

The Search For The Glitter Phenomenon

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Abstract: *This report presents the results of experiments carried out spasmodically over 14 years to investigate the glitter phenomenon. Various glitter compositions are disclosed. Some of these show that the use of sulphur in either elemental or combined form is unnecessary. Others show that similar considerations apply to antimony or any other heavy metal. It is further shown that the potassium ion may be replaced by either the caesium, rubidium, or sodium ion. Speculative broad mechanisms involved in the production of the glitter effect are discussed.*

Keywords: *Fireworks, glitter, sulphur-free, nitrate, metals, nitro-compounds*

Introduction

The earliest publication known to the author describing a formula for producing the effect now known as “glitter” is that published as British Patent number 1508 for the year 1901 granted to Frederick James Bishop who lived in the county of Gloucestershire in England. Frederick Bishop’s invention was “for producing a new kind of sparkling fires to be used in pyrotechny for designs, set pieces, and other purposes”. The formula described in the patent document is laid out with variable proportions as follows:

Gunpowder	10–20 parts
Black sulphuret of antimony (antimony trisulphide)	3–9 parts
Sulphur	2–6 parts
Aluminium	0.5–3 parts

After mixing, a composition was to be loaded into cases or dampened and made into pellets or stars. Since the date of this invention, fireworks producing glitter effects have become popular and widely used. There are now many compositions in use. They all seem to have as their core the components listed in Frederick Bishop’s invention with the exception that sulphur in addition to that contained in the gunpowder is not always present and the gunpowder can be found, either completely or in part, as its ingredients rather than as an incorporated whole. Also, the aluminium can be present as an alloy with magnesium. Sometimes, the antimony trisulphide has been replaced in part by one of the arsenic sulphides. Barium nitrate has been included as a replacement for some of the potassium nitrate. Additions of substances such as

sodium oxalate to produce a yellow glitter or the carbonates and oxalates of strontium and barium to control burning rate and glitter formation are frequently found. Other additives crop up here and there. Whatever modifications have been made, however, it seems that the essence of Frederick Bishop’s invention can always be found in the practice of producing the glitter effect. Consequent to this is the fact that sulphur in some form is always present as an ingredient. In fact it is now part of firework lore that sulphur is essential to the production of the glitter effect. No verifiable

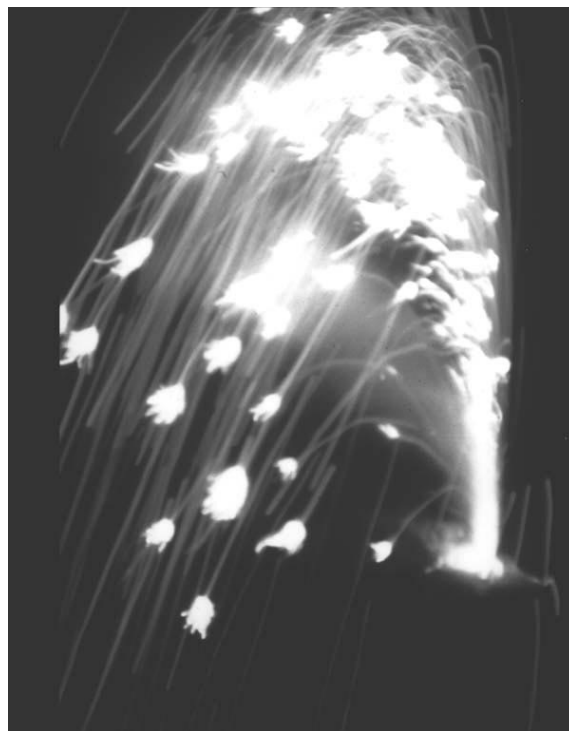


Figure 1. *Glitter effect.*

technical reason seems ever to have been presented as to why sulphur is essential; it is just one of those things which is known to be true.

In 1958, the author, purely for personal interest, began experiments to try to establish the reason for the glitter effect. Because this task was not driven by anything but mild curiosity, it was done only when spare time was available for it. In the event the work proceeded very spasmodically over a period spanning 14 years. The original aim went unrealised but some interesting facts were unearthed which belatedly are described below. Some of these facts have a bearing on the subject of the need for sulphur.

