GLITTER

Chemistry & Techniques

by Lloyd Scott Oglesby

CONTENTS

PREFACE

PART 1

PART 2

APPENDIX

oxalate effects: see p. 31

To Uncle William Oglesby and Grandpa C.O. Scott

'Wi a hundred men like these na battle is er lost
tho ever one be gone. Ya can ken the pipers toon
they fought to, an that's a lastin thing.'

I dedicate this paper to these two "Texians" of Scot blood.
'Slan na Gail!'

Left photograph illustrates the use of a brick wall in static evalua-
tions. Distance of fall equates with delay time. Upper center
photo: Streaker formula as pearl effect. Lower center: Streaker
formula as tremolante. Photo right: Streaker formula as twinkler.
All exposures 1/30 second except right photo is 1/15 sec. 5/8 inch
stars and all other conditions held constant.

Preface

In 1974 I published a hypothetical chemistry of glitter. Few comments were received on that article. In the intervening nine years the research done has validated the hypothesis. The implications of the theory have been explored; practical applications of the theory are explored in this paper.

Most of the literature of pyrotechnics contains statements to the effect that formulas are only a guide, but that is the end of the advice as to how to use the guide or progress beyond the guide. This is a *How to proceed beyond the formula guide for glitter.*

Throughout the following pages the term *sulfide melt* is used. The older term sulfide fusion could have been used, but it implies laboratory fusions in crucibles. Sulfide melt is used here to denote potassium sulfide or potassium sulfides in molten condition with or without other chemicals in solution or suspension within the molten potassium sulfide, or sulfides.

The redox chemistry of sulfide fusions is not well known. This redox chemistry has industrial application only to the fireworks industry. Since only the fireworks industry has a commercial interest in this chemistry there is no funding for research. Additionally, the sulfides share with tellurium the rotten eggs smell and other foul stenches. Few chemist are willing to tolerate the foul stench or the reactions of others to the strange reek they emit upon emerging from the laboratory where "stinky chemistry" is being elucidated. The story of the most famous tellurium chemist, his banishment from the chemistry department of his university, social ostracism, divorce, etc. is often told with humorous epithets.

The sulfide melts have unique chemical properties. Chemical reactions which occur in water do not always occur in sulfide melts. The author was surprised to find evidence of strong oxidizing ions, such as peroxides, dissolved in sulfide melts. In water, sulfide ion will reduce iodine to iodide and potassium peroxide, and superoxide will oxidize aqueous iodide solutions to iodine, or further to periodate ion. It is not surprising that much of the literature about pyrotechnically produced sulfide melt sparks is filled with reports of chemical species which do not exist at 800°C, such as the thiosulfate ion. These ions are quickly formed when the melts are dissolved in water prior to analysis. The author found radically different chemistry occurring at room temperature for spark droplets only seconds after collection by freezing. Some of the sulfide melts studied were not stable for more than one half second after capture. Special handling techniques were, and are, being developed. As techniques evolve the future may yield better data. Chemistry is an effort to be better informed tomorrow than is possible today.

Many of the effects used in fireworks involved potassium nitrate, sulfur, and charcoal reactants burning to produce potassium sulfide melt as the principle product. Gunpowder-like mixtures have been in use for approximately two thousand

years, and they are still not well understood from a chemical standpoint. The analytical chemical work that has been done, has, for the most part, used cold residues dissolved in water. The products of combustion react with water and with each other in water solution. Most of these analyses have reported potassium carbonate, but not potassium oxide. Potassium carbonate decomposes to the oxide and carbon dioxide at a significant rate at its melting point 891°C at atmospheric pressure. The rate increases at temperatures above this. The explosion temperature of black powder has a calculated value of 3880°C. T. Shimizu has reported 1800°C for atmospheric burning of a black powder mix coated on rice hulls.

Until recently the exact nature of the individual molten chemicals was a mystery. The viscosity, electrical conductivity, vapor pressure, and other physical properties of molten chemicals did not match the calculated values. Mossbauer and Raman spectroscopy have contributed to the understanding of simple salts in the molten state. Unfortunately, fireworks are virtually the only commercial products which depend upon the chemistry of potassium sulfide melts. Spectra for these are not of general interest and are unavailable.

It must be born in mind that much of what is presented here is application of modern theoretical inorganic chemistry and is a deliberate simplification of what is a complex problem. The future holds better data and from that data, better pyrotechnic effects.

PART I

Theory

When blackpowder-like mixtures of the finely divided chemicals are burned at atmospheric pressure, the nitrate crystals are flash heated so quickly that they do not decompose by the same mechanisms involved in the slow heating of the molten salt. The crystals are in part melted and in part become gaseous products, and the result is a spray of potassium oxides, nitrogen, oxygen, nitrogenoxides, etc. No nitrites have been found by the author except where the reaction was slow and crystal size too large to have been called representative of blackpowder. Apparently, in black-powder mixtures the nitrate is completely decomposed to oxides of potassium and gases. No traces of nitrite were found in the reaction residues of well made mixtures. In mixtures which contained thirty micron particles of potassium nitrate, the large crystals were projected from the original mixture surface as liquid droplets and if trapped by freezing at very short range, 5mm, were found to contain traces of nitrite. At slightly greater distance such particles were found to contain no nitrate and be nitrite free. Both nitrite and nitrate were analyzed by diaziatation color methods, nitrate by Brucine in sulfuric, and phenol disulfonic acid techniques for confirmation. Nitrite confirmation was by two unpublished methods of my own, and iodiometric analysis. The existence of potassium oxides is short-lived because the oxides react with hydrogen, water, OH -ion, carbon oxides, etc. With different physical conditions the reactions change. When potassium nitrate is flash heated alone in free fall through a furnace, the liquid and gas spray can be observed. A near colloidal spray of decomposition products (a smoke) is produced by flash heating in the furnace. It is less likely to produce much spray near the surface of the metal plates used to flash heat the nitrate, because the heating is too slow. A melt results on the plate. Small crystals of potassium nitrate embedded in the surface of a star or other powder grain are in a situation more closely resembling the plate experiment, but some oxide spray can be detected near very fast burning mixes at very short range. The force exerted by the gases within the flash heated nitrate must be small because the spray in furnace experiments does not spread far. In military research experiments at moderate pressures the nitrate appears to form melts on burning surfaces. Microchemistry of the military work was not reported. The author is aware of the many difficulties in finding traces of nitrite and nitrate in the melts which occur on burning stars or which form less than a few millimeters from the burning surface, but no evidence of nitrites and nitrates has been found.

Potassium nitrate melts or fusions have been studied by Raman spectroscopy. These studies have revealed that the ions present in molten potassium nitrate are not the simple potassium ion and the simple nitrate ion but rather the dipotassium-mononitrate ion ($K_2NO_3 +$) and the monopotassium dinitrate ion [$K(NO_3)_2 -$].

These larger ions precouple near the melting point to form chain-like ions, which helps account for the speed at which the material can crystallize. The size and complexity of these ions allow more quantumechanical J states and therefore explains many of the properties of the potassium nitrate's response on heating. The ions have more modes of energy storage than the simple ions would have. Because the ions are large, the reactions are rate moderated, both because the melt is more viscous, and because of the guarding effect of the dipotassium mononitrate ion.

If pure potassium nitrate is heated it undergoes a crystal transition at 129°C (rhombic to trigonal), melting point is 334°C, and at about 400°C the melt evolves oxygen to become potassium nitrite. Potassium nitrite melts at 440°C and at higher temperatures evolves oxides of nitrogen, leaving a residue of potassium peroxide and other oxides of potassium. Dipotassium monoxide decomposes in air above 350°C, and by reacting with air forms K_2O_2 in the melt.

Sulfur exists at room temperature as orthorhombic crystals of sulfur octets. Eight sulfur atoms bound at the apexes of a four pointed crown figure. At the melting point (130°C) the fluid consists of these so called 'sulfur crowns'. Around 160°C the crown molecules begin to break, at 193°C all crown molecules are broken, and the sulfur exists as helical ribbons, about 3.5 atoms per turn. The ribbons polymerize and reach a maximum length about 200°C. The chains become linear as the boiling point is approached. The dark red linear ribbons begin to split off even numbered groups of atoms as gas phase sulfur is evolved at the boiling point (444°). At temperatures of 2200°C the predominant species is diatomic. The gas is a deep blue color. At 2000°C and in hard vacuum the sulfur atoms exist singly. No studies of flash heated sulfur were found in the literature; flash sublimation to gas phase species of unknown structure is easily observed in aerosol burning. The tendency of sulfur atoms to associate in even numbered pairs is seen both in the sulfide ions and in the pure element. Only the monosulfide ion is stable at very high temperature, at moderately high temperature no other odd numbered sulfide ions exist. At temperatures near their melting points all of the odd numbered polythio ions decompose to yield even numbered polythio ions.

$$2\ K_2S_3 \longrightarrow K_2S_2 + K_2S_4$$
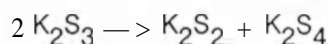
We would expect potassium sulfide melts to be formed from mono- and diatomic sulfur gas, primarily the diatomic gas, and the even numbered polythio ions or the monosulfide. Since the tetrasulfide decomposes at 850°C and higher sulfide numbers are associated with lower decomposition temperatures, their role in the chemistry discussed here is very short lived if it exists. We are reduced to dipotassium monosulfide, dipotassium disulfide and dipotassium tetrasulfide as possible sulfide species. Similarly, the possible thio-oxo ions are eliminated except for sulfate; others may have fleeting existence but if the temperatures at which they are known to

10

decompose or react with sulfide ion are taken as a guide, the probability of their being detected in the actual melts is exceedingly small. Thiosulfate ion was reported by Takeo Shimizu in his recent book in English as having been found by A. Maeda and his students in residues from the Japanese sparkler Sienko Hanabi. Sienko Hanabi is a small sparkler-type device which uses a potassium sulfide melt to produce the effect. Potassium thiosulfate does not exist in molten state, at temperatures of interest. Thiosulfate is formed in solutions which contain sulfur and sulfite ion both of which may be formed by air or peroxides reacting with sulfide solutions. The thiosulfate ion may have been formed in this way. The salt is formed when sulfide melts are allowed to react with air in the aqueous solutions normally used for analysis. The author has found no evidence of thiosulfate in Sienko Hanabi melts. Similarly the ions dithionate, tetrathionate, hexathionate, etc. do not exist as potassium salts at elevated temperature, and probably do not exist at all in the sulfide melts discussed here. Sulfites decompose to form sulfide and sulfate when the potassium salt is melted.

Potassium oxide, potassium dioxide and higher oxides are stable in the temperature range of interest. The dipotassium dioxide or potassium peroxide and monopotassium dioxide or potassium superoxide are the most probably oxygen transport species in the sulfide melts considered here. It is probable, but not proven, that the higher oxides of potassium react with the sulfide in melts to produce potassium sulfate.

Viscosity of spritzel fluids cannot be measure by the traditional techniques of physical chemistry. Forensic scientists use blood splatter patterns to assess speed and direction of blood droplets impacting surfaces at the scene of a crime. By studying the splatter patterns of spritzels impacting surfaces at constant angle of incidence and at as nearly matching velocities as possible, some assessment of melt viscosity and surface tension may be made. Firing a standard size star a set distance above a smooth concrete surface is a simple, adequate technique.

Under milder conditions of combustion the tendency to produce a spray of potassium oxides and gasses may be completely supplanted by melt and thermal degradation in a series of crucible like melts. Such conditions of milder burning rate are more typical of glitter stars. Factors such as larger nitrate crystals and more slowly reactive charcoals in the presence of inhibiting binders are typical in glitter stars. Glitter stars are often seen to accumulate droplets of molten reactants on their surfaces. In such stars any spray of potassium oxides is likely to be captured by the droplets and the concentration be low in the gases. Carbon dioxide and sulfur are likewise captured by the droplets. So it is not surprising to find no oxides of potassium in detectable concentrations forming on board the star in molten droplets. Glitter stars burning in static tests are sometimes completely covered by masses of molten dross with gasses erupting from small and transient vents. It is a moot question in such cases which type of reactions occurred with regard to the potassium nitrate.

11

Later in the paper the factors which increase the tendency to form the drossy droplets will be developed in regard to the formation of glitter.

At this point a few terms must be introduced and defined to help facilitate the discussion. Glitter effects are seen to be a continuum of achievable effects and any finely defined vocabulary to describe them would be more of a burden than a benefit. The glitter effect which produces a fiercely burning ball, or velocity elongated elipsoid shape of glitter flashes and produces the flashes near the star are called in this paper the *pearl effect*. The pearl effect stars in a shell break resemble teardrop pearls. The name derives from a formula discussed later that is often used to achieve this effect. The Italian term *tremolante* has been used to mean any type of glitter effect. Tremolante is used here to describe glitter of intermediate effect, some glitter flashes occur near the star, and most of the flashes appear in the path of the star as the droplets left behind the moving star explode to produce the flashes. The term *twinkler* is used here to indicate the type of star which has very few or no flashes near the star but which leaves a long trail of occasionally flashing lights behind it; these stars are often completely consumed before half of the flashes have occurred.

Reactions which may occur in the mixing, handling, dampening, forming, and drying of glitter mixtures are called *wet reactions.*

Reactions and conditions within or on the surface of a burning star or in gerbs during burning are called *onboard* reactions or onboard conditions. The term *onboard* refers to reactions that occur within 5mm of the star.

The term *spritz* refers to the flash of light each little droplet is desired to produce, and to the reactions and conditions which produce this brief explosive burning. A burning star produces a rain of burning droplets and spritzen is German for rain. Spritz is also an alliteration of the puffing or brief sputtering sound that the exploding droplets make.

Spritzel is the term used here for the burning droplets which form at or near the star and continue burning at low luminosity in the air at temperatures near 850°C. Spritzels are the droplets that explode in a spritz reaction. Reactions that occur in or on the spritzel are called *spritzel reactions* and the properties of the droplets such as average diameter are called *spritzel diameter. Spritzel size* means the average spritzel diameter. *Spritzel count* is the number of spritzels produced by a star, or other glitter device. *Total spritzel count* is the average number of spritzels produced by the type of star under discussion. Spritzel burn time, from the formation of the dross and separation from the star to the spritz reaction, is called *delay. Spritz size* is the average distance across the flash.

