The Senko Hanabi Sparkler: A Study Of Its Reaction Mechanisms

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Abstract: The senko hanabi sparkler was found to be a very useful tool to study glitter phenomena. It was shown that current theoretical frameworks are incapable of explaining all observations. New elements were added to the discussion about the role of critical temperature and potassium sulfate concentration on the glitter flash. Also, the role of sodium bicarbonate as glitter enhancer and coloring agent was demonstrated in the senko hanabi sparkler.

Keywords: Senko hanabi, sparkler, satori effect, glitter

Preface

This article is the second to emerge from a comprehensive study of the senko hanabi sparkler. A first article¹ gave some historical and practical background and discussed the variables that affect the performance and construction of a finished device. This second article will focus on the underlying reaction mechanisms inside a senko hanabi droplet. Insights from recent experiments are compared to data from relevant literature. I hope this review will be a starting point for other pyrotechnicians to do further studies on the fascinating senko hanabi phenomenon.

Life of a senko hanabi sparkler

The sequential chemical reactions and related effects can be seen as stages in the 'life' of a senko hanabi sparkler. These stages were already defined by Maeda for the sparkler's traditional design.² This article proposes an updated design that adds new stages (4,5,6 and 8) to the sparkler's life course while leaving the traditional effects untouched.

For each phase, the relevant theoretical frameworks will be discussed. Although many authors agree upon the main chemical reactions that take place inside the reacting melt,²⁻⁴ different views are held about specific theoretical aspects. Currently, there does not seem to be one model that explains all

observations.

(1) Birth (8–10 seconds)

A fuse-like burning of the composition that leaves a thread-like melt of reaction products (Figure 1) In this phase, all of the potassium nitrate reacts.

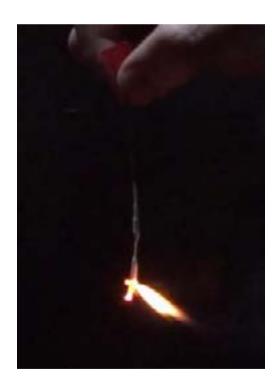


Figure 1. Birth.

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The following reaction mechanisms are proposed by different authors:

2 KNO₃ + 2 S + 3 C
$$\rightarrow$$
 K₂S₂ + 3 CO₂ + N₂
(Shimizu,¹⁰ Oglesby⁵)

4 KNO₃ + 2 C \rightarrow 2 K₂CO₃ + 2 N₂ + O₂

8 K₂CO₃ + (3n + 1) S₂ \rightarrow 6 K₂S_n + 2 K₂SO₄ + 8 CO₂

4 K₂SO₄ + 7 C \rightarrow 2 K₂CO₃ + 2 K₂S₂ + 5 CO₂
(Ito³)

Measurements show that besides CO₂ and N₂, CO is also generated.¹⁰ Therefore both reaction mechanisms are but approximations of the real reactions going on. Maeda has studied the concentration of different reaction products during the lifespan of a senko hanabi droplet. He showed that in this first stage, much potassium carbonate is present. When the reaction continues, this amount decreases and the concentration of potassium sulfate gradually begins to rise.²

From the above equation, Oglesby defines the optimal theoretical formulation as being (KNO₃ 67/ S 21/ C 12). 5 Shimizu found through empirical research that the optimal formulation is closer to (KNO₃ 60/ S 25/ C 15). He uses a mortar and pestle as the mixing method.⁶ Ito also uses this method and formulates his composition as (KNO₃ 55/S 25/ C 15–5). However, when more intimate mixing methods are used, like the slurry ball mill that was used for the current experiments, the optimal formulation now shifts towards (KNO₃ 50/ S 35/ C 15). This ratio of ingredients seems independent of the type of carbon used, an observation that Shimizu also made concerning his formulations.² This shift of the optimal formulation is analogous to the history of black powder, where the ideal ratio of raw materials changed together with the different mixing methods that were used throughout the ages.⁵ This 50/35/15 formula gives the following gross starting ratio of reactants (after minimal correction for sulfur loss by evaporation and without correcting for the ash/volatile content nor for the small amount of carbon that is used during spark generation):

$$2 \text{ KNO}_3 + 4 \text{ S} + 5 \text{ C} \rightarrow ...$$

Analogous to the theory of black powder, the search for an all-explaining equation is extremely complex. Also, this is by no means the aim of this article. However, it is clear that the proposed ratio of ingredients according to current theoretical models is too far removed from this 50/35/15 formulation to allow any of these equations to account for its high performance.