Initial Investigations

Observation of glitter fireworks when they were burning suggested that the effect was arising from particles travelling through the air which then burst with instantaneous production of light. The bursts were often associated with a slight “ploppy” sound and a thin white smoke. It was felt that the light could be arising from either intense reactions in the particles or combustion of a metal vapour escaping rapidly from the particles as they travelled through the air.

In order to investigate these possibilities, small glitter fountains made from potassium nitrate, sulphur, charcoal, antimony sulphide, and aluminium were burnt in an observation chamber in which the air had been replaced by dry nitrogen. No glitter effect was produced but some glowing particles were seen travelling through the gas. This experiment showed that air was necessary for the glitter effect to develop and supported the proposition that the glitter effect is produced by burning metal vapour although it did not entirely rule out a mechanism based on intense reactions in the particles because oxygen or water vapour in the air could be a required reactant. However, in the end it was decided that burning metal vapour was the most likely cause because it seemed that the particles were rather small as they could be bounced off a water surface still to produce the glitter effect. It was felt that particles small enough to bounce off a water surface would not produce the size of light flash that was observed if the light was produced from intense reactions intrinsic to the particles. Potassium vapour was thought to be

the agent concerned on the grounds of the general appearance of the light which was the wrong colour for antimony and not bright enough, and also the wrong colour, for aluminium.

Sulphur-free Glitter Compositions

If the flashes of light were caused by burning potassium vapour it was not clear why sulphur needed to be present for the production of the glitter effect because potassium is easily produced from its carbonate or oxide by heating with carbon but not by heating with sulphur. Any of the obvious functions that sulphur might perform, either as an element or combined as antimony sulphide, could be done by other materials.

Experiments aimed at producing sulphur-free glitter fireworks were started using mixtures of lead nitrate, potassium nitrate, and charcoal as the main energy source. Such mixtures were chosen because they were known to react vigorously and produce hot gases and molten residues which would be thrown into the air as a spray during combustion. Aluminium powder was added to these mixtures. It was thought that it would raise the temperature of the spray and might also, in conjunction with the charcoal, produce potassium by reduction of potassium compounds. Each material contained less than 0.01% sulphur. No glitter effects were produced using these materials. It was thought that it might be beneficial to introduce hydrogen into the main reacting system so that potassium hydroxide might arise which could then react with aluminium and charcoal to produce potassium. Dextrine was added for this purpose. This also produced no glitter effect but was useful for controlling the burning rate. At this stage it was thought that yet another material should be added which had the potential to promote the reduction of compounds such as potassium hydroxide, oxide, and carbonate. It was thought that iron might be a suitable agent because of the well known classical process for producing potassium by heating iron with potassium hydroxide. With the introduction of iron powder the production of a sulphur-free glitter effect was achieved. A suitable formula for demonstrating a sulphur-free glitter is

Lead nitrate	12
Potassium nitrate	6
Sugar charcoal	2
Dextrine	1
Aluminium powder	1
Iron powder	1

The lead nitrate, potassium nitrate, sugar charcoal and dextrine should be <120 mesh. The iron powder should be sulphur free and <300 mesh and the aluminium less than about 10 micron atomised powder. Flake aluminium was never tried but there is no obvious chemical reason why it should not work. The size of the iron powder is not critical: some cast irons up to about minus 60 mesh are suitable provided that they are low in sulphur content. The potassium nitrate content may need reducing with a larger size of iron. Sugar charcoal, prepared by pyrolysis of sucrose was used because wood charcoal can contain significant amounts of sulphur combined as sulphate.

The Effect of Different Nitrates

After this success it was decided to see if glitters could be produced with other metal nitrates in place of potassium nitrate. It was felt that if each of the alkali and alkaline earth metal nitrates produced glitters this would not support the burning metal vapour mechanism because lithium and the alkaline earth metals have boiling points well over 1000 °C and seemed unlikely to arise suddenly as vapour from tiny particles moving through the air. This was thought to be a good test for the validity of the burning metal vapour mechanism.