Some spritz explosions result in patterns of light. The flashes often throw incandescent material in reproducible patterns. The shapes of the light production zones can be called *spritz shapes* and described simply. Some patterns of the tiny burning masses blown away from the spritz are given simple descriptions and the following special terms. *Spurels* refers to spur-like projections of rapidly cooling debris

12

that are projected by the spritz explosion, and are visible if the star is burned close to the observer, a few feet to perhaps one hundred feet. *Spurets* are a like phenomenon but more numerous and visible for much shorter distances. Usually the particles are less massive than the projected bits of spritzel debris in spurels.

The keys to glitter are:
- Understanding and control of the spritzel formation processes;
- Control of the spritzel reactions, also called delay reactions;
- Control of the spritz reactions and the light emission.

Spritzel droplet formation occurs on or near burning stars if the conditions are favorable. In the case of stars which burn very fiercely and produce conditions where fine sprays of liquid droplets of sizes in the range of air colloids (smoke), the spritzels are formed near the star by a small nucleating droplet or particle accumulating the fine spray of material until a drop of 0.05 mm or larger is formed. This usually occurs within a distance of 5 mm from the burning surface. Accumulation of material by such a spritzel consists of aluminum which is in a molten state or is being melted. The molten mixture of salts which cover the surface of the aluminum constitutes the principle mass of the spritzel.

To discuss the reactions which create and control the spritzels we must have some background in three things: the chemistry of Sienko Hanabi, and gunpowder; some data on the most critical powder ingredient, charcoal. The nature of charcoal is all critical to gunpowder and similarly reacting mixtures.

CHARCOAL

Charcoal has been an important fuel for all recorded times in which pyrotechnics of any kind have been in use. In spite of this, very little modern research has been done and that which has been done is of little use. No other chemical or substance has so baffled the pyrotechnist. Most of the data on charcoal are found in physical chemistry research, especially the physical chemistry of surfaces.

Graphite studies and the results of graphite fiber technology of recent high strength fibers technology are the best structural data sources. Graphite industries such as high temperature and special applications of graphites such as special electrodes, etc. are also data sources.

Charcoal is basically the solids that remain after nonoxidative pyrolysis of organic material; for present purposes, the range of organic material is restricted to the cellular material of plants. Such solid residues are composed of graphite-like materials as the principal constituent, and such other inorganic compounds as are usually found between 40 and 0.02 percent of the total weight of the charcoal. The inorganic residues in the charcoal are usually expressed as so much metal oxide and

so much nonmetallic oxides. These numbers are meaningless in terms of revealing the chemical situation of such elements. Most plants have at least three different tissues. The area of charcoal research is large and complex and largely unexplored. Everything in writing on the subject can be read in less than a year. Since each tissue of each plant makes a different charcoal the field of study is vast. The author has studied the subject strictly from a pyrotechnic standpoint for years and still feels the matter needs further study to be well understood.

The pyrotechnists of the Orient, especially Japan and China, have the best selections of charcoals commercially available to them and seem the most skilled in charcoal selection and use.

Most of the literature of pyrotechnics available in English is unenlightening on the subject of charcoal. Most of the commercial producers of charcoals in the United States have no appreciation for the needs of pyrotechnists. The commercial producers seem to feel that if it is black and about the proper mesh size then it is suitable for pyrotechnics. In the author's experience no two species of wood or other plants produce charcoal with identical properties. Many pyrotechnists seem to think that particle size controls the reactivity of the charcoal. They have only to examine a fast burning composition from the Orient to realize this is not always the case. Gross particle size does have a marked effect on the reactivity, but not to the same degree that species factors and charring conditions do.

The woods most often referred to in pyrotechnic literature are grapevine, willow, alder, elm, pine, spruce, and the much less reactive oak, coke, coal, etc. The Orientals have different species of trees available and use a wide variety of woods and herbaceous plant debris as well, for reasons of economy, as well as to achieve effects.

The microscopic structure of plant materials is for the most part preserved in the pyrolysis process. Characteristic damage to the fine structures and this general preservation of micro structure allow even finely powdered charcoals to be identified.

Most of the charcoal supplied to pyrotechnists in this country is coniferous wood charcoal, most of which is made from sawdust and sawmill scrap. It is often called hardwood charcoal for the reason that hardwood charcoal brings a better price in industries where it is used for filtration. The hardwood charcoal is preferred in filtration because it does not crumble as easily in handling. The building and lumber industry use different woods in different areas of the country and the regional scrap and waste differences are fairly consistent.

Pine charcoal is nearly ideal for the glitter effects and is suitable for many spark effects. The structure of pine varies as the soft spring wood is replaced with the hard and resinous summer wood. The soft spring wood produces a fast reacting charcoal and therefore fast burning compositions. The hard summer wood produces a moderate to slow charcoal and it is this part of the pine charcoal which is found in the

14

burned residues of pyrotechnic mixtures made with this charcoal. One can observe the differences in reactivity in a fireplace or campfire. Fine charcoal will burn away deeply in the layers of spring wood and leave a relief of the hard and less reactive charcoal formed from the summer wood. Pine is a natural source of blended charcoal. With a little practice, the pyrotechnist can predict the burning rate and spark appearance from the microscopic appearance of the wood and its grain development, given a limited knowledge of plant physiology and biochemistry, and some knowledge of pyrolysis reactions.

Charcoals contain 60 to 99.6 percent carbon. It is this carbon fuel which makes most fireworks possible. Rarely does the ash content of a charcoal greatly affect the performance of a charcoal. This high ash is usually adjusted for by using more charcoal in the formula. A few charcoals contain very high silica (such as teak) and this does render them useless in pyrotechnics.

Charcoal is a special form of graphite. To be useful it must be reactive. This reactivity comes mainly from the structure of the graphite at the molecular level. Reactive charcoals have such poorly defined structure that special computer enhancement techniques are necessary to find a structure by X-ray diffraction techniques. Only in the last ten years has the solid state autogoinometerimetric digitalized diffraction machine become a commonly available tool. Digital computers can solve in a few hours the crystal structures of very complex materials. Charcoal is essentially a poorly formed graphite in more or less the physical form that the original plant material had formed.

Electron photomicrographs and X-ray crystallography of rayon fibers in various states of char and at various stages in the production of high strength graphite fiber production have been published. These studies are an excellent source of charcoal information. As the fibers of viscous cellulose are charred the X-ray pattern shows great damage to the semi-microcrystalline fiber. The fiber is heated to temperatures around 1000°C, and this high temperature allows a healing of the fine structure of the material. After thorough heat treatment the fiber becomes essentially a single molecular crystal of pyrolytic graphite, a very strong and inert material. It is the first few stages of this process that has interest to the pyrotechnist. Any charcoal can similarly be rendered nearly inert by heating to 1000°C to 1300°C for at least 24 hours.

Fairly recent studies by British researchers have probably confused cause and effect. The Britons found that the most reactive charcoals had significant volatiles and related the reactivity of the charcoals to the levels of volatiles. Such charcoals have not been heat treated at high temperature for long periods and thus have the poorly formed graphite structure. If such charcoals are stripped of their volatiles by moderate heating in high vacuum with inert gas sweeping (a low temperature process) they are found to have a higher reactivity than the low volatile charcoal from high heat treatment. The volatiles are a source of hydrogen. This is the lightest ele-

ment and therefore the fastest moving and reacting atom. It is no surprise that black powder reactions not only speed up but alter in character in the presence of the traces of hydrogen. Hydrogen has the highest heat conductivity and the fastest atoms at any temperature. Hydrogen would be the best charge transfer atom in the flame.

Introducing volatiles into poorly reactive charcoals would be expected to have another effect that would result in enhanced reactivity. The volatiles would be flash heated and would boil out of the structure of the charcoal explosively thus rupturing the carbon particles. You might call this vapor explosion grinding. Wet charcoal powder exhibits this phenomena when it is placed in the high temperature flame of an oxygen-propane torch. It is interesting to speculate that liquids which are prone to "bumping" in distillations such as aldehydes and a few amines, might be more effective at this vapor explosion grinding.

It should be mentioned that volatiles lower the temperatures at which the healing of the charcoal's graphite structure occurs. The volatiles furnish gas phase transportation of carbon and markedly speed the reordering. As charcoal is held above 700°C the structure becomes more clearly graphitic. The graphite structure is a stack of sheets. The sheets are composed of hexagonal carbon rings linked continuously by double bonds, thus graphite has greater conductivity along the axes of the plates than through the stack axes. The layers of the stack can slip one ring diameter at a time over the other layers. This gives graphite its lubricating properties.

The imperfect graphite structures that typify the more reactive charcoals are nowhere near the pure graphite structure. The distance between layers is not constant, the layers are pocked with holes, and shreds of broken rings are twisted and out of place. In the most reactive charcoals the graphite structure is more missing than present. The holes and dangling shreds are the active sites for chemical absorption, and for electrolytic hydrogenation. Probably they are the active sites for burning reactions. Stereochemically, it would be hard to imagine a shape better suited for entrapped gases to react with.

In the author's experience the most reactive charcoal is made from cotton by a rapid or flash heating process. The next best is charcoal from the balsa wood. Both are very expensive.

There is a tendency in the recent military research to refer to charcoal as an organic compound or material analogous to organic compounds. The researchers have begun to think of charcoal as an organic compound or mixture of compounds and to expect that the charcoal will react in similar fashion and by similar reaction mechanisms to those shown by other organic materials. Charcoal has an organic origin but there the similarities end. The pyrolysis process is incomplete in pyrotechnic charcoals and this leaves a good number of functional groups attached to the charcoal's underlying structure. The functional groups are so altered in their reactions by the stereochemistry of the graphitic material they are attached to, that any reaction analogies should be drawn with great care and rigorous proof.

16

The shredded structure of the graphitic material is stabilized by the remaining elements of the so called "functional groups". The dangling shreds of carbon chains would otherwise attach themselves to the main structure and well formed graphite would form. If the chains, broken and shattered rings had no attached hydrogen, oxygen or hydroxyl groups then they would be free radicals or ions, two very reactive species. The author believes the presence of such radicals is the reason for spontaneous combustion of charcoals (a well known phenomenon). Atmospheric oxygen introduced into evacuated vials of charcoal many hours after thorough cooling can cause measurable temperature changes. Industrially, the charcoal is often made wet, to retard the spontaneous heat rise. Free radicals can associate with water. The stabilized charcoal has a high oxygen content. Diatomic oxygen has a π^* orbital which can be used to react with free radicals at room temperature. The spontaneous ignition hazard is destroyed by long exposure to air. A near graphite structure with enough terminating elements other than carbon to stabilize the distorted graphite structure with oxygen best accounts for the reactions and the physical properties of charcoal. Conductive organic compounds are rare, charcoal is a moderate conductor and conductivity changes are observed as one would expect with physical chemical changes and these follow the unstably terminated broken graphite model. Surface chemistry reactions and absorption techniques of surface measurement follow the model. The model explains why the absorbates cannot be fully recovered. The model may explain the D.T.A. data from charcoal experiments, but the author has not seen the data charts, only the tabulated peak data which has very limited value since the size and shape of a peak are often more useful diagnostically than the temperature alone.

At least the military is not treating charcoal as a defense secret; it has been in use for at least five million years and is hardly secret. It is unfortunate that their research is so limited in scope; all they want is fast powder. By careful charcoal selection, special pyrotechnic mixtures for ignition, delay elements, and infrared or optical energy emission can be made to fit special purposes. Charcoal kept the magic fire going overnight for our ancestors and since it is renewable in chemically sealed environmental systems and is a compact high energy fuel capable of reactions over a wide range of temperatures, it will be of use in interstellar human efforts. Charcoal was used in the vehicles which landed on the moon. It would seem logical to understand charcoal in greater detail.

Lampblack and oven black are very similar to charcoal. The same healing of structure by heat to produce a less reactive material is observed. The best source of information on these materials is the rubber tire industry research.

Lampblack and oven black are useful illustrations of the molecular structure controlling the reactivity. Electron micrographs and X-ray diffraction reveal a very poorly defined structure for lampblack made at low temperature and quickly quenched. This is the preferential production sequence for pyrotechnic lampblack. The structure of such materials has been shown to be bulbous groups of imperfect

rings and straggling twisted shreds of crooked chains with many branches coiling back on themselves and each other. Recent research indicates that lampblack formation occurs as a special type of polymerization of acetylene.

The same types of studies made on lampblacks produced at temperatures in the range of 800°C show a much more graphite like structure. On continued heating, the structure shows a gradual approach to the perfect graphite structure. As these changes in structure occur the material changes in physical properties (such as electrical conductivity and reactivity).

In charcoal spark effects, the charcoal, as carbon, is added in excess of stoichiometric requirements. In glitter effects, the charcoal is added in nearly stoichiometric quantity with a ten percent excess to compensate for the normal levels of ash content, volatiles and moisture. In flitter, by contrast, the charcoal is normally added in less than the amount required to reduce the potassium nitrate stoichiometrically with respect to carbon dioxide. This can be used as a test of the theory given here: if the charcoal in a glitter formula is reduced to one third the prescribed level, a flitter type of effect should be observed. It is possible to formulate glitter mixtures which have large percentages of antimony sulfide or arsenic sulfide that could also glitter with one third the normal charcoal, but these would be rather unusual, and expensive. In such mixtures, antimony sulfide would chemically perform the reductions normally performed by carbon in the charcoal.

GUNPOWDER

Many of the older formulas for glitter were worked out in the luxurious days of cheap meal powder. Ammonium nitrate and smokeless powder have forever eliminated the economics of inexpensive gunpowder. Fortunately most glitter formulas actually perform better with mixtures of the chemicals instead of using meal powder. This gives a star which fills a larger column of fire and is particularly effective in comets to be fired near the audience. Meal powder burns much faster than hand mixed chemicals and it throws the spritzels further, and the spritzels are characteristically smaller. Naturally, stars which contain large percentages of meal tend to produce very small spritzels which have a high surface to mass ratio and therefor somewhat shorter delay. Small percentages of meal or grain can be marbled through a mixture to produce local differences in burning rate. This can be used to create cavities in the burning surface which help promote larger spritzels. These cavities can be the puddling site for the formation of large spritzels. Large spritzels have less surface to mass and therefore the delay reactions take longer for physical reasons. In small shells the meal powder type mixtures are useful but in large shells the hand mixed chemical mixtures are more appropriate from an artistic stand point. The technique of cavity formation by nonuniform mixing of small quantities of meal or grain is useful in achieving the twinkler effect which is useful in all sizes of shells. Combin-

18

ing the meal powder marbling trick with other control techniques to be discussed later is especially recommended.