The melting temperature of K_2S_2 is 470 °C. The reaction temperature is high enough to keep it in a molten state. The surface tension then makes the worm-like melt contract into a drop that soon afterwards begins to boil.

(2) Infancy (3–4 seconds)

The melt contracts to a droplet that boils and sizzles (Figure 2)

This is the moment where the magic of the senko hanabi phenomenon starts. The following reactions are also responsible for the persistent and potentially dangerous afterglow of reaction products after the burning of black powder-type compositions, e.g. in a mortar.

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2$$

(Oglesby⁵)

The temperature of the drop now rises to about 860 °C,^{2,8} a temperature where potassium disulfide as well as potassium monosulfide (melting point



Figure 2. Infancy.

840 °C) are in a liquid state.

The fact that atmospheric oxygen is essential for the senko hanabi phenomenon to occur can be illustrated by holding a sparkler in pure oxygen and pure carbon dioxide respectively. In the oxygen rich atmosphere, the sparkler starts reacting fiercely and even ignites the paper string. The inert atmosphere immediately stops the reaction. One can also stimulate this polysulfide oxidation by blowing on the drop or holding the sparkler in a light breeze. In still air, fresh oxygen is provided solely by convection around the drop. It was observed that a senko hanabi sparkler ignited in micro-gravity performed poorly. In this study, convection processes inside the droplet were of course inhibited as well.

In designing a senko hanabi sparkler, it is therefore necessary to allow plenty of oxygen to reach the reacting melt but also to provide enough support (paper) to keep the drop suspended. These 2 opposing conditions are met in the current 'satori' design as discussed in the previous article. Folding back the end of the gampi-paper strip to where the soot composition ends, leads to regions where the composition (and afterwards also the melt) is covered by only one layer of paper and

other regions where multiple layers can provide support for the drop to hang on. It was observed that this design also allowed the jet of reaction gases to be pointed sideways. In contrast, if one just used a wider paper strip, a tube is created that would direct the exhaust gases towards the drop with the risk of blowing it off.

(3) The first phase where sparks are generated

Maeda² divides this phase into:

(3a) First youth

(This phase lasts for 8–11 seconds in a traditional sparkler, 2–10 seconds in a split-composition sparkler, depending upon the moment of rebirth): sparks shoot approximately 10 cm away from the fireball and explode into small densely branched 'bushes' (Figure 3). The effect produces a puffing sound.

(3b) First middle age

(9–10 seconds in a traditional sparkler, 0–3 seconds in a split-composition sparkler, depending upon the moment of rebirth): shorter sparks with smaller bushes are ejected at a higher frequency (Figure 4).

Until now, part of the original amount of carbon



Figure 3. First youth.



Figure 4. First middle age.

(and any metal present) was latent. These particles were shielded from atmospheric oxygen by a layer of polysulfide melt. When the reaction is stopped at this time, these particles can be observed microscopically.⁵ In this phase, the particles react.

2
$$K_2S + 2 O_2(g) + carbon \rightarrow explosive burning + CO_2(g) + K_2S$$
(Oglesby) [sic]

Ito also states that in this phase the polysulfide melt makes the carbon react with oxygen to form carbon dioxide. According to him, the potassium ion is capable of splitting adjacent carbon grids. He used X-ray diffraction to show that their interatomic distance is increased from 3.35 angstrom to 8.5 angstrom. This way, their susceptibility to oxygen is increased and the carbon dioxide that is evolved shoots away fragments of the polysulfide drop. It was shown that for classic metal glitter compositions, the potassium ion seems to be crucial. This finding is similar for senko hanabi compositions. In a recent review however,⁴ Jennings-White showed that beryllium nitrate is also capable of producing an effective glitter. Because of the toxic nature of beryllium salts, they were not tested in the current experiments. For theoretical reasons, it might however be interesting to substitute potassium nitrate for beryllium nitrate in senko hanabi compositions and to see if the sparks have the same appearance.

