmission; 3) no requirement for batteries; 4) facile coupling with certain kinds of chemical sensing. We have described two infochemical systems that do not require external electrical power (they use only chemical interactions or reactions) to transmit alphanumeric information. The first system—which we call an "infofuse"—is based on a strip of flammable polymer (nitrocellulose).[1,2] In this system, patterns of spots of thermally emissive salts encode information. The second—which we call a "droplet shutter"—is a microfluidic device that capitalizes on the high stability of operation of a flow-focusing nozzle to generate bubbles and droplets.[3] In this system, windows in an opaque mask encode information. The combination of optically transparent droplets and windows serve as optical shutters. A third system—a frequency-agile microdroplet-based laser—requires electrical power to operate the pump laser, and is intended for different applications.[4]

In our previous design of infofuses, information was encoded as patterns of ions (Li^+, Rb^+, Cs^+) on a strip of nitrocellulose.[1] Ignition of one end of a nitrocellulose strip initiated propagation of a flame-front (at $T \approx 1000\,°C$) at 2–3 $cm\,s^{-1}$. As this moving hot zone reached each spot containing added metal ions, it caused the emission of light at wavelengths characteristic of the thermal emission of the corresponding atomic species. The pattern of emissive salts, ordered in *space*, therefore, became a sequence of pulses of light at characteristic wavelengths, ordered in *time*.

We have described infofuses that used three thermal emitters (the perchlorate or nitrate salts of Li, Rb, and Cs, with Na as an internal standard for intensity) to encode and transmit alphanumeric messages. Because each of these three ions can either be present or absent in a particular spot, there are seven unique combinations (2^3-1; we have chosen not to use 0,0,0 to avoid ambiguities between a pulse and a space between pulses). Seven unique pulses allow an encoding scheme that assigned alphanumeric characters to combinations of two ($7^2=49$) sequential optical pulses.[1,5]

The infofuses fabricated according to this design demonstrated the principle of a successful strategy for coupling chemistry with the encoding and transmitting of chemical information, but suffered from a number of weaknesses. Two were of primary concern to us:

1) While burning, the flame-front had to remain far (> 1–2 mm) from surfaces, so that the heat transfer from the flame to the surface did not cool and extinguish the flame. When the flame-front of nitrocellulose infofuses with dimensions we used (1–3 mm wide, ca. 100 μm thick) came close (< 1–2 mm) to any solid surface, their rate of propagation decreased, and the flame frequently extinguished. This characteristic required that the burning infofuses have a vertical orientation, and be out of contact with solid surfaces; these restrictions limited the practical applicability of these infofuses. 2) The rapid propagation of the flame-front (ca. 3 $cm\,s^{-1}$) precluded times of transmission longer than about 1 min (an infofuse on which the flame propagated at this rate would require a length of 2.6 km to transmit continuous or repetitive messages for 24 h).[6]

Here we describe a new experimental platform for infofuses that addresses these weaknesses by using a "dual-speed" arrangement (Figure 1), in which a fuse that burns slowly and continuously (a "SlowFuse") and that does not transmit information, intermittently ignites fuses (strips of nitrocellulose) that burn quickly and transmit information

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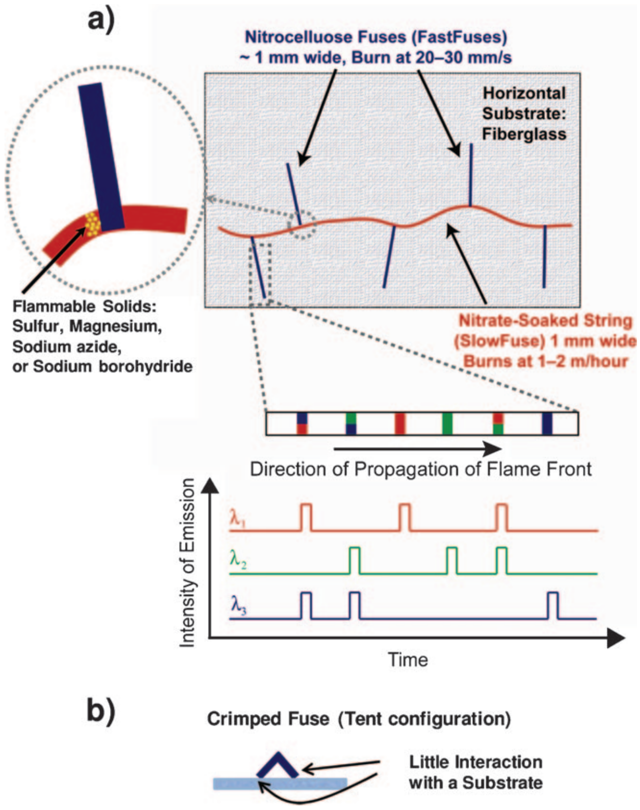

Figure 1. a) Diagram of a slow-burning, nitrate-soaked cotton string (SlowFuse), with appended fast-burning nitrocellulose fuses (FastFuses) that transmit information as optical pulses of light characteristic of thermally emissive alkali metals. b) Diagram of a crimped fuse (tent configuration) with little interaction with a substrate.