The best way to study the effect of the techniques which involve non-homogenous mixing is to prepare cross sections or slabs of stars. The star is sawn into sections with a jeweler's saw or fine tooth coping saw. The sections are ground flat with abrasive paper or grinding stones by hand, with care taken to avoid heating and ignition. It should be kept in mind that the aluminum being ground away from the star surface is highly reactive and in the presence of oxidizers. Aluminum is a tough metal which heats greatly on abrasion. A series of abrasives are used to speed the production of flat sections and quickly achieve a highly polished section of sufficient fineness to make possible the easy observation of the individual component particles of the star. Finely polished sections are not needed when fine crystal growth during drying is to be observed. Let the specimen preparation and magnification used be fitted to the information being sought. A hand lens and low power microscope are sufficient for most observations. Magnification of five, ten and twenty power are the most useful for developing a valid understanding of cause and effect relations in glitter devices. Not being able to see the particulates in pyrotechnic compositions is a simple thing to correct. Several cause and effect relations given here are best studied and used with low power magnification for observation.

In the long history of gunpowder many formulas have been used. Tartaglia gave the formula as four of saltpeter and one each of sulfur and charcoal. The Spanish conquistadors used the ratios five, one, one, to conquer half the planet. The German artillerist used six, one, one. At about the end of Spain's imperial era, this formula ended the gradual increase in saltpeter percentage which had held for centuries. The reasons for the preference of most of these formulas are easily found in the nature of the charcoal used and the manner of mixing and granulation used at the time and place. The powder makers always had the best formula for the conditions of mixing and use at their time. The literature on gunpowder's history shows a remarkable disregard for simple experimentation, suppositions are rife, and facts correlated to the nature of such mixes are few. The powder makers have always sought speed, then uniformity of burning, and then power, in that order. It is no surprise that these are the criteria of modern powder mills which still make this ancient material, and it is still a challenge to make good powder. In Tartaglia's time the mixing was done very crudely, hot water being used to distribute the nitrate in fairly coarse charcoal. This mixing technique will yield the fastest mixture at about the ratios he gave. The Spanish were still using hand mixing and pounded the ingredients with wooden pestles in stone or bronze mortars in a damp or wet condition, after which the material was wet granulated and sun dried. With the microchemical conditions, this technique produces the greatest speed at a ratio of about five, one, one. The Germans were using very good charcoal and mechanical hammer milling. The French before Napoleon used grapevine charcoal which has high ash and their formula was

ten nitrate, two sulfur, three charcoal. According to Bob Cardwell, the Maltese pyrotechnicians use the same grapevine charcoal and similar mixing techniques to the French in the period before Napoleon and have found the best formula to be the old French formula. At about the time of Napoleon the French powder makers switched to the use of alder charcoal and adjusted the formula to nearly the famous Waltam Abbey formula of fifteen, two, three. The microchemistry of the ingredients is greatly affected by the physical factors created in the processing and the nature of the charcoal used. In a recent series of experiments reported in the publications of the P.G.I.I., a mix of twenty-five, four, five was found to be best for the commercial charcoal available in the U.S. and processed by simple ball milling and wet granulation. The table which follows shows these formulas as percentages and compares them with a theoretical mixture which will be discussed later.

TABLE #1: COMPARISON OF HISTORIC MIXTURES AND THE THEORETICAL BEST MIXTURE.						
	EQUATION ONE	15,2,3	5,1,1	6,1,1	25,4,5	10,2,3
POTASSIUM NITRATE	75%	75%	71%	75%	74%	67%
SULFUR	12%	10%	14%	12.5%	12%	13%
CHARCOAL	13%	15%	14%	12.5%	14%	20%

Analysis of modern powder usually runs 74%, 11.5%, 14.5% when the moisture is added to the charcoal.

Clearly the formulas are all in the range of Equation One's formula, and the ratio of potassium nitrate to sulfur is nearly constant. The variations are necessitated by the variations in the charcoals. The message is simple: hold the ratio of potassium nitrate and sulfur constant and adjust for the nature of the charcoal used. The more nearly a charcoal approaches being pure carbon the more nearly the formula is optimized at Equation One ratios, if the materials are ground to two microns average particle size or finer.

The most ancient formulas are often faster than the Waltham Abbey formula, if the mixing, grinding and processing are crude. For instance, if a poor charcoal such as oak is used and mixing and grinding are crude and incomplete, the formula 4, 1, 1 will burn faster and make a better firecracker than 15, 2, 3. It is difficult to grind and mix two batches to the same degree by crude means; the results may be monitored by use of the microscope. The formula 5, 1, 1, or its very close analog 25, 4, 5, will often

20

yield faster powder than 15, 2, 3, with the simple methods of mixing and grinding used in fireworks. This is especially true if the commercial charcoals are used without further grinding. Present day fireworks mixing techniques are very similar in results to the Spanish process in use circa 1650. It is a simple thing to establish this by experiment. During this discussion the term speed has been used as if it had only one meaning and one method of measurement. This is a gross misconception, but it is necessary to make generalizations. Since the methods of measuring powder speed depend upon the physical arrangement of testing, the entire subject is too lengthy to pursue here. It is interesting to observe the affect of different measuring techniques over the centuries, upon the formulas used.

From the literature on blackpowder, the analytical chemistry data on ignition products is expected to contain a wide variety of chemicals. The average chemist would look at the laundry list of previously reported chemicals and despair of ever generating better data. Most of the analyses of products do not give the conditions of burning used in the experiments. Blackpowder is found to yield different products at different pressures and durations of confinement at temperature. There are simple chemical reasons for these differences in products. Applying the principle of Le Chatelier we find that the reactions should shift to compensate for the conditions of reaction. Examination of the literature shows the following list of products.

SOLIDS	GASES	UNREACTED MATERIALS
Potassium sulfide	Nitrogen	Sulfur (trace)
Potassium carbonate	Carbon dioxide	Charcoal (trace)
Potassium sulfate	Carbon monoxide	
Potassium cyanide	Sulfur dioxide	
Potassium thiocyanate	Hydrogen cyanide	
Potassium nitrite	Hydrogen	
	Hydrogen oxide	
	Hydrogen sulfide	
	Ammonia	
	Nitrous oxide	
	Nitrogen dioxide	

There are undoubtedly others, under conditions not investigated, in at least trace amounts. It is unknown what importance the trace materials may have. As previously noted, the analytical problem is made more complex by reactions which occur after the samples are prepared for analysis. There are many questions to be asked about each analytical result. Questions as to when and why the analyte formed are important. A few observations can easily be done to develop an understanding of the types of reactions which are typical of these mixtures. Clearly a detailed study of the
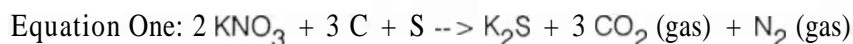
physical chemistry of black powder is needed but for the present purposes, a simplification of the actualities is all that is required. Perhaps a nonequilibrium thermodynamic analysis done numerically in multidimensional analysis format could be made to closely fit very carefully determined analytical data by regression techniques, but for now a simplified view will at least give a rational starting point for further understanding. By using simple semi-quantitative techniques and simple chemical theory, useful information can be derived.

Mention has already been made of the formation of potassium oxides from the potassium nitrate. This is found when loose piles of finely mixed powdered chemicals are burned with no significant confinement. Most of the potassium compounds are not oxides but finding any oxides at all is a clue to the initial fate of the potassium compounds. The same experimental conditions will yield potassium carbonate and potassium sulfide. The carbonate will be the predominant compound. If the gases are captured they will be found to contain sulfur in the elemental state, and much of the carbon is simply scattered as unreacted particles. As the physical state of the mix is brought closer to the condition of hard dense grains the potassium oxides are no longer found. They have all reacted more thoroughly with the other materials. The most prominent compound of potassium becomes first the carbonate, and then the sulfide, as conditions change. At mild pressure, the predominant compound of potassium becomes the sulfide. At pistol conditions, carbonate and sulfide, with some sulfate, are found. At rifle conditions, the cyanide and thiocyanate as well as the carbonate, sulfide and some sulfate are found. At shotgun proof loads, the solids and liquids begin to flow on gun barrel surfaces, cyanides increase, and the principal residue becomes potassium sulfate.
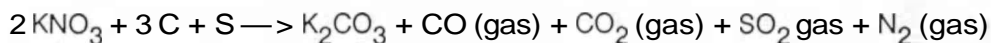
Now we can look at equations to determine why the reactions change with conditions.

$$2\,KNO_3 + S \longrightarrow K_2O + 3\,CO \text{ (gas)} + N_2 \text{ (gas)} + S \text{ (gas)}$$

This equation produces five moles of gas.

Equation One: $2\,KNO_3 + 3\,C + S \dashrightarrow K_2S + 3\,CO_2 \text{ (gas)} + N_2 \text{ (gas)}$

Equation One produces four moles of gas.

$$2\,KNO_3 + 3\,C + S \longrightarrow K_2CO_3 + CO \text{ (gas)} + CO_2 \text{ (gas)} + SO_2 \text{ gas} + N_2 \text{ (gas)}$$

This equation also yields four moles of gas, and in addition, makes four different kinds of gases, which is indicative of higher entropy than Equation One. We find that Equation One is predominant if temperature and pressure are held for longer reaction periods, and carbonate products drop correspondingly. Just as the oxides are

22

never found to be exclusive products, the carbonate and sulfide are never found to be exclusive products. The sulfide is 80% to 90% of the material found in low pressure fireworks guns. Gerbs, rockets, etc. yield similarly high percentages of sulfide. The longer the gases have to react the higher the sulfide; the higher the pressure, the higher the sulfide. The slower the comp burns, the higher the sulfide.

$$2\ KNO_3 + 3\ C + S \longrightarrow 2\ KCN + CO_2\ (gas) + SO_3\ (gas) + N_2\ (gas)$$
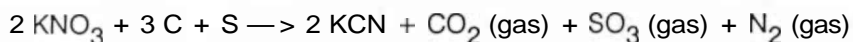
The formation of cyanide is catalyzed by iron. This equation yields three moles of gas. Traces of these products are found in the smoke of heavy rifle loads.

$$2\ KNO_3 + 3\ C + S \longrightarrow K_2SO_4 + 2\ CO\ (gas) + C + S\ (gas) + N_2\ (gas)$$
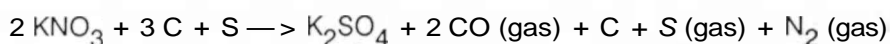
This equation yields three moles of gas. The high cyanide and high sulfate residue are typical of loads above the maximum pressures recommended for heavy rifles. These loads typically formed yellow liquid slags that tended to plug the vents of large naval guns and shore batteries in the days of black powder military propellants.

Naturally, none of the equations above are the only reactions occurring when black powder burns, but it is interesting that the equations reveal mechanisms for shifting the gas volume produced, and shifting the energy released when this old mixture is burned at different conditions. It was this ability to shift chemistry that made the development of firearms possible. Black powder does not shift from one equation to another like a transmission shifts gears. It's a smooth continuum of changing chemical reactions that has made this mixture a very versatile composition for centuries.

$$\text{Equation One: } 2\ KNO_3 + 3\ C + S \dashrightarrow K_2S + 3\ CO_2\ (gas) + N_2\ (gas)$$
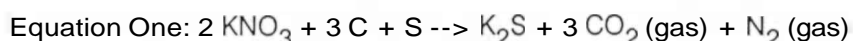
is the predominant reaction in fireworks devices. It is the main onboard reaction of glitter mixes based on meal powder with aluminum and antimony sulfide. These are the early forerunners of modern glitter mixtures. The antimony sulfide does play an important part in the chemical reactions of these mixtures but the initial reactions are those of burning meal powder. Antimony sulfide has the most complex chemistry of the materials used in glitter and it's chemistry is handled later in the paper.

SIENKO HANABI

Sienko Hanabi is the next item we will undertake in the examination of the gunpowder ingredients and glitter. Its range of chemical stoichiometry is similar to glitter mixtures. An understanding of this phenomena is fundamental to the understanding of delay in glitter.

23

Equation Two: $2 KNO_3 + 3 C + 2 S \longrightarrow K_2S_2 + 3CO_2$ (gas) $+ N_2$ (gas)
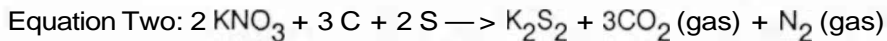
The calculated formulation (two significant figures) represented by the above equation is:

Potassium nitrate	67%
Sulfur	21%
Carbon	12%

The calculated center of the triangle diagram Takeo Shimizu gives for the phenomenon is:

|	
Potassium nitrate	60%
Sulfur	24%
Charcoal	16%

Comparing these two we find a remarkable fit and the differences in the two are logical. Sulfur is volatile and not all of the sulfur used in the mixture could be expected to react as Equation Two indicates. The devices are small and the sulfur is easily lost as a gas. The carbon is slightly higher and this is expected from the nature of charcoal. It is not pure carbon so extra weight of charcoal would be logically required to produce Equation Two-type reactions.

The theoretical formula is very near the center of the diagram. Analysis of Sienko Hanabi compositions residues shows them to be largely potassium disulfide in the first part of the reaction. Potassium disulfide is combustible and burns to yield the potassium sulfide as the reaction continues.

Now we can give a simple chemical explanation for the observed phenomenon of this device. Experimental results of studies on Sienko Hanabi have shown that the reactions may be written:

$2 KNO_3 + 3 C + 2 S \longrightarrow K_2S_2 + CO_2$ (gas) $+ N_2$ (gas)
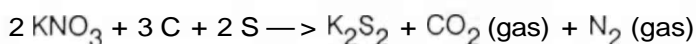
After the reactions that form the disulfide are complete there is a continuation of burning in reactions with air.