The mixtures in Table 1 were made. With the exception of the mixture containing lithium nitrate, the mixtures were prepared by sieve mixing and then dampening evenly with water in the amount of 3 g of water to 100 g of dry mixture. The dampened mixtures were run around with slight pressure in a pestle and mortar for about 1 minute and then spread out onto sheets of paper into layers about half-inch thick. They were then dried for a half-hour at 102 °C in a hot air oven, removed and allowed to cool. Each mixture was then filled into cases and ignited. To prepare the lithium nitrate mixture, all ingredients except the nitrate were sieve mixed. The nitrate was ground in a pestle and mortar, added to the other mixed ingredients and blended in with a spatula. The complete mixture was then processed with water as before.

The aluminium was <10 microns atomised powder. The lithium nitrate was crystal of about 20 mesh. All other ingredients were minus 120 mesh. The charcoal was sugar charcoal prepared by pyrolysis of sucrose, chosen to avoid potential effects from contamination by the potassium usually present in significant quantity in wood charcoal. All nitrates except for the caesium and rubidium nitrates were analytical grade materials. The caesium and rubidium nitrates were prepared from nitric acid and the corresponding carbonates. The rubidium nitrate contained some slight contamination by potassium as determined by flame spectroscopy. The sulphur was ground roll sulphur and the antimony trisulphide was prepared by fusing antimony of 99.5% purity with the calculated quantity of sulphur and grinding the product.

Table 1. *The effect of different nitrates.*

Lithium nitrate	15						
Sodium nitrate		18					
Potassium nitrate			22				
Rubidium nitrate				32			
Caesium nitrate					42		
Strontium nitrate						23	
Barium nitrate							28
Charcoal	4	4	4	4	4	4	4
Sulphur	3	3	3	3	3	3	3
Aluminium	3	3	3	3	3	3	3
Antimony trisulphide	6	6	6	6	6	6	6

The mixtures prepared from barium, lithium, and strontium nitrates did not produce a glitter effect but, not surprisingly, gave rise to considerable amounts of rather infusible residues. The mixtures prepared from caesium, potassium, rubidium, and sodium nitrates produced glitter effects. The effect from the sodium nitrate mixture was particularly interesting because of the brilliance of the yellow colour which was much more intense than that obtained by the addition of sodium oxalate to an ordinary glitter mixture. It was more in similarity to the depth of colour produced by sodium metal burning in the air. This fact obviously gave some support to the view that the glitter flashes might be due to burning metal vapour and that aluminium was not the source, or at least not the major source, because if this were the case the colour would not have been so saturated.

If the glitter effect were due to burning alkali metal vapour it was thought that appropriate investigations might indicate how and where the metal was formed, why, if the metal were formed in the main burning layer, it did not burn immediately on reaching the air, and why the metal burnt with a flash.

The Effect of Different Sulphides

It was decided to see if antimony trisulphide was critical to the production of the glitter effect in sulphur-containing glitter mixtures. With suitable adjustments to proportions of ingredients it was found that a glitter effect could be produced by replacing the antimony trisulphide with the sulphides of arsenic, bismuth (trisulphide), cadmium, iron (pyrites), lead, mercury (cinnabar), tin (stannic), and zinc. No other sulphides were

tried. The only chemical feature common to all of these materials seemed to be that they were sulphides.

The Effect of Iron and other Metals

It was next decided to do some experiments to see if iron would promote glitter formation with sulphur containing mixtures as it had done with the sulphurless mixtures containing lead nitrate. It was quickly found that iron did behave similarly with sulphur containing mixtures and that cobalt and, possibly to some extent, copper also behaved in the same way. The effect with copper only produced small sized flashes of light. Manganese, nickel, and chromium did not produce a glitter effect at all. The effect with nickel was pretty. No other metals were tried. During these experiments it was found that the inclusion of metal sulphides was unnecessary. A typical set of mixtures that were tried is listed in Table 2 below.