("FastFuses"). This design enables us to repeat a message, or transmit different messages, periodically. The design we use here—in which FastFuses are supported on a thermally insulating support (fiberglass), or separated from the surface by some other methods (e.g., crimping)—also increases the mechanical and thermal stability of the devices, and allows them to be used in a range of orientations.

Protecting nitrocellulose infofuses from extinguishing upon interaction thermally with a substrate is critical to their application in transmission of information. Flat fuses ignited on flat thermally insulating polymers, such as Kapton ($k = 0.12\ \mathrm{W\,m^{-1}K^{-1}}$)[7] or Teflon ($k = 0.25\ \mathrm{W\,m^{-1}K^{-1}}$)[8] extinguished after 1–2 cm of burning, as did fuses ignited on planar substrates of borosilicate glass ($k = 1.0\ \mathrm{W\,m^{-1}K^{-1}}$)[8] and on aluminized poly(ethylene terephthalate). The observations that flat fuses extinguished on planar glass, and that they burned reliably on fiberglass (see below), are consistent with heat transfer from the flame-front to the substrate as causing, in some part, extinction.

There are three potential mechanisms by which extinction could occur: 1) heat transfer to the substrate, 2) quenching of the flame by thermally generated compounds from the fuse or substrate,[9] and 3) mass transport limitations in diffusion and convection of O_2 to the fuse. Because thermal (and perhaps chemical) interactions between the flame-front of a burning nitrocellulose infofuse and the substrate on which it rests can cool and extinguish the flame, we developed several strategies for minimizing these interactions physically: 1) burning it on a good insulator with a low thermal conductivity and heat capacity (e.g. fiberglass or glass wool), 2) crimping the nitrocellulose fuse (to separate the flame-front physically from the support), and 3) burning it over a trench.

Fuses burned much more reliably on fiberglass than on other substrates. Out of 70 10 cm long, 1 mm wide nitrocellulose fuses ignited on fiberglass, 65 burned completely.[10] On other substrates, less than 40% of the fuses burned completely. Fiberglass has a low thermal conductivity ($k = 0.04\ \mathrm{W\,m^{-1}K^{-1}}$) and high softening point (720–850 °C), and should generate little volatile organics.[11] Although fuses burned reliably on fiberglass, the proximity of the flame-front to fiberglass did cause the propagation of the flame to slow from 2–3 $\mathrm{cm\,s^{-1}}$ to 1–1.5 $\mathrm{cm\,s^{-1}}$. A flame that burned slowly on fiberglass often gave multiplets from a single spot (possibly a source of error) when short integration time (10 ms) for the detector was used.[12] To ensure that a single spot generates only a single pulse, we either used long integration time (30–40 ms) for a flat fuse, or fabricated the fuse so that the nitrocellulose supporting the deposited metal salts could burn at a rate of 2–3 $\mathrm{cm\,s^{-1}}$ (at the fabricated region, nitrocellulose had little interaction with a substrate; so the propagation of the flame did not slow) (Supporting Information, Figure S1).

Fuses folded once along their long axis and resting on the substrate in a tent-like configuration resisted extinction by heat transfer. In a set of ten experiments, all of these "tent" fuses (ca. 10 cm long, 2–3 mm wide) burned completely while resting on Kapton, but only 30% (3 out of 10) of the corresponding flat fuses burned completely (Figure S2). Crimping the fuse in this manner prevented the majority of the flame-front from transferring heat to the substrate; only the edges of a crimped nitrocellulose film contacted the substrate, whereas the much of the surface of a flat nitrocellulose film did so. As for the fuses on fiberglass, use of crimped fuses in a tent configuration did cause the propagation of the flame to slow from 2–3 $\mathrm{cm\,s^{-1}}$ to 0.5–0.8 $\mathrm{cm\,s^{-1}}$. We achieved a single pulse from a single spot either using long integration times (50–80 ms) or a fuse fabricated so that the nitrocellulose supporting the deposited metal salts had little interaction with substrate (Figures 2 and S3).[12] A complementary strategy, in which a 2 mm wide strip of nitrocellulose rested on a 1 mm wide rectangular trench between two glass slides, also protected the flame from extinction (a 1 mm wide fuse resting on a 0.5 mm wide trench, however, extinguished quickly).