$2 K_2S_2 + O_2$ (air) $\longrightarrow K_2S + SO_2$ (gas)
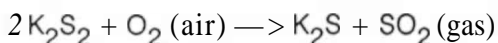
Recall that a very small excess of carbon is usually used in these mixtures.

$2 K_2S + 2 O_2$ (gas) $+$ excess carbon $\longrightarrow$ explosive burning $+ CO_2$ (gas) $+ K_2S$

24
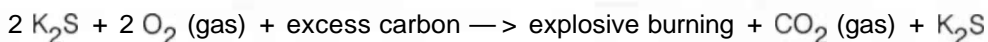
We will develop an understanding of the spark producing explosive burning mechanism, but first consider that the above equation indicates that the potassium sulfide is regenerated and the process can continue until the carbon fuel is consumed. This explains the relatively long lasting nature of the Sienko Hanabi. Normally, if a great deal of excess carbon is used, the phenomena will cease before the carbon is fully consumed.

$$2 K_2S + 3 O_2 \longrightarrow 2 K_2O + SO_2 \text{ (gas)}$$
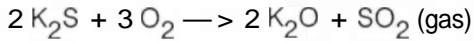
During the burning of Sienko Hanabi, the generation of sulfur dioxide is greatest at the quiet period before the generation of the sparks becomes intense. Sulfur dioxide is, however, given off throughout the active burning of the materials. This competing reaction will eventually consume enough potassium sulfide to block the reaction mechanisms of Sienko Hanabi. In practice the dross globule can pick up carbon from the tissue paper or rush halm used to support the dross globule. We now have an explanation for the duration of the phenomena and it's eventual termination. The melting points of the materials involved play a role in determining the reaction temperatures of the mixes and a critical role in the spark production mechanisms.

TABLE #2: MELTING POINT OF SELECTED POTASSIUM SULFUR COMPOUNDS
POTASSIUM DISULFIDE: RED-YELLOW CRYSTALS, MELTING POINT 470 C POTASSIUM SULFIDE : YELLOW-BROWN CRYSTALS, MELTING POINT 840 C POTASSIUM SULFATE : CLEAR WHITE CRYSTALS, MELTING POINT 1069 C

Shimizu reports that A. Meada, *et alia,* gave a temperature of 860°C as the burning temperature of the globules of Sienko Hanabi drosses after the initial reaction subsides and that the reaction continues for 8-10 sec.

At the temperature given by Maeda, the sulfides will be molten and the sulfate would be a solid, as would the carbon. Carbon sublimes at 3652-3697°C.

The droplet burns quietly until much of the disulfide has oxidized to the sulfide. At this point, the concentration of sulfate begins to rise. The tiny explosions which occur in the primary reaction mass cast out droplets of material which continue to burn in the air to form the sparks.

FIRST FORMULATIONS

Now we can predict a valid and operating formula for glitter, then compare the formula with one or two formulas used in the past, pick up some further data on more chemicals and examine the formulas published to date. At that point, the theoretical limits of glitter can be approached.

Simple things first. Empirically, most glitter formulas contain between five and fifteen percent metal fuels so we assume ten percent and calculate the percentages of materials needed to create a mix that will yield Equation Two residues.

Formula One:

Potassium nitrate	60%
Charcoal	11%
Sulfur	19%
Atomized aluminum	10%

The formula does produce glitter and it produces better glitter than the same aluminum and meal powder or hand mixed 15, 2, 3; naturally it is advisable to increase the charcoal to compensate for the fact that the formula assumes the charcoal to be pure carbon. This base fire is the same as was found for Sienko Hanabi, so Equation Two becomes the first consideration in the chemistry of this simple glitter mix.

Equation Two: $2 KNO_3 + 3 C + 2 S + [Al] \longrightarrow K_2S_2 + 3 CO_2 + N_2 + [Al]$
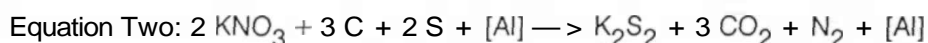
The brackets are used to indicate that a chemical is present but not reacting. In the next set of brackets a small letter "l" will appear to indicate that the aluminum is in the liquid state. The spritzel is formed of the above and continues to burn in air. The equation used to simply state the first and simplest type of delay reaction can be written as:

$$K_2S_2 + O_2 + [Al,l] \longrightarrow K_2S + SO_2 + [Al,l]$$
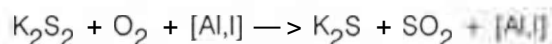
In the experimental section later in the paper are simple experiments that prove the mixture of potassium sulfate and aluminum is capable of explosive burning if some potassium sulfide is present. Aluminum can exothermically and explosively reduce all sulfates to sulfides but in the case of potassium sulfate it is usually a slow reaction similar to the flitter effect and is indeed typically taking place in most flitter stars whose formulas have the three formula ingredients of black powder type mixtures and aluminum. The presence of potassium sulfide causes a change in reaction types and reaction speed. Please see the test tube experiments.

26

Before the reaction indicated in the last equation has occurred to more than half the potassium sulfide (typically about one fifth to one third) the flash reaction occurs.

The stoichiometry:

$$3\,K_2SO_4 + 8\,Al \longrightarrow K_2S + 4\,Al_2O_3$$
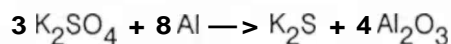
Notice the brackets are gone. Here is the high light output flash. Incidentally, the reaction can be used to make firecrackers but it is disappointing and difficult to initiate properly.

In all but the last equation the aluminum has been essentially inert. The temperature of the molten material has been about 850°C; aluminum melts at 660.37°C. The aluminum particles can easily be recovered from the molten spritzels by dissolving the spritzel in nitric acid. The aluminum can be filtered out or separated by sedimentation or centrifuging.

Microscopic examination of the spritzels after quick freezing on microscope slides will allow the examination of the aluminum. The spritzels can be frozen on contact with slides at room temperature. The four hundred Celsius degree or more drop in temperature is nearly instantaneous, so fast that the materials do not sort themselves out well enough to produce crystals visible at one hundred diameters. The spritzels are extremely hygroscopic. They will often have picked up enough water from the flame and air that reactions will occur within 3 seconds from collection. Spritzels which contain higher oxides of potassium are as hygroscopic as phosphorus pentoxide, which is the world standard for total desiccation. All handling and analytical work must take into account this exceedingly hygroscopic condition. Most of the work reported here was done at humidity of six percent or less, which is low enough to dry calcium chloride, the most common laboratory desiccant.

The potassium sulfides hydrolyze in the water they absorb from the atmosphere to form potassium hydroxide solution which dissolves the aluminum. A drop of water placed on a fresh spritzel will quickly cause the reaction. Hydrogen and hydrogen sulfide bubbles will be observed. By covering the splatter of frozen spritzel with oil, air and moisture can be occluded for enough time for observations. (Remember that oils often dissolve a percent or so of water.) The spritzel can be ground away with emery paper of 200 grit, then 400 grit, and then 600 girt, always under oil. Often a small hand lens is enough magnification to see the shiny aluminum particles. Aluminum particles become more spheroidal. Flake aluminums often melt and leave very thin sheets of aluminum around a globule which contains most of the mass of the aluminum in the particle. These particles somewhat resemble fried eggs. A few grams of these fried egg-shaped aluminum particles were found to be easier to ignite than the original form. Much more sophisticated chemical testing can be done,

27

but the findings are that no important consumption of aluminum occurs until the flash reaction.

Equation #3 is found never to go to completion; as soon as enough sulfate accumulates Equation #4 is activated and the droplet is blown apart violently. In poorly formulated, mixed or formed glitter, one can observe spritzels which are not entirely reacted. These spritzels, if large enough, yield interesting debris for microscopic study.

Winokur calls this burning of the spritz reaction comma or asymmetrical flashes. The reasons for such performance are obvious under the microscope. The accumulation of sulfate in a high viscosity spritzel, or one which contains large particles or aggregates of particles which block mixing in the droplet, produce uneven distributions of sulfate and aluminum in the droplet. Thus when the explosive reaction occurs, the explosive is poorly mixed and the slower burning or nonburning particles act as casings or loads to be driven by the microscopic explosions. The small (less than 2 cm) lacy effect I call *spurets,* and if two centimeters or larger, *spurels.* *Lacy* implies crisscrossing. The phenomena is radial and spur-like. The coma effect mentioned by Winokur is similar but more often occurs when the viscosity of the droplet is high and physical obstructions, often metal particles of aluminum too large to burn quickly, are thrown from the droplet. There is microscopic evidence that after the spritz flashes, the particles in the unreacted mass are heated greatly and that this increase in temperature causes a shift in type of reaction to that of aluminum flitter burning reactions. This is not completely investigated. Present data indicates that the thickness of the melt covering the aluminum particles is the differentiating factor between flitter and glitter, where the molten sheath is composed of sulfides. Thin films react with air to lose sulfur, and this causes a transition to flitter reactions. (Later studies confirm that the ratio of sulfide to other compounds, such as oxides, controls the change of mechanism).

28

MORE COMPLEX FORMULATIONS

Now that the simplest case has been handled, we can proceed to make investigations into the more complex glitter formulations.

Barium nitrate is often added to glitter formulas. For example, a very cheap formula that is used in Class C comets, given to me many years ago by Bill Withrow is called "Pearl Mix".

PEARL MIX:

Potassium nitrate	48%
Barium nitrate	16%
Sulfur	10%
Charcoal	11%
Aluminum	10%
Dextrin	5%

This formula produces little delay in the spritzels. The spritzels are small and very numerous when a uniform atomized aluminum is used. The flashes are brighter than those of formula #1.

After a few simple chemical calculations, we can begin to explain the observed facts. First divide through by the approximate formula weights, truncating to a reasonable number of digits. Calculate the molecularities of the ingredients.

KNO_3	48/101 = 0.475
S	16/32 = 0.500
$Ba(NO_3)_2$	10/261 = 0.038
C	11/12 = 0/917
Al	10/27 = 0/370

Since the Equation #1 has two moles of nitrate, we adjust to that convenience. Change the molecularity of barium to its equivalence, then set the total equivalence of barium and potassium to two, and find the factor by which to multiply all of the formulas molecularities to maintain their respective ratios of concentration.

0/475 + (2 X 0.038) = 0.551
2/0.551 = 3.6297 (or 3.63 to 3 significant figures)

$$KNO_3 : \quad 0.475 \times 3.63 = 1.724$$
$$Ba(NO_3)_2 : \quad 2 \times 0.038 \times 3.63 = 0.276$$
$$S \quad : \quad 0.500 \times 3.63 = 1.815$$
$$C \quad \quad 0.917 \times 3.63 = 3.328$$
$$Al \quad : \quad 0.370 \times 3.63 = 1.393$$

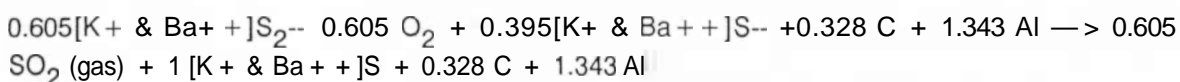Since barium nitrate has similar reactions to potassium nitrate we set up the equation as:

$$KNO_3 + Ba(NO_3)_2$$

$$(1.724 + 0.276) = 2$$
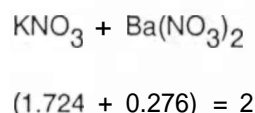
or: $2[K+, Ba++ \text{ nitrates}] + 3.328\,C + 1.815\,S + 1.343\,Al \longrightarrow [K+ \& Ba++]S_2 + 0.395[K+ \& Ba++]S + 3\,CO_2 + 0.328\,C$ and ash $+ N_2 + 1.343\,Al$

Now oxidation to monosulfide ion:

$0.605[K+ \& Ba++]S_2^{--}\; 0.605\,O_2 + 0.395[K+ \& Ba++]S^{--} + 0.328\,C + 1.343\,Al \longrightarrow 0.605\,SO_2$ (gas) $+ 1[K+ \& Ba++]S + 0.328\,C + 1.343\,Al$

Carbon oxidation requires approximately 0.328 moles of oxygen and the sprit-zel becomes:

$$1[K+ \& Ba++]S + 1.343\,Al$$
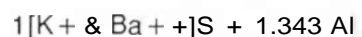
Similarly, the numbers for other glitter formulas work out so closely with the theory that you might suspect a chemical conspiracy. The formula is a little high in charcoal and a little low in sulfur; it is improved by adjusting these not quite to theoretical. The reason is, of course, ash content, etc. of the charcoal, and the high volatility of the sulfur.

A better **Pearl Mix** formula is:

|	
Potassium nitrate:	47
Barium nitrate:	10
Sulfur:	18
Charcoal:	10
Aluminum:	10
Dextrin:	5

The spritzels are low viscosity because of the high total nitrates, therefore they are usually small and numerous. The formula is nearly stoichiometric and usually burns fast, spraying the small droplets a fair distance. The flashes are bright because the barium nitrate forms a refractory sulfate and this sulfate does not react with aluminum at spritzel temperatures. It requires the higher temperature of the spritz reaction to start reacting the barium sulfate, melting point 1580°C, with the aluminum. The potassium spritzels never completely convert to sulfate before Equation #4 begins. Only a fraction of the sulfate and other refractory sulfates which require the high temperature spritz to react, therefore store oxygen in the spritzel. This additional stored oxygen creates a better explosive in the spritzel. They explode better. The formation of $BaAl_2O_4$ in the flame of the spritz helps the illumination power of the spritz reaction.

Similarly, strontium salts result in refractory sulfates and improve glitter. Strontium sulfate's melting point is 1605°C. Calcium sulfate is still solid at 1193°C and its effect is less pronounced but observable. Magnesium sulfate decomposes at 1124°C and is therefore of use. It has other properties which help, such as the lowering of viscosity of the spritzels. Metallic magnesium would be one of the reaction products (see Shimizu on strobe, *Pyrotechnica*) and would be expected to give flashes more closely resembling magnalium glitters, as indeed it does.