The potassium nitrate, sulphur, and charcoal were <120 mesh, the aluminium was <10 microns, the chromium and manganese were <100 mesh and the cobalt, copper, iron, and nickel were <300 mesh. The potassium nitrate, sulphur, and charcoal were processed separately as described for the previous set of nitrate, sulphur, and charcoal mixtures and the dried mixture was then combined with the appropriate metals. The charcoal was wood charcoal made from willow.

It was found during this series of tests that, although not necessary for the production of the glitter effect, the inclusion of either antimony, bismuth, or tin metal modified the appearance of the glitter flashes in interesting ways.

Table 2. *The effect of iron and different metals.*

Potassium nitrate	15	15	15	15	15	15
Sulphur	2	2	2	2	2	2
Charcoal	4	4	4	4	4	4
Aluminium	2	2	2	2	2	2
Chromium	2					
Cobalt		2				
Copper			2			
Iron				2		
Manganese					2	
Nickel						2

Following on these experiments the effect of replacing the iron by either cobalt, nickel, or chromium in the sulphur-free lead nitrate mixture quoted above was investigated. It was found that nickel and chromium each produced no glitter effect but that some glitter effect was produced by replacing the one part of iron by three parts of cobalt. The effectiveness of cobalt was not nearly as good as with the sulphur containing glitters.

Alternatives to Lead Nitrate

Obviously, the use of lead nitrate in fireworks is undesirable due to the poisonous nature of both lead nitrate and the products of combustion. A less troublesome formula for sulphur-free experiments and possible practical use was therefore sought. It was found that mixtures based on 3,5-dinitrobenzoic acid would provide the necessary conditions for glitter formation. A mixture that should easily demonstrate this is as follows.

Potassium nitrate	6
3,5-Dinitrobenzoic acid	4
Iron	1
Aluminium	1
Antimony	1-3

The iron should be <300 mesh, the aluminium about 5-10 microns, and the antimony <100 mesh. The remaining ingredients should be <120 mesh.

In the author's experiments, replacing the 6 parts of potassium nitrate with 5 parts of sodium nitrate gave a mixture which produced a glitter with a good yellow colour. Replacing the potassium nitrate with 4 parts of lithium nitrate or 12 parts of caesium nitrate gave no glitter. Replacement with 9 parts of rubidium nitrate did produce a glitter effect. In the case of caesium nitrate, an incipient glitter effect was obtained by increasing the iron content of the mixture.

A disadvantage with this type of mixture is that smoke production during combustion is greater than is usually found with similar mixtures containing sulphur.

Possible Broad Mechanisms

At this point, some more thought was given to possible ways by which alkali metal vapour could be suddenly released in the air. Three possibilities

were selected for consideration. These were:

1. The transport of alkali metal in solution or suspension of droplets or metal fog, in molten alkali metal salts or oxides which on cooling would precipitate the alkali metal and also form a solid contracting crust. The resulting increase in internal pressure of the droplet might cause the crust to crack and the alkali metal to be ejected into the atmosphere where it would burn rapidly. Or the particle might absorb water from the atmosphere which might then react sufficiently exothermically with the alkali metal to bring about ignition.
2. Droplets containing alkali metal carbonyls which would react with the air in an explosive manner to produce a flash of light.
3. The bursting of droplets of molten alloys of alkali metal and other metals formed in the burning mixture.

Scheme 3 was considered to be very unlikely because alloys of alkali metals and other metals that might be present in the burning mixture were believed to contain insignificant quantities of alkali metal at the temperatures which would be attained. Scheme 2 was thought to be possible. Even though sodium is not believed to form an analogue of the well known potassium hexacarbonyl, it has been reported to form a carbonyl which is explosive in air.

In order to obtain information of relevance to schemes 1 and 2 of the above, a series of mixtures was made using a base mixture which did not produce a glitter effect when burnt and adding to this various organic materials which might be expected to increase the carbon monoxide concentration in the burning mixture and/or to produce salts which would lower the melting point of oxide and carbonate slag.