These approaches (crimping the fuse, and burning the fuse on a trench) to protecting nitrocellulose fuses from extinguishing have two advantages: 1) they can work on a variety of substrates: it is not necessary to provide a special substrate on which crimped fuses will burn reliably, and 2) crimping the fuses is a simple process that is straightforward to implement.[13] In controlled situations, where an insulating material such as fiberglass is readily available, burning flat fuses on an appropriate material is also a useful tactic. In our opinion, however, crimped fuses are the most general strategy, since they can operate while resting on most solid materials without extinction.

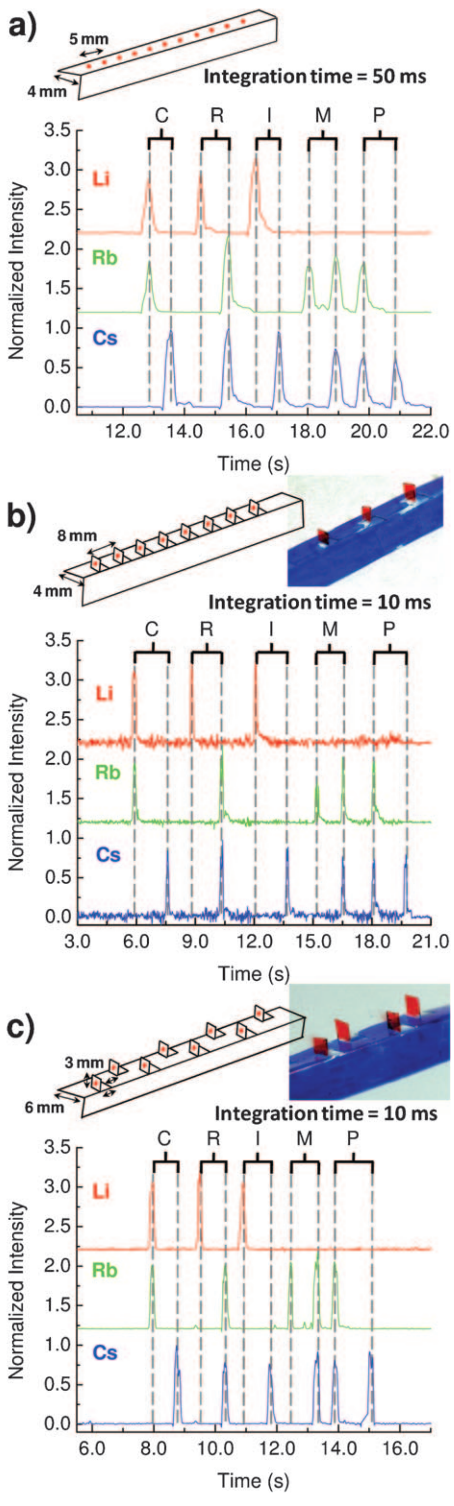

Figure 2. Two strategies to generate a single pulse from a single spot for crimped fuses (tent configuration) on glass substrate. a) Using long integration time (50–80 ms) for collecting data: diagram of a crimped fuse (top), and transmitted light detected from a crimped fuse (bottom). b,c) Fabricating fuses so that the nitrocellulose supporting the metal salts could have little interaction with a substrate: diagram of a fabricated fuse (top), and transmitted light detected from a fabricated fuse (bottom); inset images show blowup photographs of fabricated fuses. We colored the fuse blue (part that sits on glass substrate) and red (part where metal salts are deposited) with permanent marker for easy visualization. In all schematic diagrams of fuses, red dots indicate deposited metal salts. In the encoding scheme used here, two consecutive optical pulses represent one alphanumeric character.