The current observations show that increasing the airflow around the droplet makes phase 3 start earlier. In still air, charcoal-based compositions almost always proceed to phase 3, while sootbased compositions are more inclined to stop at phase 2. Since the reaction temperature of sootbased compositions is lower than that of charcoalbased compositions,³ it seems that the temperature of the melt influences the occurrence of phase 3. When the airflow increases, the reaction temperature increases, hereby allowing even sootbased compositions to react properly. In analogy, it was shown for classic metal glitter formulations that the light intensity and therefore temperature of the spritzel rises just before the flash reaction.⁴ (Analogous to its definition by Oglesby, ⁵ a spritzel is a burning drop consisting of polysulfide melt ejected by a glitter star or, in the case of a senko hanabi sparkler, suspended on a paper string. It burns at low luminosity in the air at temperatures around 850 °C.)

Reactions 3a and 3b most likely have similar reaction mechanisms. The reason for the differences in length and size of the sparks may be caused by the fact that during this phase, the dross ball gets smaller. Because of this, the generated gases have less distance to travel before reaching the surface of the drop and therefore have less time to expand and accelerate. That evolved gases



Figure 5. *Rebirth – umarekawari.*

are responsible for the emission of the sparks was proven by the observation that senko hanabi sparks shoot less far when atmospheric pressure is increased. The place where the gases are evolved seems equally important. Given the need for atmospheric oxygen, their formation most likely takes place in the outer layer of the droplet. The deeper the gases are formed, the longer they can expand. In windy conditions it is observed that phase 3a very quickly gives way to 3b. Possibly, the airflow makes the most superficial layer of the dross ball heat up quickly, thereby ejecting numerous but smaller sparks.

Both Oglesby's and Ito's equations describe the regeneration of reactants. According to Oglesby, this explains the long duration of the senko hanabi phenomenon. He also describes two reaction mechanisms that compete for the available K_2S and eventually end the reaction:

2 K₂S + 3 O₂
$$\rightarrow$$
 2 K₂O + 2 SO₂ and
K₂S + 2 O₂ \rightarrow K₂SO₄

Although Oglesby states that K_2SO_4 is a reactant for the metal flash reaction in classic glitter compositions, he does not propose a similar reaction mechanism for the reaction of the carbon source. Ito, however, explicitly describes K_2SO_4 as a crucial reactant. During this second oxidation phase, the temperature of the dross

ball rises to about 940 °C. 2,8 At this temperature however, potassium sulfate is still solid (melting point 1069 °C). This would plead against a major role for K_2SO_4 in this phase. Further research will hopefully shed more light on the relative importance of melt temperature and potassium sulfate concentration.

On the pictures that were made during this phase, the light trails of the sparks exhibit a peculiar tubein-tube appearance. This will be discussed more in detail in phase 6.

(4) Rebirth, 'umarekawari' (4–5 seconds)

The second composition is consumed by the reacting droplet and no more sparks are generated.

A difficult point in creating an effective composition for a senko hanabi sparkler is the charcoal/soot ratio. Charcoal is needed for its reactivity in the polysulfide reaction. Soot on the other hand gives the largest and most beautiful sparks. There exists an optimal ratio that Shimizu experimentally defined to be 4:1 for a Paulownia charcoal: anthracene soot composition. This ratio is the best compromise between reactivity and aesthetics. However, this article introduces a new production method that splits the total amount of composition (typically 85 mg) into two separate and sequential compositions: the first one only contains charcoal, the second one only soot. The



Figure 6. A horizontal >40 cm spark.