A base mixture was prepared from

Potassium nitrate	22.0
Sulphur	3.4
Wood charcoal	4.0
Aluminium	0.3

Mixtures were prepared by adding each of the following materials to the base mixture in the proportions of 5.5 parts of base mixture to 0.3

parts of additive: citric acid, oxalic acid, tartaric acid, biuret, iminodiacetic acid, glycine, potassium bitartrate, potassium glyoxylate, antimony sodium tartrate, sodium oxalate, lithium formate, potassium formate, and sodium formate.

When burned, only mixtures containing sodium formate, antimony sodium tartrate, and sodium oxalate produced good glitters. Mixtures containing tartaric acid, potassium bitartrate, potassium formate, or potassium glyoxylate produced incipient glitters, while the others produced no glitter effect at all. The fact that lithium formate produced no glitter effect and potassium formate only an incipient one while sodium formate and sodium oxalate both produced good glitter effects indicated that carbon monoxide played little or no part in glitter formation but that reduction of slag melting point was important. Sodium formate and sodium oxalate would both produce sodium oxide and carbonate in the burning mixtures and these would reduce the melting point of the slag due to formation of the known relatively low melting mixtures with the corresponding potassium salts. If a low slag melting point was a key factor for producing the glitter effect it was thought that adding sodium bicarbonate to the base mixture would also produce a glitter effect on burning. This was confirmed by mixing 0.3 parts of sodium bicarbonate with 5.5 parts of the base mixture and burning the product. A good glitter effect was produced confirming that low melting slag was required.

This result pointed the way to the next set of experiments. If low melting slag was required then a mixture of sodium nitrate and potassium nitrate mixed with appropriate quantities of sulphur, charcoal, and aluminium should also produce a glitter effect when burnt. This proved to be the case as was shown when the following mixtures were burnt.

Sodium nitrate	1.7	2.9	4.6	
Potassium nitrate	5.5	3.5	2.0	
Wood charcoal	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5
Aluminium	0.4	0.4	0.4	0.4

The first mixture occasionally produced an incipient glitter. The second and third mixtures

produced glitters. The fourth mixture produced a bright yellow flame.

The results from these various experiments were not specific enough to eliminate any of the three proposals mentioned above. Each proposal depended upon a molten slag with the property of being easily dispersed into droplets for projection into the air. However, the results from the experiments where an increase in carbon monoxide concentration in the burning mixtures might be expected hinted that the alkali metal carbonyl mechanism was not very likely.

In order to obtain information that might be useful in discriminating between possible mechanisms of glitter formation, it was decided to investigate the products of the reactions in the firework tubes.

First, an attempt was made to capture whatever was producing the glitter, or at least its reaction products with water, by projecting the spray from a burning glitter firework at a slant angle to a water surface separated from the firework by about 1 to 2 feet so that dross dropping from the firework would not contaminate the water. It had been discovered earlier, as stated above, that particles producing glitter bounced off water surfaces. It was thought that the problem might be overcome by increasing the angle of attack or by reducing the surface tension of the water with a suitable additive. This procedure was quickly abandoned because it was found that the particles producing the glitter effect still bounced off the water surface and travelled on to produce the glitter flashes even when the angle of attack was 45 degrees and an agent to reduce surface tension had been added. The fact that the particles had insufficient energy to overcome the surface tension of the water, even when the surface tension was reduced, suggested that they were very small indeed.

Next, an attempt was made to recover all combustion products by burning glitter fireworks inverted in an argon atmosphere and collecting ejected material on a cool surface. A plywood box (see Figure 2) was made for this purpose such that its internal dimensions were 20 inches high by 8 inches square. One end was fixed permanently in place while the other end was oversize and rested loosely in place so that it could easily be slid away. A gas inlet was arranged by the fixed end. One side was made of glass for purposes of