In addition to the extinction of the infofuses through heat transfer to a substrate, another practical limitation of nitrocellulose infofuses is that they burn at a rate of several centimeters per second: the length of the strip of nitrocellulose determines the length of time that the infofuse can transmit data continuously, and for long intervals of transmission, is impractically long. To overcome this limitation, we developed a "two-speed" configuration for infofuses (Figure 1), in which patterned, fast-burning strips of nitrocellulose (FastFuses) branched off from a central, slow-burning fuse (SlowFuse).[14]

For our SlowFuse, we used a formulation similar to "slow match", a type of matchcord used in the early days of firearms:[15] cotton string (diameter ca. 1 mm) soaked in a 6% (w/v) aqueous solution of $NaNO_3$ for about 20 min and dried at 125 °C. When ignited, the hot zone of this SlowFuse smoldered with a red-hot ember (Figure S4) instead of with a flame, and propagated at 1–2 m h^{-1}. The SlowFuse emitted a substantial amount of smoke when it smoldered, and although it did glow with a red-hot ember, it did not produce a significant amount of background optical emission, and was not hot enough to cause the embedded sodium to emit. The SlowFuse did not extinguish when burning on fiberglass, and continued to burn even while held loosely between two pieces of fiberglass or while wrapped in glass wool. The smoldering flame of the central SlowFuse was more resistant to extinction than the rapidly burning flame of the FastFuses. In particular, blowing air on the hot zone of the SlowFuse increased the rate at which it burned, while blowing air on the FastFuse extinguished the flame.[9] This design therefore has the characteristic that the extinguishing of one nitrocellulose FastFuse does not prevent the entire system from continuing to transmit information.

For two-speed configuration of fuses, we glued FastFuses to the SlowFuse by applying a solution (5% w/v) of nitrocellulose in acetone and allowing the solvent to evaporate. The SlowFuse was not always able to ignite the FastFuse directly: the heat from the SlowFuse caused the film of nitrocellulose to combust locally (the nitrocellulose disappeared), but without the creation of a self-propagating flame. Small quantities ($<$10 mg) of flammable solids at the junction of the two fuses allowed the SlowFuse to ignite the FastFuses (Figure 1). This "handoff" of ignition worked in 100% of trials when we used any of four additives at the junction: 1) sulfur (S_8) powder, 2) magnesium powder, 3) sodium borohydride ($NaBH_4$) powder, and 4) sodium azide (NaN_3) powder adsorbed on the surface of nitrated tissue paper (flash paper).[16,17] To illustrate the generality of the two-speed approach, we also demonstrated that a cigarette could act as the SlowFuse, with the combination of NaN_3 and nitrated flash paper at the Slow–Fast junction (Figure S5).

To demonstrate using this two-fuse system to transmit information, we appended seven FastFuses to a SlowFuse using flash paper for ignition. Each FastFuse was encoded with its distance from the beginning of the SlowFuse, i.e., the FastFuse that was 1.5 feet (ca. 45 cm) from where the SlowFuse was ignited transmitted the message “1.5 FEET”. For this two-speed fuse on a glass wool, the five-foot long SlowFuse did not extinguish until it burned completely (after 45 min). Figure 3 shows the transmitted intensity (at a pulse frequency of 6 ± 1 Hz) of lithium, rubidium, and cesium for the fuses that encoded for “1.5 FEET” (which transmitted at 10.7 min) and “4 FEET” (which transmitted at 35.7 min).

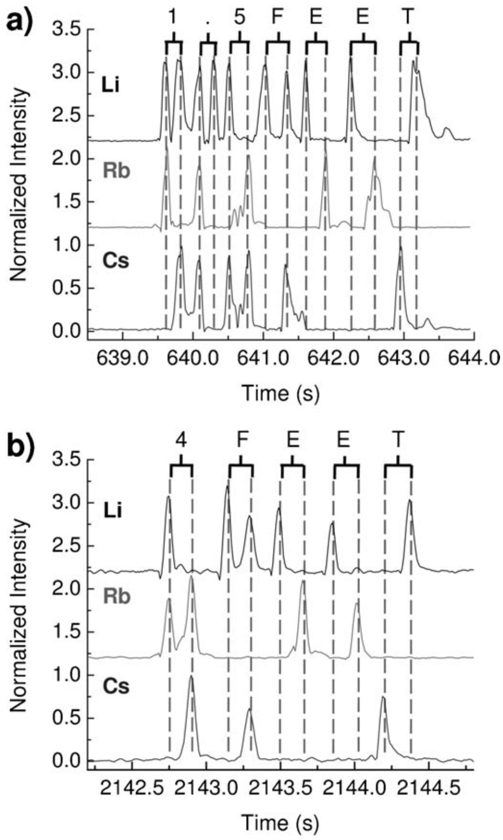

Figure 3. Transmitted light detected from a two-speed infofuse when a) a FastFuse ignited after 1.5 feet of the SlowFuse had burned (10.6 min), and b) a FastFuse ignited after 4 feet of the SlowFuse had burned (35.7 min). In the encoding scheme used here, two consecutive optical pulses represent one alphanumeric character. The fuse burned on a glass wool and was ignited once at $t=0$ s.