Another simple topic is that of the oxalates: Why do they help? Oxalates of magnesium, calcium, barium, and strontium all help by furnishing the ions to form sulfates of refractory character. They help lower the viscosity of the sulfide melts. Lithium oxalate helps lower viscosity but does not form a refractory sulfate. Onboard reactions of the oxalates have the effect of cooling the flame of the star. This cooling effect is beneficial in three ways. One, the delay reactions similar to, or identical with Equation Two, are initiated at lower temperature and therefore, at least initially, they are slower. Slower delay reactions mean greater delay. Second, particularly in stars which contain high aluminum percentages the oxalates help lower the temperature of the onboard reactions and this helps block aluminum loss. Finally, the onboard reactions are slower, giving longer burn times and usually larger spritzels, because the slower, less violent reactions do not tend to atomize the slag on the star as finely. Calcium oxalate is often used as a laboratory source of carbon monoxide. Its decomposition is endothermic and typical of the oxalates.

$$CaC_2O_4 + heat ---> CaCO_3 + CO$$
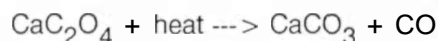
The calcium carbonate formed endothermically decomposes at temperatures below spritzel temperature.

$$CaCO_3 --> CaO + CO_2$$
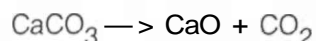
Calcium oxide forms calcium sulfide in potassium disulfide melts.

$$2 \, CaO + 3 \, K_2S_2 \longrightarrow 2 \, CaS + SO_2 \, (gas) + 3 \, K_2S$$
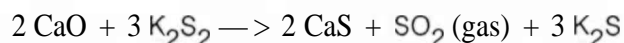
This reaction explains the advisability found in the literature of unusually high sulfur in mixtures involving oxalates. In calculations of glitter mixtures, the oxalates should be treated as other ion sources for sulfides.

The crystallization energy of barium sulfide is large, therefore the formulas which produce it evolve hotter slag than the corresponding potassium formulas. Barium sulfide is a solid at spritz temperatures and acts as a fluid reaction barrier. This enhances delay with increasing barium sulfide concentration until the barrier effect completely blocks the spritzel reactions and it does not fire. Other high melting sulfides form similar blocks. In general no more than one-third of a spritzel's sulfide melt should be a refractory sulfide. The higher the melting point of the sulfide, the lower its concentration should be. In gerbs, the initial temperature of the melt tends to be higher due to a longer contact time with more completely reacted gases at higher pressures. This creates special formulation problems. At the higher temperatures, destruction of the aluminum by oxide and/or sulfide generation becomes more probable. Aluminum oxide and sulfide form refractory slags which block fluid flow in the tube. This raises both pressure and temperature. More aluminum is destroyed. Gerb formulas must be designed to burn at lower temperatures than star formulas typically require. Most of the standard pyrotechnic techniques for lowering reaction temperature are effective in glitter gerbs. Bicarbonates, carbonates, and oxalates, are endothermic in decomposition, so if this is not offset by the production of refractory sulfides the overall reaction can be cooled when they are added to a formula. Potassium bicarbonate and oxalate are effective and often used. Carbohydrate materials as carbon sources, rather than charcoal, produce lower temperatures of combustion. High antimony sulfide content helps protect the aluminum chemically, and lowers the combustion temperature. Since potassium sulfate reacts with sulfur or charcoal to produce potassium sulfide, and the reactions are low energy, an interesting theoretical prediction that they might be useful or cause very adverse reactions, depending upon competing rates of reactions, offers interesting experimental material.

Barium sulfide's melting point is close enough to the temperature range required to be useful in larger proportion than any of the other suitable ions, other than lithium. Lithium has too low a melting point to be useful as a sulfate storage crystal. Potassium sulfide is therefore a necessity from the theoretical view and has been experimentally determined to be necessary.

The glitter enhancers: sodium, magnesium, and strontium, all help increase the percentage of the star which is available for spritzel solutions. Other elements

which theoretically might be useful are too expensive. The equivalent weight of lead is too large for it to be useful in anything but small percentages. Zinc in very small percentages might be interesting. Tiny crystals of the sulfides which have too high a melting point to be liquid in potassium sulfide solutions would act as tiny physical barriers to chemical reactions and fluid mobility restrictors in the spritz. This would enhance delay.

Tin oxide has the effect of lowering the viscosity of the sulfide melt but it inhibits the spritz reactions of the aluminum.

By comparing the weights involved in the equations for decomposition of oxalates, carbonates, and bicarbonates, the utility of each can be assessed. The best glitter will be achieved with those compounds which contain the least weight per metal ion equivalence, if all other factors are equal.

TABLE #3: EQUIVALENT WEIGHTS OF USEFUL ANIONS	
NITRATE ION (NO_3-)	62.0652 G/EQUIVALENT
OXALATE ION (C_2O_2--)	44.0099 G/EQUIVALENT
CARBONATE ION (CO_3--)	30.0046 G/EQUIVALENT
BICARBONATE ION (HCO_3-)	61.0173 G/EQUIVALENT

The carbonates are preferable except where they cause pH problems in the mixtures and spoil the aluminum by wet reactions. Barium carbonate is very refractory and is therefore useful in small quantities. However it has too little advantage over the nitrate and oxalate to warrant much study.

The oxalates are next best and have more suitable chemical properties. Sodium oxalate is 34% sodium and the gases produced are carbon dioxide, as is the case with sodium bicarbonate, and carbon monoxide. Carbon monoxide is a powerful reducing agent and acts upon the nitrate's oxygen to help produce heat for the melt. The overall stoichiometry of oxalates in glitter are analogous to that given for calcium oxalate but the reaction mechanisms are different.

The bicarbonates are cheap but prone to wet chemical problems and have too high equivalent weights. Sodium bicarbonate for example is 27.3% sodium by weight. The remainder of the chemical is essentially waste and is lost in the gases.

The nitrates of metal ions suitable for use in glitter are well known and will not be discussed.

Lithium oxalate produces a near red-pink glitter. Lithium sulfate has a melting point of 845°C which is below the melting point of its sulfide (900-975°C). Magnesium oxalate is useful with the sulfide decomposing without melting at 2000°C and the sulfate melting at 1124°C with decomposition. Obviously only quantities small

enough to remain in solution or as a fine suspension in the sulfide melt may be used. Calcium sulfate has a crystal transition at 1193°C. The melting point is not listed in the "Handbook of Chemistry and Physics" for calcium sulfate or calcium sulfide. The sulfide decomposes before melting but no temperature was listed; it is probably above the range of interest. Calcium sulfate and sulfide, like the magnesium salts, can only be used in small quantities.

TABLE #4: MELTING POINTS OF VARIOUS SULFIDES AND SULFATES.		
METAL	SULFIDE	SULFATE
LITHIUM	900-975·	845·C
MAGNESIUM	>2000°C (DECOMPOSES AT 2000·C)	1124·W/DECOMP.
CALCIUM	NOT AVAILABLE	>1193°C
STRONTIUM	>2000·C	1605·C
POTASSIUM	840·C	1069·C
BARIUM	1200 C	1580·C

Potassium sulfide melts below the melting point of potassium sulfate and that is what it takes to make glitter. Barium sulfide also melts below the sulfate but is useful only in potassium sulfide solutions.

In generating glitter formulations, it is important to remember that most of the glitter enhancers based on alkali metals give refractory sulfides. These sulfides are useful in percentages increasing with decreasing melting point of the sulfide. Compositions containing one-third barium sulfide and two-thirds potassium sulfide are nearly too viscous for use in glitter. The presence of antimony sulfide in such mixtures lowers the melt viscosity. It should be remembered that the spritzel looses almost all of the antimony before spritz and it is apparently this factor which determines the upper limit of useful concentrations for these additives. The refractory nature of the carbonates and their endothermic decompositions limit these ion sources usable concentrations. The carbonates are typically supplied in larger crystals with increasing solubility in water. The larger the crystals of these materials, the longer it takes for them to decompose and become sulfides. This last factor and the refractive nature of the compounds greatly influences the usable upper percentages in glitter. Generally the solubility of the carbonates increases with decreasing atomic weight of the ions. Refractory properties increase in order of increasing atomic weight until at barium carbonate the carbonate melts with some decomposition rather than decomposing entirely at 1450°C. Microchemical evidence suggests that barium carbonate is most useful as a physical barrier-type delay additive.

All of the oxalates decompose readily at or below spritzel temperature so their upper limits of usable concentrations are more nearly in order of their corresponding sulfide melting point.

The alkali metal oxalates are similar but tend to produce sulfides with low melting points. Sodium sulfide present in the spritzels imparts the sodium spectra to the spritz, causing it to appear yellow. Lithium sulfide imparts the lithium spectra to the spritz and produces a deep pink (commercially called red) to the spritzel reaction. Lithium pink or red glitter is difficult to achieve because most charcoal contains enough sodium to render the flash orange or yellow. The spectra of lithium and sodium may be deliberately combined to yield true orange and true gold flashes. Calcium and strontium produce even weaker spectra in glitter spritz and usually produce very weakly colored flashes or white. Indium could be used for its blue spectra if the price were not prohibitive. Blue tints might be possible with lead compounds but a clear and intense color is probably only possible with indium salts. Copper salts do not yield the green copper spectra in sulfide melts. Barium salts are used to produce clear whites. Thallium is too poisonous to be of any interest. Rare earth metals could become useful as prices continue to drop. Zinc-aluminum alloys looked promising for green production but are found to produce a different effect, similar to iron in iron gerbs, but do not glitter. No other sources of green coloration are economically feasible at this time.

Calcium oxalate gives glitter a rich golden color which differs perceptibly from sodium oxalate gold or yellow. Lithium oxalate with most commercial charcoals gives reddish gold closely resembling high pressure sodium-mercury vapor street lamps. Achieving a good pink-red with lithium requires very low sodium chemicals. Charcoal must be washed free of sodium.

The use of arsenic sulfide in glitter has not been investigated by the author for lack of a suitable supply of the material. It is probable that its chemistry would be similar to that of antimony sulfide. Potassium arsenate's melting point is 1310°C.

IMPORTANCE OF ANTIMONY SULFIDE

Paraceleus said that antimony is a fascinating element and that one could spend a lifetime studying its compounds and chemistry. Antimony sulfide is an unusual material. It is a naturally occurring semiconductor. It is usually given the formula Sb_2S_3. The compound is usually nonstoichiometric, that is, it is nearly Sb2S3 but not quite. If a crucible full is melted and allowed to resolidify, there is usually a multitude of natural diodes in the mass. The author found a crude transistor formed in such an experiment. The material is of the n-type if sulfur is above the stoichiometric and of the p-type if antimony is in excess. The n-type is much more sensitive with chlorates.

35

Lancaster stated that the naturally occurring sulfide was much better in glitter. Unless he was remarking the difference in the orange allomorph versus the black form, the statement is in error. The sulfide forms ribbon-like polymeric thiosulfides with alkali sulfides. The exact nature of the reactions of antimony sulfide in glitter is not elucidated to my satisfaction. The matter is under study. Well established facts are the following: The onboard star reactions occur at lower temperatures; the adhesion of the spritzel melt is improved; viscosity of the melts is at least lower onboard; and for part of the spritzel delay period much of the antimony leaves the spritzel and reacts with air to form antimony oxide near the spritzel. This oxide is reflective and the combustion of the antimony is exothermic. The spritzel is heated by the blanket of antimony oxide smoke forming at approximately a millimeter from the spritzel and is insulated by its reflectance. Antimony is a heavy element; as it leaves the spritzel, heat energy is required. Spritzels of high antimony content appear to burn at lower temperatures. These temperature effects have not been adequately studied. Antimony remaining in the spritzel at the time of spritz is reduced and evaporated to form a second luminous fuel. The antimony flame is often used for white stars. Because of this, antimony sulfide is the most popular chemical for enhancing delay. Formulas usually contain between 5% to 35% antimony sulfide. Droplets of the pure chemical falling through air burn at about the same temperature as normal spritzel reactions. It is therefore no surprise that glitter formulas will tolerate very large amounts of this substance.

Antimony sulfide is normally supplied in two forms, a fine powder best used for lowering onboard temperatures, and a Chinese needle best used (as explained later in the paper) under complex mixing. For the first 3 to 7% of a star mixture, antimony is best added in fine powder form. If a formula calls for more antimony than seven percent, the remainder is advantageously added as Chinese needle for reasons that will become obvious later in this paper. Antimony sulfide dissolves in potassium sulfide melts to form polymeric thioantimonates. These are apparently the best protectors against flitter reactions between potassium sulfate and aluminum. Only one thioantimonate is listed in the *Hand Book of Chemistry and Physics* and that as the hydrate! Information on the series of compounds is difficult to obtain or does not exist. Tripotassium tetrathioantimonate hydrate is listed as a yellow salt. The most probable ionic form of antimony in the sulfide fusions is SbS_3-3 and ribbon-like polymeric ions where each antimony is bonded in planar array with three sulfurs, and sulfur bridges between antimony atoms are the cause of the polymerization. The degree of ionization of such compounds would probably be highly variable with the chains catalyzing electron transport reactions like a 'button, button who has the button' game. Electron transfer along the chains would occur at speeds of 60-80% of the speed of light. Small wonder these ions are useful in fireworks. Stoichiometric considerations of the simplest case are:

$$3 K_2S + Sb_2S_3 \longrightarrow 2 K_3SbS_3$$

$$2 K_2S + Sb_2S_3 \dashrightarrow K_4SbS_5$$
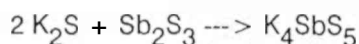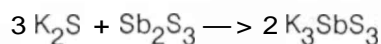
In melts of potassium disulfide, the chemistry will remain entirely a mystery until IR and Raman spectral studies and X-ray crystallographic studies are made. Even then, the temperatures involved in spritzels are high enough to make hash of room temperature stable compounds. Antimony polysulfides are known; they are not completely analogous to the arsenic polysulfides. The chemistry of the arsenic compounds is better studied.

Recently Winokur and others have used antimony oxide and oxalate in glitter. These react to form the sulfide and therefore require the formulas to include sulfur and charcoal for that purpose. They are inferior to the sulfide in glitter, and are very poisonous. Less than 20 mg/kg is the lethal dose.