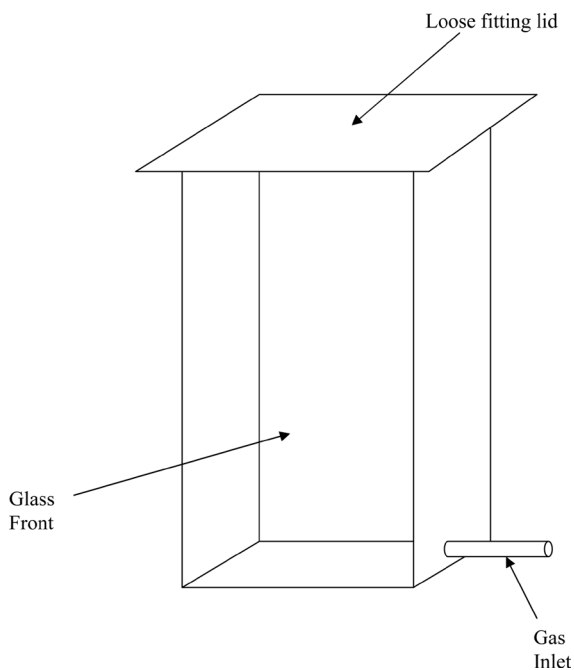


Figure 2. Apparatus for collection of combustion products.

observation. In use, the box was stood upright on its fixed end which thus formed a base. A receptacle to solidify and retain molten matter issuing from a burning firework was made in a form which could be easily dismantled by placing a 4 inch square piece of steel plate (0.25 inches thick) on the base and holding two similar pieces of steel plate upright such that the three pieces were brought together at one corner. The upright pieces of plate were supported by wooden blocks on their outside surfaces. The firework under test was arranged for electrical ignition and held so that its burning end would be aimed at the corner of the steel plates. After putting the lid in place, the box was filled with argon and the firework ignited. The material collected on the steel plates was then removed and examined.

Two glitter mixtures were tested as shown in Table 3. Mixture A was used as an example of a sulphurless glitter and mixture B as an example of one containing sulphur. A mixture containing combined sulphur rather than elemental sulphur was used because it was thought that any elemental sulphur appearing in the collected combustion residue might react with the glitter forming material so that it could not be identified.

When tested as described, mixture A gave a black deposit interspersed throughout with small shiny metallic looking spheres. Some residue was added to water held in a 1 inch diameter test tube. The residue reacted immediately and exothermically with vigorous evolution of an odourless gas. The test tube was closed with a bung before gas evolution had ceased. After gas evolution had progressed for a short time the bung was removed and a burning splint held at the mouth of the test tube. The gas burnt violently producing the squeak characteristic of hydrogen. The flash was not luminous. It was assumed that the gas was hydrogen. The experiment was repeated using mixture A without an iron content. This mixture produced no glitter but the residue collected after burning in argon looked the same as the residue obtained from the normal mixture A and reacted similarly with water. It seemed therefore that whatever was producing the gas was not responsible for producing the glitter effect unless the iron was responsible for favourably affecting the physical properties of the molten slag.

The residue obtained from when mixture B was burnt was a black material which had relatively large white spheres dispersed throughout. When treated with water there was a slight evolution of gas but insufficient for flammability tests.

The above results did not seem to be immediately useful for unravelling how glitter formation occurs so another attempt was made to collect the particles responsible, this time by using self-adhesive tape as a collector. Strips of double sided self-adhesive tape were fixed to one side of a square paper board

Table 3. Glitter mixtures.

	A	B ^a
Potassium nitrate	6	7.8
Potassium 3,4-dinitrobenzoate	4	
Sodium 3,5-dinitrobenzoate		6.2
Sodium 4-nitrobenzoate.		2.4
Sodium hydrogen sulphite		3.8
Aluminium	1	1.0
Iron	1	
Antimony	2	

^a Note: Mixture B does not keep for more than a few hours in humid conditions.

of 7.5 inch side. A glitter firework was arranged for electrical ignition and to fire upwards from the centre of the box base. The board, with the self-adhesive tape facing towards the firework, was held with heavy duty self-adhesive tape 2 inches below and parallel to the box lid. The box was filled with argon and the firework ignited.