soot composition is put at a short distance from the charcoal composition, so that the latter reacts first. What happens now is that the soot composition is consumed at the moment the first polysulfide drop is in phase 2 or 3. This way, the less reactive soot composition is given a boost by the vigorous charcoal melt. By carefully choosing the spacing between compositions and the way the sparkler is rolled, one can define the moment at which the soot composition is reached by the ascending fireball. The combined polysulfide melt then uses the soot as the spark-forming carbon source. The sparks that are generated this way are far larger and more beautiful than sparks generated by a mixed carbon-source composition. To illustrate this, I refer to Shimizu's 'studies on senko hanabi', where his optimal composition emitted sparks a little more than 12 cm in length. Nakaya and Sekiguti say their sparks travel 10 cm.8 By splitting the composition, the author succeeds in creating sparklers that throw out sparks 15-40 cm in length, even horizontally (Figure 6).

Another benefit of using this split composition technique is that it brings diversity to the spark effects of a senko hanabi sparkler. The sparks typical for the type of charcoal used as well as those typical for the type of soot are emitted separately. I named the effect 'umarekawari', Japanese for

rebirth. Because spectators appreciate this effect and because it also makes the integration of pure magnesium possible (see below, 'satori' effect), the author now produces all senko hanabi sparklers this way.

The optimal formulation for a single-composition sparkler (50/35/15) seems to lend itself very well for split composition sparklers as well. However, further experimentation may even generate better formulations that take into account that the first composition already lived through some phases.

(5) Second infancy (2–3 seconds)

The combined melt continues to boil and sizzle (Figure 2).

Analogous to the first infancy, the dross ball boils and sizzles. This phase is a little bit shorter than the first, because the temperature of the combined melt is already higher from the start.

(6) The second phase where sparks are generated

Analogous to the first spark phase, one can distinguish two sub-phases:

(6a) Second youth (8–11 seconds)

Sparks shoot approximately 20 cm away and explode into large fire pompoms. The effect



Figure 7. Second youth.



Figure 8. Second middle age.

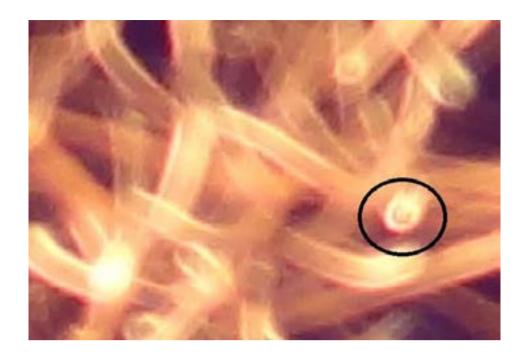


Figure 9. *Tube-in-tube appearance of light trails.*

produces more of a gushing sound (Figure 7).

(6b) Second middle age (9–10 seconds):

Shorter sparks with smaller pompoms are ejected at a higher frequency (Figure 8).

In this phase, the sparks shoot much farther away from the melt (on average 20 cm in the youth

phase, occasionally up to 40 cm) and explode to give much bigger 'fire pompoms' than the charcoal sparks. They also make more of a 'rustling' sound where the charcoal sparks tended to produce small 'puffs'. Upon analysing pictures taken from this phase, it is seen that the sparks share their anatomy with the charcoal sparks: their light trail also has a

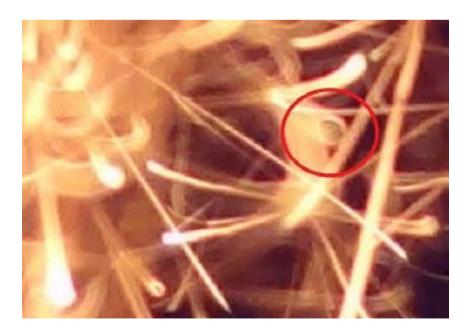


Figure 10. *Dot-in-tube-in-tube appearance of a light trail.*

tube-in-tube appearance (Figures 9 and 10).