The oxides of iron were proposed by James Finkbone; I communicated this to Winokur. Both oxides of iron have been used. They are both reduced to iron and magnetic nonstoichiometric sulfides. The iron serves as a low energy fuel after the spritz and as a simple physical barrier to fluid motion in the spritzel, often causing the spurel effect explained earlier. They are very nice in small items where the diminished light output is no disadvantage. Spritzels from these formulas may be dissolved in water, the magnetic sulfides and iron particles removed with a magnet, washed and then reacted with dilute hydrochloric acid to yield hydrogen sulfide and hydrogen. Microscopically, they consist of poorly formed dendritic crystalline fronds and weakly bonded filigree fronds of very small crystals. The tendency to aggregate into the above fronds enhances the effectiveness of the material as physical barriers to mixing and transport within the spritzel.

Very recent experiments by the author have found nickel compounds to be of interest. The microchemistry of the nickel compounds is under study. Nickel carbonate and nickel oxides have the unusual effect of enhancing the violence of the spritz flash reactions to such a degree that they make crackling noises. The brilliance of the spritz reaction is affected by the presence of the nickel compounds usually, but not always, adversely. Cobalt compounds are too expensive at present for practical formulations, but are under investigation.

If antimony and sulfur leave the spritzel as atomic gases they have recombined to form antimony sulfide 50 microns from the spritzel surface. Antimony bonds in molecular and ionic species with sulfur in trigonal planar arrays. Each antimony atom shows marked tendency to surround itself with three sulfur atoms. These trigonal planar groups can polymerize with more antimony and sulfur atoms to form larger groups. Sulfur atoms between antimony atoms are called bridging sulfurs and these are rarely ionized, but nonbridging sulfurs can be ionized. The antimony sulfide polymers tend to form ribbon-like structures.

37

The sulfur atoms external to such groups may combine with other sulfurs and produce an entire series of poly-thio antimonates. All of these structures would be in a maze of rapidly reacting equilibrium in the temperature range of spritzel chemistry. Because such a mixture should have many species present in significant concentrations, eutectic properties are found to be important factors in spritzel melts. The liquidous to solidous range of spritzels containing significant antimony sulfur compounds is much larger than the melting point range of the simple sulfides. This undoubtedly helps maintain a fluid condition on the exterior of the spritzels as they lose heat by air conduction and radiation. Spritzels of the following formula undergo a curiously complex series of reactions as burning proceeds.

Potassium nitrate:	44%
Charcoal:	8%
Antimony sulfide:	48%
Aluminum:	5-10% additional

At first the formula produces a melt that loses antimony (as the metal and the free metal are found in quick frozen spritzels). Then a series of reactions occur which go through a stage where the spritzel is largely K_3SbS_3 and the spritzel loses antimony sulfide apparently as the compound in gaseous state. Then another series of reactions occur where antimony is lost as the metal and the spritzel approach the formula K_2S at which time sulfate begins to accumulate and spritz follows shortly. At the time of the spritz, a trace of antimony as the metal can be found in the spritzel. During the first series of reactions where antimony is lost as the metal aluminum particles in the spritzel are coated with a thick black deposit of antimony. The subsequent period of antimony loss does not show such a strong tendency to deposit antimony metal on the aluminum. The heavy deposit of antimony metal is dissolved during the period of loss as sulfide. Note that this mixture has so much of the high heat capacity antimony sulfide that it rarely makes effective glitter in stars. The initial temperature of the melt is too low. By adding a higher temperature mix such as one which produces barium sulfide, the glitter phenomenon is achieved. Glitter gerbs can be made with this formula and the delay achieved is remarkable.

```
TABLE #5:  PHYSICAL PROPERTIES OF ANTIMONY TRISULFIDE

CRYSTAL CLASS: RHOMBIC OR ORTHORHOMBIC
MELTING POINT: 510°C
HEAT CAPACITY IN CAL/DEG MOLE AT 298-821°K: CP = 24.2 + 13.2T
HEAT OF SUBLIMATION: 51.2 KCAL/MOLE AT 510 C (MELTING POINT)
HEAT OF FORMATION AT 25 C: -43.5 KCAL/MOLE
SPECIFIC GRAVITY:  4.64
```

FLITTER VS. GLITTER

Flitter compositions based on potassium nitrate are not a principal topic of this paper. However, since flitter effects often intrude in discussions of glitter and since the flitter effect is often seen in experimental mixtures, a short discussion is necessary. The basic difference between glitter and flitter effects is that glitter effects burn the metal fuels in a sudden flash reaction, while flitter effects burn the metal fuels more gradually, thus the flash and associated sound are not found in flitter effects.

The sparks from flitter mixtures have been found to consist of aluminum particles covered or coated with potassium oxides and small quantities of potassium sulfate. Potassium sulfide is found only on sparks very near the star and never in a sufficiently high ratio to the aluminum that it completely bathes the aluminum in a molten sulfide melt and thus protects it from air oxidation. Very thin coatings of sulfide melts react with air quickly to lose the sulfur atoms or ions and become oxides. This is the reason that almost any glitter mix can be overloaded with aluminum and become a flitter type mixture. When a glitter formula is overloaded with aluminum the spritzels produced will have insufficient sulfide melt material to cover and chemically isolate the aluminum from air. A very thin coating of sulfide melt is easily oxidized to the oxides with the escape of sulfur to the air as sulfur dioxide. Evidence of this is seen in the smoke particle size of sulfide melts that show an increase in potassium oxides with distance from the source of the sulfide melts. The best device for observing this is a gerb. The pressure and time of reaction in the gerb case can be used to assure near total conversion to sulfides and total elimination of oxides. The sulfide melt from the gerb will show oxidation to oxides of the very fine smoke particles some distance from the gerbs vent. The oxides thus produced do react with carbon dioxide and sulfur dioxide in the cooler portions of the gas cloud produced by the gerb and with moisture from the air, but it is possible to detect the oxides produced. Similarly the aluminum containing melt droplets can be shown to contain only sulfides and later oxides in gerbs which contain aluminum in ratios too high to produce good glitter effects. It is often noted in the literature that the aluminum content of gerbs is held to about half the ratio the same formula would tolerate in stars. The reasons for this are complex but it should be obvious that the high velocity of the gases at the vent do not allow the formation of large droplets. This produces spritzels of high surface-to-mass ratio. It is well known that unchoked or moderately choked glitter gerbs will tolerate higher aluminum percentages and that glitter effect gerbs become problematical at high choke, or high pressure burning conditions. Flitter-like burning reactions can occur inside a high pressure gerb and the resulting refractory mixture precipitate a solid slag in the gerb. This blocks the vent and the fluid flow of spritzel materials out of the vent or case.

39

Potassium nitrate reacts with charcoal to produce potassium carbonate, potassium oxides, and potassium cyanide. More cyanide is formed at high temperature and pressure or in the presence of iron or its compounds. Potassium oxides are formed whenever potassium carbonate is held molten at atmospheric pressure. The rate of reaction is low, and the reaction is an equilibrium reaction which is easily reversed. At atmospheric pressure the molten material produced is predominantly potassium carbonate. The temperature achieved are sufficient to ignite aluminum. Flitter stars can be made with potassium nitrate and aluminum but charcoal is often added to lower the ignition temperature and render the stars more easily ignited. Similarly sulfur, antimony sulfide, or arsenic sulfide is used to start and control the burning of aluminum in flitter stars. Microscopic and microchemical examination of the sparks of such stars show a thin film of potassium oxides and potassium aluminates with some traces of liquid potassium oxide and potassium sulfide films over the mass of molten unreacted aluminum.

In most formulas for potassium nitrate-based flitter effects, the sulfur content of the stars will be found to be below the stoichiometric requirements for the formation of sulfide from all of the potassium nitrate. In most of the formulas of this type there is insufficient carbon to perform the total reduction of the potassium nitrate to form sulfides. Potassium nitrate can react with sulfur to produce sulfate directly and this is common in flitter effects. In all cases flitter effects will be found to have insufficient molten sulfide melts to protect the aluminum from direct reaction with oxygen from air. A thin layer of potassium sulfide at the melting point is quickly oxidized and thus there is rapid loss of the sulfur content. A thin layer of potassium sulfide on aluminum is insufficient to cause delay. The oxidation of the aluminum takes place first through a rate moderating oxygen transport system liquid layer covering the aluminum and then must later take place within the solid jacket of potassium aluminate that forms over the aluminum. This explains the observation that most flitter sparks lose incandescence in a smooth decent of temperatures at the end of their burn. This can also explain why some formulas appear to produce sparks at more than one temperature. Adjustment of flitter effects is easily made with an understanding of the phenomenon involved.

Typically the flitter mixtures are so loaded with aluminum, usually the flake type, that the formula does not produce enough volume of liquid potassium compounds to thoroughly coat the aluminum with a thick film. This is especially true where flake aluminums are used. The aluminum is in a molten condition but retains the original form to a large extent due to the oxide coat remaining intact as oxide or potassium aluminate. In gerbs the oxide coat is often dissolved in the liquid melts as complex aluminates due to the longer reaction times and higher reaction temperatures. Gerbs are correspondingly less sensitive to the form of the aluminum used. Gerbs often throw the melt with such violence that the layer of liquid sulfide is blown off to such extent that the flitter effect is seen. This is a typical problem of heavily

choked gerbs. Gerbs, because of their higher pressure, are more likely to produce sulfate at the burning face of the powder grain. The higher pressure and temperature and greater depth of molten slag a particle of aluminum must escape from, makes transitions to flitter reactions more probable. Excessive choke and too high a content of aluminum are typical problems in glitter gerbs.

Thin films of potassium sulfide are quickly oxidized with significant loss of the sulfur content to the oxides of potassium. The dipotassium monoxide or normal oxide is not stable in air at or above the melting point of 350°C. This salt reacts with oxygen from the air to form dipotassium dioxide, or potassium peroxide and higher oxides. Potassium peroxide melts at 490°C and reacts with air at that temperature to form the potassium superoxide, i.e., monopotassium dioxide. Both of these compounds can react with aluminum and probably play a role in oxygen transport and reaction moderation in flitter effects. It is doubtful that potassium sesqueoxide, etc. are formed in flitter effects to a significant degree.

All of the sparks from formulas producing flitter effects from potassium nitrate mixtures have been found to go through a stage near the end of their burning where the spark has the composition of aluminum coated with alumina and aluminates coated with a very thin film of potassium oxides.

It can be concluded that flitter effects will be generated by any of the following conditions:

1. Too much aluminum surface is present for the melt to cover to a depth or thickness sufficient to cause delay reactions. This is why the atomized aluminums are preferred in glitter mixtures and the flake types in flitter mixtures.

2. The sulfur and sulfide ratios to potassium nitrate are too low to form the potassium sulfide melt. The potassium sulfide melt causes the delay reactions and blocks the flitter reactions.

3. Charcoal or other reducing reagent is not present in stoichiometric ratio or excess of stoichiometric ratio to reduce the nitrate and thus allow the formation of the sulfides.

By the use of the Equations One and Two and an understanding of the causes and effects involved, a great degree of control over the pyrotechnic effects of glitter can be achieved.

Flitter stars can be made with only potassium nitrate and aluminum and will naturally form sparks that consist as above.

ALUMINUM

Aluminum is a complex topic and useful simplifications are few. Until the trigger reactions which begin the flash reactions and their physical chemistry are well known, the mysteries of metal choice will continue, and glitter will not be optimized to the extent chemically possible.

The aluminum most often cited in the glitter formulas in print is *bright*. A variation of the nonterm *bright* is the equally unenlightening term *light pyro*. This is essentially a meaningless term. The other popular term is *medium* and is totally without meaning. U.S. Bronze number 810 is sometimes called medium bright aluminum and some type of flake aluminum similar to 810 is usually meant by the popular terms *bright* or *medium*. Microscopic examination of one lot of 810 is given here to serve as an example of the mixture that can be found in a barrel. In general, tighter sieve cuts and better reproducability of properties are necessary. In general, you cannot buy two barrels of identical aluminum flake powder.

TABLE #6: MICROSCOPIC EXAMINATION OF U.S. BRONZE #810		
FOUR FIELDS ON A SLIDE MOUNT OF U.S. BRONZE #810 CIRCA 1968. TOTAL NUMBER OF PARTICLES MEASURED WAS 962.		
AVERAGE FINES PER FIELD	AVERAGE VOLUME	AVERAGE μG/PARTICLE
192.50	9.34×10^{-9} MM3	2.52×10^{-11}
27.75	5.84×10^{-7} MM3	1.59×10^{-9}
13.00	4.78×10^{-6} MM3	1.29×10^{-8}
6.25	5.67×10^{-5} MM3	1.53×10^{-7}
<1	7.80×10^{-4} MM3	2.10
36% OF THE SAMPLE MASS WAS FOUND IN 3 PARTICLES! WEIGHTED AVERAGE MASS: 0.03 μG/PARTICLE.		

TABLE #7: MICROSCOPIC EXAMINATION OF U.S. BRONZE #808.	
AVERAGE FIELD COUNT FLAKES: 44 FINES : 57	AVERAGE MASS 1.62×10^{-7} G 2.00×10^{-9} G
COUNT WEIGHTED AVERAGE MASS: 0.06 μG/PARTICLE PARTICLE EXTREMES: 0.002 μG/PARTICLE AND 0.16 μG/PARTICLE NUMBER OF PARTICLES COUNTED AND MEASURED: 306	

Glitter effects can be made with both of these aluminums. Flake aluminums are difficult to produce with batch to batch uniformity and in general the same formulas produce much better glitter with atomized aluminums. In general, high percentages of antimony sulfide are necessary to obtain even fair glitter with these and other flake aluminums. In general, flake aluminums have too large of a surface-to-mass ratio. A good way to evaluate aluminums for glitter is to pick a formula, make a large batch without the aluminum, cut the batch into 90 gram lots and add ten grams of each trial aluminum. Then you can begin blending aluminums. Each glitter formula will perform differently with a different aluminum. Until the spritz trigger reactions are elucidated, the theory of glitter will not allow full explanation of the observed phenomena. Observations to date indicate the following aluminum parameters are critical: (listed in order of importance)

1. Most important is the surface-to-mass ratio.
2. Size, shape, and quantity of the fines.
3. The overall shape of the particles.
4. Uniformity of particle shape.
5. The degree of oxide coat.