In these experiments, mixture A produced an area of continuous black deposit surrounded by a few black spheres. No metallic looking particles were visible. The tapes were quickly removed and placed in water. The black deposit reacted with rapid evolution of an inflammable gas. The residue stuck to the self-adhesive tapes from mixture B was a collection of white spheres of widely varying size and black debris of random shape. When placed in water a few pinpoint sized regions evolved gas for about 2 seconds. It was speculated that these pinpoint regions might have held particles with the potential to produce glitter flashes. It was realised that a much more refined experimental technique would be necessary to explore this.

Experiments were then done to find out what happened when glitter fireworks were burnt in an atmosphere of argon such that after travelling through the argon particles from the burning firework would pass into the air. To do this a firework arranged for electrical ignition was placed upright at the centre of the box base. The lid was put in place and the box filled with argon. The lid was removed with a gentle sliding motion just before the firework was ignited. The effect was observed through the glass side of the box and in the air just above the box opening. Two glitter mixtures were tested, mixture B above and:

Potassium nitrate	6.0
3,5-Dinitrobenzoic acid	4.0
Aluminium	1.0
Iron	1.0
Antimony	2.5

When a firework containing mixture B was burnt no effect was visible in the argon at the beginning of combustion except for a short flame at the firework mouth. However, almost directly above the top of the box a display of glitter flashes appeared without noticeable delay. As the burning continued glitter flashes began to appear inside the

box just below the top. The line of demarcation moved down rapidly to the region of the firework. This behaviour was clearly due to air being sucked in by the upward displacement of argon in the central region driven by the materials issuing from the firework. Fireworks containing the mixture based on 3,5-dinitrobenzoic acid behaved similarly although there were some golden coloured sparks visible in the argon from the beginning of combustion and before glitter flashes were seen in that gas. The experiments were repeated twice with each mixture with the same results. The fact that mixture B did not produce visible sparks in argon suggested that the particles producing glitter flashes from this mixture were very small and cooled quickly. Yet some and perhaps all of these particles ignited on entering the air. This behaviour was considered to be compatible with the view that the glitter flashes were produced by combustion of alkali metal vapour mixing rapidly with air. If, for example, a very small particle containing or coated with potassium were ejected into air an oxidation reaction would begin. Due to the high surface area to mass ratio the temperature might rise to the ignition temperature of potassium and the large increase in heat of reaction might then vaporise the remaining potassium which would ignite with a flash. Two observations lend some support to this general mechanism.

First, when the fireworks containing mixture B were burnt in argon and the particles allowed to travel into air it was observed in one case that the first indication of chemical reaction in the lower part of the argon, where the rate of increase of air would be slowest, was the appearance of sparks which increased in size somewhat with a surrounding glow but did not develop into flashes. They simply burnt to extinction. If this observation was real rather than an illusion it would support the vaporisation mechanism. If the supply of air were sufficiently limited by dilution with argon the oxidation rate of the alkali metal would only be high enough to produce a relatively prolonged production of vapour resulting in a small diameter combustion zone maintained over a longer time hence not producing a flash.

Second, during experiments aimed at producing different sulphurless glitter mixtures it was found that the distance between the firework tube mouth and the point where glitter flashes developed

Table 4. *Use of different alkali metals.*

Potassium nitrate	6	6	6	6
Lithium 3,5-dinitrobenzoate	4			
Sodium 3,5-dinitrobenzoate	–	4		
Potassium 3,5-dinitrobenzoate	–		4	
Caesium 3,5-dinitrobenzoate				4
Aluminium	1	1	1	1
Iron	1	1	1	1
Antimony	2	2	2	2

might be influenced by the ease of ignition of the alkali metals in the mixtures. This can be shown in the series of mixtures shown in Table 4.

Glitter flashes only occur in the vicinity of the firework tube opening and for a short distance above it in the case of the mixture containing caesium. With the mixture containing only potassium the flashes still occur close to the tube opening but extend upwards to a greater extent. With the mixtures containing sodium and lithium some separation between the tube opening and the region of glitter appearance is evident while the effect extends much further upwards with lithium producing the most distance between the firework tube opening and the furthest flashes. The mixture containing caesium is interesting because in addition to the localised glitter effect it also produces reasonably large reddish sparks which spread out from the firework in all directions in a manner suggesting that they might be self-propelled.