So the type of carbon used does not seem to alter the microscopic structure of the senko hanabi sparks. A possible explanation for their different macroscopic appearance might be that soot has the ability to lower the viscosity of the polysulfide melt.^{3,7} This would make the evolved gases move more freely and possibly eject the polysulfide fragment further away. The lower reactivity of soot compositions may in turn explain why these fragments can travel further before exploding themselves into pompoms. In summary, the type of carbon used changes the physical properties of the melt which in turn determines the appearance of the sparks. The explanation for the tube-in-tube form of the light trails may be found in theories of fluid dynamics. At first glance, there are striking similarities with the trail of what is called a 'toroidal vortex'. Perhaps the sudden release of gases under the surface of the polysulfide melt makes 'rings' of melt shoot away. More specific research can hopefully shed more light on this in the future.

(7) Old age (8-20 seconds)

The droplet gets smaller and silently, long streaky sparks are ejected (Figure 12).

In this phase the drop, which has shrunken substantially, loses its vivacity. The shape of the sparks changes: now they draw long narrow lines in the air. No sound is emitted any more. The temperature of the melt drops to 850 °C.^{2,8}

(8) Metal glitter phase, 'satori' (fractions of a second)

One or more crackling flashes are observed and ejected melt material explodes at a distance. The magnesium sparks have a peculiar corkscrew appearance. The flashes are occasionally accompanied by a metallic whipping sound (Figure 13).

During the 'old age' phase, one or more crackling flashes are suddenly observed. There are little drops of polysulfide melt ejected from the mother drop that explode themselves into more sparks. Also, from the micro-droplets as well as from the mother drop, sparks are emitted that have a typical corkscrew appearance. This reaction does not interfere with the traditional effects and adds diversity to the sparkler. It even adds an element

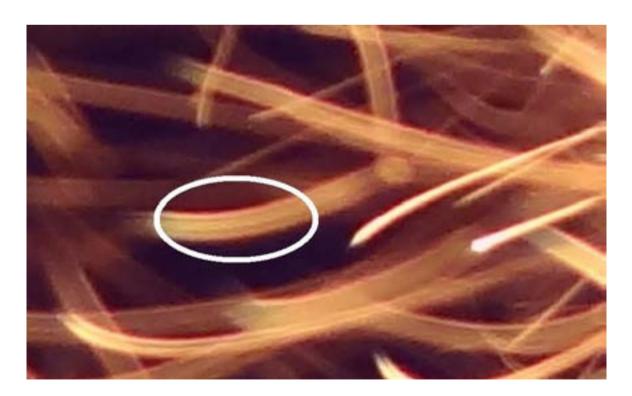


Figure 11. Tube-in-tube appearance of light trails.



Figure 12. Old age.

of excitement during the burn and it makes for a spectacular finish. Because it is frequently absent in still air but always present in the slightest breeze, it seems to adapt itself to the setting.

In this phase the magnesium reacts. Until now it has been present in the melt as liquid drops (melting point 600 °C) covered by a layer of polysulfide melt that shields it from atmospheric oxygen.

Analogous to Shimizu's proposed flash reaction of aluminium, ¹⁰ we could write the satori reaction as:

$$K_2S_2 + Mg \rightarrow K_2S + MgS$$

Or, in accordance with Oglesby's theory,⁵ this would be:

$$K_2SO_4 + 4 Mg \rightarrow K_2S + 4 MgO$$

Even though no gases are evolved, the sparks are fiercely blown away. This might be caused by the extreme heat evolved by the oxidation of the magnesium. The spritzel heats up and the remaining carbon is oxidised to produce carbon dioxide which divides the mother drop and propels fragments away. If at this stage, the droplet falls to the ground, a single explosive flash is seen which generates a perfect smoke ring in the air. This might be caused by the instantaneous division and thereby flash heating of the total mass of melt. The same effect is observed when one shoots the drop from the string with one's finger. Also, if the air flow is suddenly increased just after the rebirth phase, satori flashes can be provoked. On the other hand, in still air the satori phase often does not appear, even though the sparkler goes through all stages of its life, all the time building up potassium sulfate. These observations indicate that temperature rise, more than a critical buildup of potassium sulfate, seems to be the necessary factor for initiating the flash reaction, much like Shimizu stated for classic glitter effects: "when small particles of molten residue pass through the air, they increase in temperature while being oxidized by atmospheric oxygen. If they achieve a sufficiently high temperature, then blooms are produced". Another theoretical objection to the potassium sulfate theory is that it would still be solid at the temperatures that were measured on the surface of a reacting senko hanabi droplet. However, it might be that sudden local heating liquefies the potassium sulfate and starts the reaction. Further research measuring surface temperatures at the moment of the satori effect may prove useful in clarifying this point. As a side note, these experiments do show that a true glitter effect is possible by only using potassium nitrate, sulfur, charcoal and metal.⁴

If pure magnesium powder is burned in a Bunsen flame, a typical corkscrew appearance of the sparks is observed (Figure 14).

The corkscrew sparks ejected from the melt are larger but have the same appearance (Figures 15 and 16). This observation is concordant with theories that postulate that the metal itself is the fuel for the reaction, and not some reaction product.⁴ The sparks are sometimes bright white, other times orange. Other sparks start off as white–yellow corkscrews and then explode



Figure 13. *Enlightenment – satori.*

themselves into a very bright white corkscrew and a few straight orange sparks. It thus seems that even droplets containing both magnesium and polysulfide melt are capable of spiraling away from the droplet. Like the peculiar shape of the charcoal and soot sparks, these spiral sparks show similarities with the appearance of what is in fluid mechanics called a positively buoyant jet.

Pure magnesium powder also gives off a typical sound while burning freely, kind of like a very high 'zing'. This sound is sometimes heard in the course of a satori reaction but then it sounds more like a metallic whip.

The experiments have shown that only magnesium is reactive enough to cause a glitter effect in windspeeds that senko hanabi sparklers can be fired in. Until now, the integration of pure magnesium in glitter formulations was thought to be impossible, because it immediately reacts away

in the birth phase.^{4,5} Indeed, this also seems true if magnesium is added to a composition that contains charcoal or mixed carbon sources (charcoal/ soot). However, now that the total amount of composition is split according to the type of carbon, magnesium can selectively be added to the soot composition. Because soot lowers the reaction temperature,³ the magnesium is allowed to integrate into the melt without reacting. From the experiments it is seen that this is the case even if a hotter-burning charcoal composition follows the soot composition. This can be explained by the fact that the magnesium is protected from the fresh reactants and the atmospheric oxygen by a layer of soot melt. Whether this protective effect of soot would also apply in stars and fountains has yet to be tested. In these devices, wind speeds are of course much higher.

The current experiments show that the satori effect consequently comes behind the spark phase of the

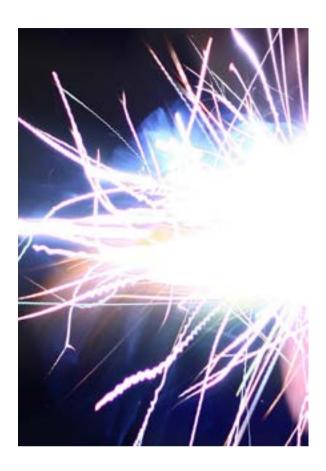


Figure 14. Magnesium powder in Bunsen flame.

carbon source. Between these two phenomena, the temperature of the polysulfide melt drops from 940 °C to 850 °C.^{2,8} A few explanations for the higher reactivity of carbon are possible. Carbon could be more reactive because of the special ability of potassium to separate its layers. Or carbon reacts using another reactant than magnesium $(K_2S_n vs. K_2SO_4)$ or needs a lower concentration of potassium sulfate to react. However, the critical role of potassium sulfate was already questioned in a previous paragraph. Another explanation could be that when the polysulfide drop gets smaller, the chance of magnesium metal touching the outer surface of the drop gets bigger. This theory is supported by the observation that the quantity of magnesium added determines the nature of the satori effect. The addition of just a few specks of magnesium makes the fireball give off separate sparks that after a short distance explode themselves. This reaction tends to happen in the old age phase and perfectly lends itself for integration in a finished sparkler. When more magnesium is added however, the satori phase tends to start earlier and the polysulfide drop reacts totally, more like a classic glitter flash in stars or fountains. Jennings-White also showed that the delay of the flash reaction in classic glitter