If the oxide coat is not sufficient, it becomes the most important factor because significant quantities of aluminum will be lost to wet reactions during mixing. The remaining aluminum is coated with a hydrated alumina jacket which, although it increases delay, spoils the brilliance of the spritz. This is the cause of the low light intensity pinkish flashes which are often asymmetrical. This effect is usually seen when wet reactions cause mild heating of the mix. An interesting example of the effect of the oxide coat is German black aluminum. The particles are much too small; the surface-to-mass ratio is much too large; but it has such a tough coat of oxide that it glitters in some formulas.

This paper is not the proper forum for comprehensive aluminum data, but in developing any theory of glitter the theory must account for most observed phenomena. The phenomena of the wet reacted aluminum has been handled in part. Additionally it is observed that such aluminum does not react as quickly with a drop of water or sodium hydroxide solution after it is removed from the spritzel reactions. Dye absorption techniques confirm this microscopically. Can the theory of oxidizer accumulation in the spritzel reactions account for this damaged aluminum performance? Asymmetrical spritz with flitter-like residues would be expected, diminished brilliance of the spritz and greatly increased delay would be expected, and a failure to fire in a spritz-like flash would be expected in the extreme case. All of these are observed. Aluminums of high surface-to-mass ratio would be expected to fire as spritz in the spritzels at relatively low sulfate concentrations unless other factors override this condition, such as viscosity and mobility of fluid transport in the spritzel. This is

observed when *spherical* atomized aluminums are used. The delay reactions increase in time required (for any one formula), if the aluminum concentration is deliberately kept low as the particle size of aluminum is increased. If the aluminum is of the flake type, interferences with fluid transport in the spritzel is expected at lower concentrations due to the shape of the particles. Due to the higher reactive surface per gram for flake aluminum, a tendency to block spritzel reactions and make transition to flitter burning at lower concentrations should exist. Due to interferences in mixing or fluid transport, flake aluminums should show asymmetrical spritz flashes at moderate concentrations of aluminum. Both of these are observed. These are the classic problems of flake aluminums in glitter.

With either type of aluminum there should be a maximum particle size at which glitter spritz reactions are too slow to call a flash, and above this size most of the spritzels should fail to fire. This is easily observed with spherical and other atomized aluminums. Blockage occurs more readily with flake aluminums and transitions to flitter occur more readily. Blind or no flash spritzels occur at spherical aluminum particle diameter of 150 microns and above. Aluminum of this size may be made to fire in the spritz if enough of a finer aluminum is used with it in a formula. The finer aluminum will allow it to burn in the explosion debris of the spritz reaction. Flake aluminum of 3000 micron diameter nearly always produces flitter, but often with delayed brilliance. Fine spherical aluminums should produce a lessening in delay, and they do. Spherical aluminum particles should display a short range of sizes which work in all formulas; they do. At mass-per-particle of 3 nanograms all formulas function, and a range of 2-5 nanograms/particle functions in almost all formulas.

Microscopic studies of blown or atomized aluminum reveal that no single aluminum product on the U.S. market is ideal. The author made studies of air separated aluminums and found the following factors to produce empirically better effects. Aluminum products were separated in a forty foot trough by air flow separation. Microscopic examination was used as a quality of separation control. Aluminums used for the study were Alcoa 101, 123 and Reynolds 120, all circa 1968. Ten pound batches of each were separated into six size ranges. Various formulas were made up with each cut, and known blends of aluminum cuts were similarly made into stars and fired as comets and in 3-inch shells. Samples of all star batches were burned statically. Microscopic examinations of residues of spritz debris collected on plastic film were used to evaluate combustion efficiency.

It was found that often as much as half of the aluminum failed to react and could be recovered by panning the boric acid solutions used to wash the plastic collectors. Cuts of the larger particles from Alcoa 101 and 123 failed to give glitter spritz when used alone.

This study indicated the following are beneficial:

1. The coarse particles should be distorted from spherical-dimpled spheres, slightly cigar-shaped particles, dumbbell shapes, twisted broken spherical segments, potato-like particles and rain drop shaped particles are preferred in the given order. The larger particles are suspected of yielding the most unburned aluminum. Slightly twisted platelet shapes are desirable in the larger to intermediate sized particles.

2. Smaller intermediate particles should be slightly more spherical.

3. Spherical fines are very desirable.

4. Desirable weight ratios of fines, small intermediates, large intermediates and coarse particles are largely determined by aggregate density and particle shape.

5. Aluminums low in fines produced the greatest delay and often the most wasted metal.

6. Aluminums with excessive fines, too small fines or poorly shaped fines produced very short delay and spur or spurel spritz, again with poor metal utilization. The larger particles in these mixes were often blown clear of the spritzel intact and unchanged in unreacted portions of spritzels. Light ball milling and hammer milling of coarse particles usually improved the effects achieved.

Maximizing the aggregate density helps in two ways. Just as in concrete made with Portland cement, control of fluidity and therefore overall spritzel viscosity is achieved by creating a mixture of particle sizes that most efficiently fills a given volume. Increasing the fines slightly makes the material flow more easily. Alcoa 101 aluminum is typical of aluminums which need more fines and intermediates to flow well. Not surprisingly aluminums can be tested for this property of proper aggregation by methods similar to the slump test used for concrete. A sample is placed in a short segment of tube on a soft rubber or plastic sheet. Fill the tube with aluminum and add water until the tube is full. The tube is then removed. A good glitter aluminum usually slumps quite dramatically. It must be remembered that many factors besides the aluminum affect glitter performance. Good glitter aluminums usually slump well, but slumping is not the only criteria. Bird shot slumps very well but does not make glitter.

The proper aggregation blending of aluminums assures that enough fines are present to quickly heat the spritzels fluid mass to the boiling point of aluminum. The flash of the intermediate particles will produce enough heat to evaporate the large particles.

Aluminums which contain particles of less than five microns average diameter do not function optimally in glitter. Aluminums which contain fines of seven to ten microns average diameter are best used in formulas which contain some antimony and are intended for intermediate delay. Aluminums with fines of 10-12 microns average diameter are best in most compositions especially those which contain little or no antimony sulfide. At about 15-20 microns average diameter of the fines, the longest delay and brightest spritz can be achieved if the remainder of the aluminum is properly adjusted. Gerbs follow approximately the same pattern but in general perform best with fines in the 15-20 micron range. Aluminum choice and blending for gerbs depends largely on the intended operating temperature and pressure of the burning device. Gerbs of all sulfur delay are especially difficult. Aluminums which contain particles up to 200 microns average particle diameter can be used, but generally about 150 micron particles is the upper limit. Shape and surface-to-mass ratio of coarse particles are most important. How large a particle of aluminum may be utilized depends more upon the selection of intermediate particles than any other factor.

Mixtures of sizes and shapes in the intermediates are difficult to evaluate. Surprising inconsistencies occur which do not fit an overall theory yet. Generally a variety of shapes is best. A mixture of conic, tear drop, potato, spherical and biscuit shapes provides high fluidity at high density of overall packing.

The exact ratio of particle sizes present to the weight is quite critical. Each formula and degree of delay of each formula requires slightly different blends of common commercial aluminums. Commercial aluminums on the market have to have limited ranges of utility and vary greatly from one barrel to the next over the years.

Coarse grain aluminum functions best in long delay formulas, finer grain in short delay formulas. Generally aluminums with 10-30% fines (5-20 microns), 30-100% intermediates (20-50 microns) and 0-30% coarse particles (50-300 microns) as percent by weight are the limits of useful proportions. The aluminum blend seems to be responsive to initial spritzel viscosity and the percentage of material the sulfide melt will lose as it burns to become K_2S. Low viscosity of spritzel slag permits a wider range of aluminum blend compositions to be utilized. Larger particles are more useful in mixtures which have a large loss of mass in the spritzel reactions. Other factors such as flake aluminum and coarse charcoal complicate the issue but in general, the longer the delay the larger the fines should be and more tolerant the mix will be of intermediate and coarse particles.

In gerbs, aluminum is subjected to temperatures well above the melting point of the metal. Turbulence in the slag subdivides the molten metal even while it is in the case. As the slag is blown through the vent, more subdivision occurs. It is therefore difficult to achieve much delay in the spritzel. Coarse atomized aluminums are advisable, preferably devoid of fines. Aluminums of larger particle sizes than can be

used in stars are preferred in gerbs.

Magnalium substituted for the coarsest particles of aluminum produces outstanding effects. Blown or atomized magnalium is preferred to the more angular ground product of the same size because of the fluid flow properties. Because magnalium is more volatile and flammable, larger particles can be used.

Photomicrographs of glitter spritzels near spritz range make it obvious that glitter will occur when finely divided aluminum or magnalium is completely covered with molten burning K_2S at a particular sulfate concentration. The most important consideration in any glitter formulation therefore, becomes the creation of spritzels which will consist of aluminum aggregates well covered with sulfide melt. Formulas high in delay materials will produce spritzel melts which lose a great deal of volume as the delay chemicals burn out of the spritzels. It is not unusual for aluminum particles to be found on the surface of the spritzels. As the antimony and sulfur burn out of such spritzels the volume of melt diminishes and the spritzel collapses until the aluminum may jam together to form an outer wall of aluminum drops and potassium sulfate crystals. Such structures often result in spurels of sparks and poor flash size. If fluidity is maintained the entire mass shrinks and collapse is uniform until the aluminum particles accumulate sulfate coatings and jam together the coated aluminum aggregate. Aluminum aggregates that allow this uniform collapse are superior. The percentage of aluminum which can be used in a formula depends therefore on the total spritzel melt volume, its fluid properties and upon the aluminum's ability to pack densely in the collapsing spritzel. This later property is very difficult to measure directly. It can be approximated by a wet vibration packing test. Similar tests are used by the Portland concrete industry to regulate aggregates. A simple version of these tests can be adapted for glitter aluminum testing. The ultimate packing density, the ease of packing and the speed of packing are important. As particles fall through a fluid the surface-to-mass ratios cause sorting of the particles. Coarse particles fall faster than fine particles. Place a carefully weighed amount of aluminum in a test tube that has about four times the aluminum's volume capacity. Fill the tube with water and shake in a uniform manner by inversion. The aluminum should be uniformly distributed. Allow the tube to stand and measure the rate of sedimentation. Measure the final volume of the sedimented aluminum. Next use a vibrator to cause compaction, measure the time necessary to pack the aluminum to its smallest volume. Measure this volume. In general aluminums that settle quickly, vibration pack quickly to form dense (small volume) sediments are best for glitter. Remember, there is no one simple, easy test for glitter aluminum, but this is a good guide.

The aluminum in a spritzel is molten and only retains a resemblance of its original shape. The more violent the forces the liquid aluminum is subjected to, the less important the aggregation properties of the original aluminum are. In hand held sparklers the aluminum particles retain shape very well, also stars that burn slowly and are fired on the ground, change the aluminum very little. Stars moving at high

speed produce spritzels that are violently stirred and the aluminum is torn apart in such spritzels. In gerbs, even large particles are reduced to fine spherical drops by the violence of the fluid flow within the case and by being blown through the nozzle. One interesting proof of this is to load gerbs with chopped aluminum wire and measure the particle size of the aluminum blown out in the spritzels. Aluminum droplets below 5 microns in diameter are often found in gerb spritzels.

For each formula a fixed amount of sulfide melt will result. For each aluminum a maximum quantity of that aluminum in that application will be found. This adjustment of aluminum content to maximum is the most critical factor in creating great glitter effects. No glitter formula should be considered to give the exact best aluminum level. Each formula should be matched with a particular aluminum by experiment. A formula is a guide, understanding is a better guide, and guided experimentation is the best available at this time. By adjusting aluminum levels to optimum performance with a particular formula and aluminum aggregate, and then introducing complex mixing and other techniques, glitter is easily controlled and optimized for the desired effect.

MAGNALIUM

```
TABLE #8:  PHYSICAL PROPERTIES OF MAGNALIUM

MACNALIUM: ALUMINUM, MAGNESIUM ALLOY. 50/50% IS MOST COMMON,
           70/30% IS ALSO AVAILABLE.
BOILING POINT (50/50%): 1150 */- 25·C.
CRYSTAL FORM: CUBIC (?) (50/50).
IGNITES IN AIR AS A DUST CLOUD AT 535·C (50/50%).
```

Magnalium is often substituted for aluminum in glitter mixtures. This alloy is much more reactive than aluminum and is prone to heating up when a glitter mixture is wetted. Magnalium 50/50 boiled in water produces hydrogen, magnesium hydroxide, aluminum metal and some alumina hydrate. Electrolytes such as potassium nitrate speed the reaction. Boric acid is used to block analogous reactions in straight aluminum comps and is best added as a water solution. Boric acid is less effective with magnalium mixes but is helpful. Boric acid esters of dextrin are more effective than the boric acid solution. This matter needs further study.

Magnalium creates large, more brilliant flashes in spritz reactions and is the only way to introduce magnesium into the sulfide melt. Pure magnesium added to glitter mixes will burn in the initial gunpowder reactions and is not available for spritz reactions. When magnalium burns in air, magnesium vapor is oxidized, then in part reduced by the aluminum which reacts more slowly. The reduced magnesium is then oxidized again and the flame duration is typically longer for this reason. The particle size of magnalium is typically larger than most effective aluminums.

48

Most pyrotechnists prefer 50/50 magnalium in mesh range 60-80. Magnalium is cubic (according to manufactor's literature) in crystal structure and easily powdered even by hand in a mortar and pestle. The larger, angular, grains of magnalium have interesting consequences in glitter spritzels. They present less surface per gram of material than fine flake particles and the spritzel loss of magnalium is therefore slower. Very fine magnalium powder often gives flitter-type effects. The low surface-to-mass and therefore low reactivity-to-mass allows the use of higher percentages of metal fuel in the spritzel than is typical for aluminums. Star formulas may contain up to 16% magnalium whereas aluminum is typically 5-12%. The high percentage of large angular particles acts as a barrier to the transport mechanisms in the spritzel and thus contributes to delay. The large angular particles also help produce large spritzel globules. Magnalium seems to perform best in stars containing antimony sulfide and is sometimes problematical in all sulfur delay mixtures in which it may produce flitter effects.