In conclusion, we have described approaches that are major improvements in a previously described system of “infofuses”. Burning fuses on a thermally insulating substrate, or preventing physical interaction between fuses and a substrate, reduced thermal interaction (heat transfer) between fuses and substrate; the fuses thus resisted accidental extinction. We also achieved long-duration transmission of information by joining fast-burning strips of nitrocellulose containing encoded messages to slow-burning cotton string.

This work is important to materials scientists and engineers interested in research at the interface between information science and chemistry (infochemistry). Improved functionality and potential for practical use of infofuses demonstrated here could ultimately contribute to achieve infochemical systems that can sense and process chemical or biochemical inputs from the environment and transmit the results optically over a distance.

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[5] For detailed encoding scheme, see Supporting Information of ref. [1].
[6] Other weaknesses on which we have not yet focused include low thermodynamic efficiency (for details, see Supporting Information) of coupling the free energy of combustion of nitrocellulose to the emission of photons at frequencies characteristic of atomic emission for the metal ions and sensitivity of the system to the environment (temperature, water content).
[7] C. J. Cremers, H. A. Fine, *Thermal Conductivity 21*, Purdue Research Foundation, New York, **1990**.
[8] J. S. Wilson, *Sensor Technology Handbook*, Elsevier, Amsterdam, **2005**.
[9] Nitrocellulose contains insufficient oxygen to oxidize completely. The oxygen deficit is increased when the solvent is not completely removed from the nitrocellulose. Products of combustion of nitrocellulose such as CO, CO_2, and NO_x could quench the flame. J. B. Bernadou, *Smokeless Powder, Nitro-Cellulose: And Theory of the Cellulose Molecule*, University of Michigan Library, **2009**, p. 102.
[10] Fuses also burned reliably on glass wool. Since fuses have little physical interaction with glass wool due to its texture, propagation of the flame maintains the burning rate of 2–3 $cm\,s^{-1}$ on glass wool.
[11] S. T. Peters, *Handbook of Composites*, Chapman & Hall, London, **1998**, p. 135.
[12] After depositing/drying 100 nL of an aqueous solution of metal salt on nitrocellulose infofuse, the resulting spot size is ca. 500 μm. For the fuses held vertically (burning rate ca. 3 $cm\,s^{-1}$), it takes about 17 ms to burn each spot; so we can achieve a single pulse from a single spot using integration time of 10 ms for the detection. On the other hand, it takes about 50 ms to burn each spot from flat fuses on fiberglass (burning rate ca. 1 $cm\,s^{-1}$); so we can achieve a single pulse by increasing the integration time from 10 ms to 30–40 ms.
[13] Fuses crimped into a “tent” configuration must obviously be in the orientation that minimizes contact between the fuse and substrate.
[14] Using dual-speed arrangement of FastFuses with SlowFuses on a 8.5″ × 11″ (ca. 21.5 cm × 28 cm) rectangular piece of fiberglass, we can transmit about 800 characters (with the pulse rate of 10 Hz) of messages for ca. 1 h with efficiency of ca. 0.01 % (for the calculation of efficiency, see Supporting Information).
[15] J. S. Wallace, *Chemical Analysis of Firearms, Ammunition, and Gunshot Residue*, CRC, Boca Raton, **2008**, chap. 3.

[16] To ignite the FastFuse directly from the hot zone of SlowFuse, we tried a variety of additives at the junction as well as physical methods. Other additives to the junction of the SlowFuse and FastFuse did not assist the SlowFuse in igniting the FastFuse included hydrocarbons (hexanes), alcohols (ethanol), aluminum powder, Zn powder, dicyclopentadiene, 2-butyne-1,4-diol, 1,5,9-cyclododecatriene, and other oxidants (nitromethane, hydrogen peroxide, di-*tert*-butylperoxide, sodium perborate, and sodium pyrophosphate). Physical methods for "handing-off" ignition from the SlowFuse to the FastFuse were not successful; we tried four methods: 1) wrapping nitrocellulose around the SlowFuse up to three times, 2) resting the FastFuse on the SlowFuse in a collinear arrangement, 3) permeating the SlowFuse with the FastFuse, and 4) wrapping aluminum foil or aluminized mylar around the junction.

[17] The formulations (nitrocellulose + NaN_3) combine highly flammable materials, strong reducing agents, and oxidizing agents. Although we have not observed any unexpected reactions, care must be exercised in handling such systems. We ***do not*** mix the oxidants and reductants directly in solution, and use only several milligrams at a time.