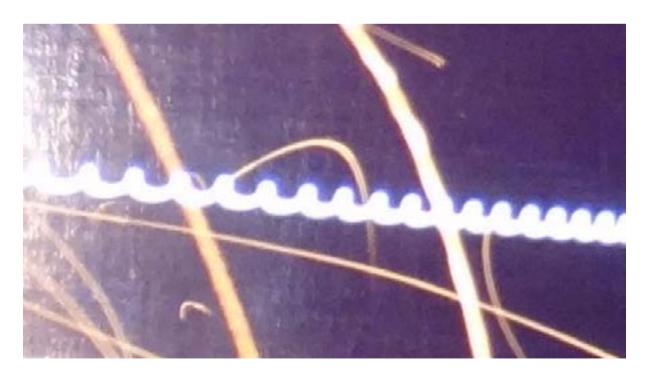


Figure 15. Corkscrew appearance of satori spark.



Figure 16. 'Sinusoidal' satori spark.

formulations is shortened by the addition of more metal.⁴

Because a reacting senko hanabi sparkler containing magnesium can be seen as a stationary 'spritzel', experiments were done to see if flash coloration is possible by using pure magnesium. Although some authors claim to have made non-yellow colored glitter using salts such as strontium nitrate, strontium carbonate, strontium oxalate

and lithium salts, these findings could not be reproduced by Jennings-White who studied the subject extensively.⁴ The results from the current experiments with a soot based and therefore sodium-free senko hanabi formulation with pure magnesium as the metal show identical results. Pure magnesium gives a bright white flash. Addition of just a little sodium bicarbonate colors the flash vividly vellow and doesn't influence the spark generation too much. Lithium carbonate, strontium carbonate, strontium oxalate and strontium nitrate do not significantly color the flash. Strontium oxalate perhaps gives off a slightly pinkish light but in live sparklers, the flash is observed as being white¹ (Figure 17). These salts also dramatically change the polysulfide chemistry so that the spark effects are ruined. Therefore they seem useless in senko hanabi formulations.

Interestingly, the addition of sodium bicarbonate to a senko hanabi formulation with added magnesium makes the magnesium much more reactive. Classic spark effects are absent, and even in still air, the magnesium very quickly reacts to produce yellow flashes. This observation further questions the role of a critical potassium sulfate concentration to be reached before the flash reaction can occur. Seemingly, the protective nature of the polysulfide melt can be influenced and this makes the metal react easier. This might also explain the role of sodium bicarbonate as a glitter enhancer in classic glitter compositions.

Conclusion

The senko hanabi sparkler was found to be a very useful tool to study glitter phenomena. It was shown that current theoretical frameworks are incapable of explaining all observations. New



Figure 17. *Indirect light from satori flashes with added salts.*

elements were added to the discussion about the role of critical temperature and potassium sulfate concentration on the glitter flash. Also, the role of sodium bicarbonate as glitter enhancer and coloring agent was demonstrated in the senko hanabi sparkler.

The remarkable microscopic appearance of classic senko hanabi sparks was documented and raises further questions about the nature of the polysulfide melt and the mechanism of spark generation.

The possibilities for further research are many. Other salts might be introduced into the composition, influencing melt properties and flash coloration. Different sources of carbon may be tested for their spark-forming abilities. Also, the specific properties of soot in senko hanabi glitter phenomena might prove useful in larger pyrotechnic devices.

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All pictures were taken by the author except Figure 14, 'Magnesium powder in Bunsen flame', which was taken by Ken Kohl.

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