It was clear at this point that to progress further in finding out how the glitter effect came about would require a more rigorous approach and a refinement to experimental equipment that would be too costly and time consuming. Therefore no further work was done.

In the late 1970s sulphur-free glitter fireworks were demonstrated to Ronald Hall and his colleague Edith (Dai) Ison of Brock's Fireworks. During a discussion about glitter fireworks Mr Hall mentioned that he had discovered that a mixture of meal powder, aluminium, and sodium oxalate produced a glitter effect. He gave the following mixture as an example:

Meal powder	10
Aluminium	1
Sodium oxalate	2

This confirmed in part the experiments reported above in relation to low melting slags where it was also found that sodium oxalate stimulated glitter formation.

During the progress of the work reported above many mixtures not recorded in this report were produced. Some that may be of interest are recorded below.

An example of a glitter mixture containing no heavy metals is:

Meal powder	10
Sulphur	4
Aluminium	1

Other examples of sulphur-free glitter mixtures are given in Table 5.

Mixture B produced small bright sparks which burst to produce golden rays but no glitter flashes. The addition of 1 part of antimony (mixture C) produced glitter flashes with bright rays. The addition of 2–3 parts of antimony (mixture D) produced glitter flashes without significant rays.

Potassium nitrate	6
3,5-Dinitrobenzoic acid	4
Lead cyanamide	3
Aluminium	1
Iron	1
Antimony or Tin	1–2

The above mixture produces no glitter unless either antimony or tin is included.

Table 5. *Sulphur free glitter mixtures*

	A	B	C	D
Potassium nitrate	6	3.5	3.5	3.5
Potassium 3,5-dinitrobenzoate	2			
2,4 Dinitrophenylhydrazine	4	1.5	1.5	1.5
Aluminium	1	0.5	0.5	0.5
Iron	1	0.5	0.5	0.5
Antimony	2		1.0	2.0–3.0
Wood charcoal		0.5	0.5	0.5

In the case of sulphur-free glitter mixtures it was found in the author's experiments that antimony could not be replaced by either of the metals bismuth or lead. Antimony could be replaced by tin usually with a change to the detail of the flashes. Iron could not usually be replaced by cobalt and when it was possible to do so there was always a decrease in effectiveness.

Conclusions

The experimental results obtained prove that:

1. Sulphur is not essential for the production of the glitter effect.
2. The glitter effect can be produced when the potassium ion is replaced by either the caesium, rubidium, or sodium ion.
3. Iron, cobalt, and, possibly, copper can promote the formation of glitter flashes, iron possibly being the most effective.
4. Heavy metals such as antimony are not essential for the production of the glitter effect.
5. The material ejected from burning glitter mixtures reacts spontaneously with air to produce the glitter flashes, air being an essential ingredient for their manifestation.

The results obtained when investigating the mechanistic aspects of glitter formation are unable to discriminate definitely between the possible broad mechanisms suggested. There is some experimental support for the view that glitter flashes are produced by the reaction of alkali metal vapour with air. It is suggested that the alkali metal vapour might be carried into the atmosphere in solution or suspension in droplets of an oxide or a salt.

Experimental Details

The mixtures described in this report were burnt in tubes rolled from paper. The tubes usually had an internal diameter of 0.4 or 0.5 inch and were unchoked. Some experiments were carried out with lead nitrate mixtures using tubes with an internal diameter of 0.75 inch provided with clay chokes of 0.375 inch diameter.

Author Biography

John Wraige designs and supplies explosive and pyrotechnic special effects for use in the film industry. This work sometimes requires the design of unique devices or the production of fireworks that are no longer available from commercial sources. He was responsible for the development of tapematch and its introduction into use. Also, he has developed novel powder filling, resin bonded, and extrusion techniques employed in the production of explosives and fireworks and other pyrotechnics.