Typically, an all aluminum mix will produce spritzels 0.1 mm to 3 mm in diameter; substituting magnalium produces spritzel diameters of 3 mm to 30 mm. Magnalium stars therefore typically invest their spritzel material in much fewer but larger flashes. Magnalium is seldom used in glitter gerbs because it is lost in onboard reactions with sulfur.

Magnalium is present in glitter spritzels as molten material. Magnesium is lost from the molten magnalium to become magnesium sulfide and then magnesium sulfate. Magnesium salts are known to benefit delay processes and reactions in a fashion analogous to calcium, strontium and barium salts. Magnalium glitter is more effective in producing color effects from sodium and lithium.

Magnalium substituted for the coarsest particles of aluminum produces outstanding effects. Because magnalium is more volatile and flammable, larger particles can be used. Most of the magnaliums used cause very large spritzels by nucleation effects. In the extreme case a star may produce a very few but spectacularly large spritzels. Often these glitter mixes produce flash reactions audible at 1000 feet.

Magnalium is available in narrow mesh range cuts of excellent shape uniformity. Blends of aluminums and magnalium are very versatile and usually permit greater total metal fuel loading, 10% aluminum and 5% or more magnalium are commonly used.

Magnalium is often supplied in very reactive surface condition and is therefore a great hazard. The surface of magnalium, and zinc dust as well, may be made less reactive by dampening the metal and allowing it to dry in shallow trays. Deep or large capacity bowls are not advisable for handling wet magnalium. Heat accumulation has caused fires with many wet reactive metals. For safety, maximize heat loss surface when handling wet magnalium, therefore large shallow trays are advisable.

Magnesium-aluminum alloys with higher aluminum content may soon be available. Alloys such as "AlMg" used at sea for cast ship fittings are likely to be less

hazardous in wet mixtures with nitrates. Such alloys will probably be more stable in storage. Since aluminum particle size and shape are more difficult to produce in uniform assortments, such alloys could well be the only type of metal fuels used in glitter in the future.

BINDERS AND WET REACTIONS

Carbohydrate binders have interesting effects upon glitter formulations and gunpowder-like mixtures. Their effective equivalence as carbon sources is negligible in the small percentages usually used. They furnish hydrogen and/or water to the reacting gases and liquids. Water is found to make large differences in viscosity of volcanic lava and in general in pyrotechnic slags. Often tiny fractions of a percent of water cause dramatic changes in reaction types, rates and viscosity. Water from moisture in a mix or from carbohydrate thermal decomposition suppresses the formation of potassium superoxide and potassium peroxide. Water enhances the formation of sulfides rather than carbonates in glitter mixtures. Water or potassium hydroxide suppresses the formation of potassium oxides in potassium carbonate fusions. Potassium hydroxide fusions do not yield superoxide or peroxide even near the boiling point. Glitter effects are known to be enhanced by atmospheric humidity.

The author has found the carbohydrate binders (e.g. starch, dextrin) superior to phenol formaldehyde resins, maleic and phthalate type resins, polyester, glyptal resins, shellac, vegetable rosins, urea formaldehyde resin and melamine resin in all experiments to date. Dextrins and starches combine good binding properties and low cost with simple handling requirements.

It should be noted that boric acid, often used to control pH of wet mixtures, combines quickly with carbohydrates to form water and ionic esters more strongly ionizing than the original acid. Unless the metals used are pretreated with the boric acid, the mixtures will actually contain boric carbohydrate esters. Boric acid is best added as a solution to mixtures which contain only aluminum as the rnetal fuel.

Lancaster mentioned the reaction in water of nitrate ions and reactive metals to form nitrites. Actual analysis of several batches of stars which had heated up or shown other signs of wet chemical problems revealed that nitrite and ammonia were rarely produced by aluminum and only slightly more frequently produced by magnalium. Mixtures containing both aluminum and magnalium metals produced nitrites more frequently than either metal alone.

Most of the wet reactions observed by the author were simple reactions with water. Water in the presence of electrolytes causes corrosion of aluminum, magnalium, and most active metals. Water used to perform binding and processing is present in the mixtures as saturated solutions of all soluble materials present. Much of the water used in processing glitter mixtures is associated by hydrogen bonding

50

with the carbohydrate binders. The water hydrating the binders has lower solvent effect for potassium nitrate and other ionic salts.

The most important factors in metal corrosion in wet mixes are pH and temperature. High temperature increase the ionic strength of the saturated nitrate etc. brines, and the reactivity of the metal. It is essential that glitter mixtures remain cool from the first additions of water until they are totally dry. Sunlight, infrared heaters, hot air blowers etc. are ill advised. Since glitter mixtures are among the safest mixtures used in fireworks and do not constitute great explosion hazards, most commercial production should be done during winter months. Thoroughly dried stars and compositions should be stored in moisture proof packaging or containers. Careful attention to thorough drying is necessary as any moisture remaining in the articles will cause corrosive loss of active metal fuels.

Sodium bicarbonate evolves water and carbon dioxide very slowly at room temperature. The material slowly accumulates sodium carbonate on the surface of crystals. The resulting sodium carbonate is quite basic and can cause faster corrosion of active metals. Sodium salts of organic acids invariably present in dextrin as fermentation products, are often very hygroscopic and are usually basic in solution; both factors which create drying and storage problems. Sodium oxalate is sometimes supplied with sodium hydrogen oxalate present in large quantities. This material is hygroscopic and of no use in glitter.

Sunlight seems particularly effective in causing the destruction of glitter metals in damp stars. Sun drying of glitter comps is not advisable.

The longer time glitter mixtures are damp, the more likely the aluminum and magnalium are to be damaged. Glitter stars are best made with the minimum amount of water practical and should be dried by induced cool air flow, well protected from heat. If excessive moisture is used, the dextrin binder tends to migrate to the exterior regions of the star. Unless the mixture is to be granulated, the water used for forming the material into stars should be no more than the weight of the charcoal used in the mix. For example: a mixture containing eleven percent charcoal and two kilograms of mix is being prepared; maximum water is approximately 220 ml or 220 grams. Letting the dampened mix stand a few minutes is advisable if dextrin is used for a binder. Dextrin is slow to take up water evenly.

Mg:Al 50:50 Reade -60 mesh
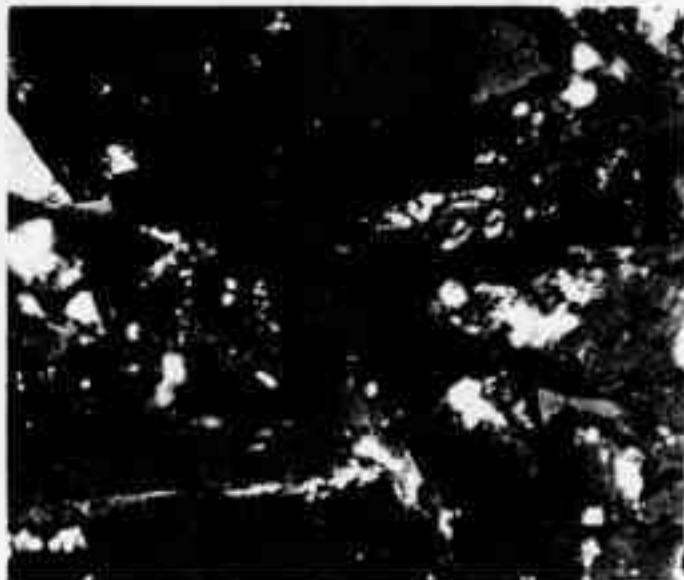
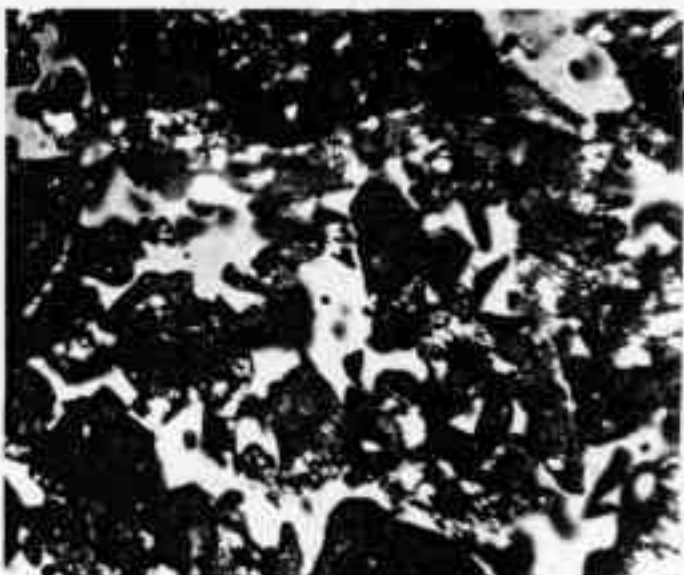Mg:Al 50:50 Reade -20 mesh

Mg:Al 50:50 Reade -22 mesh

Mg:Al 50:50 Reade -32 mesh
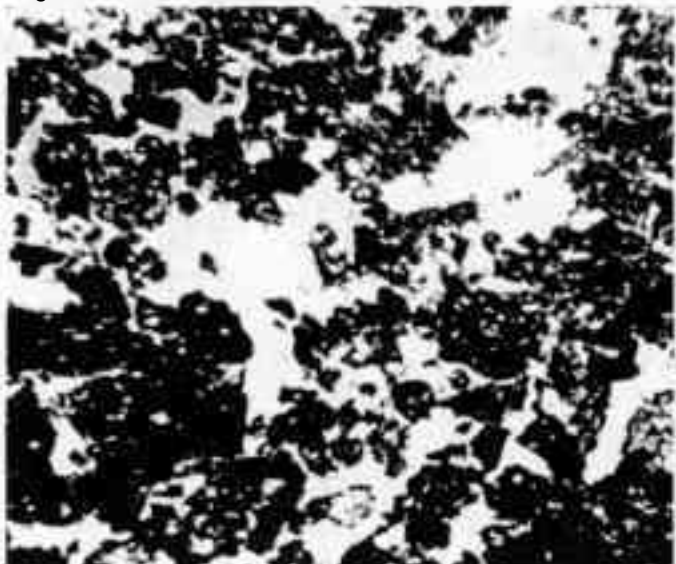
Aluminum; Alcan 2000
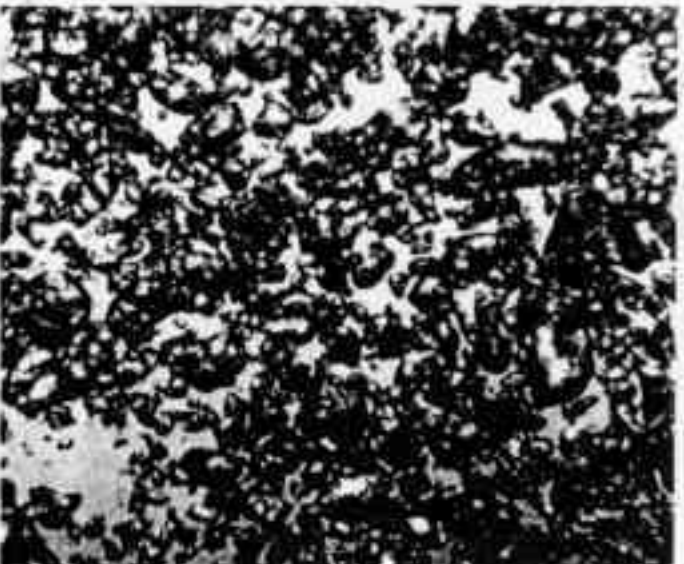
Aluminum; Alcan 101

All photomicrographs on this page - 1mm = 5 microns

Aluminum; Reynolds 4-301
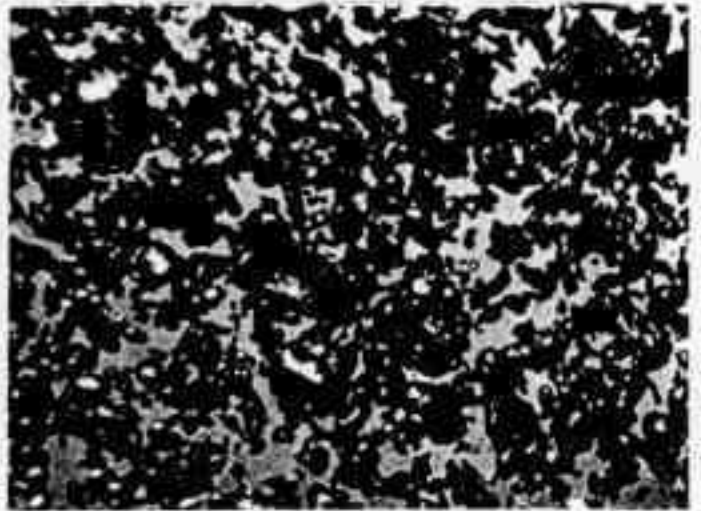
Aluminum; Reynolds 200 atomized
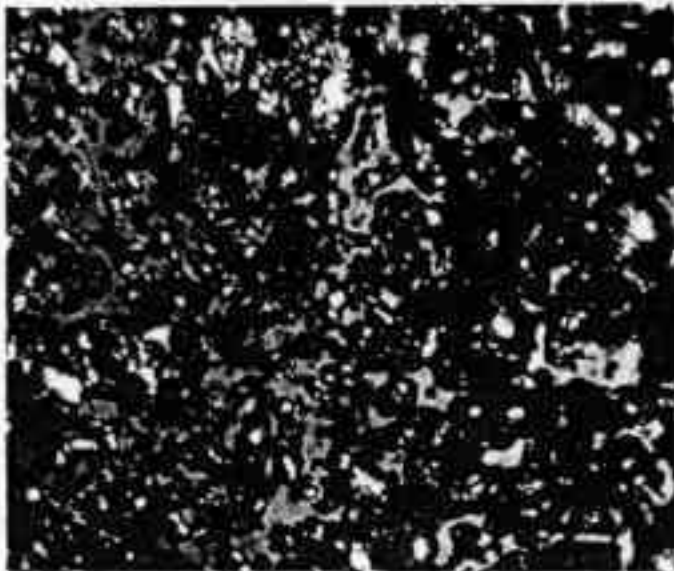
Aluminum; Alcoa 120
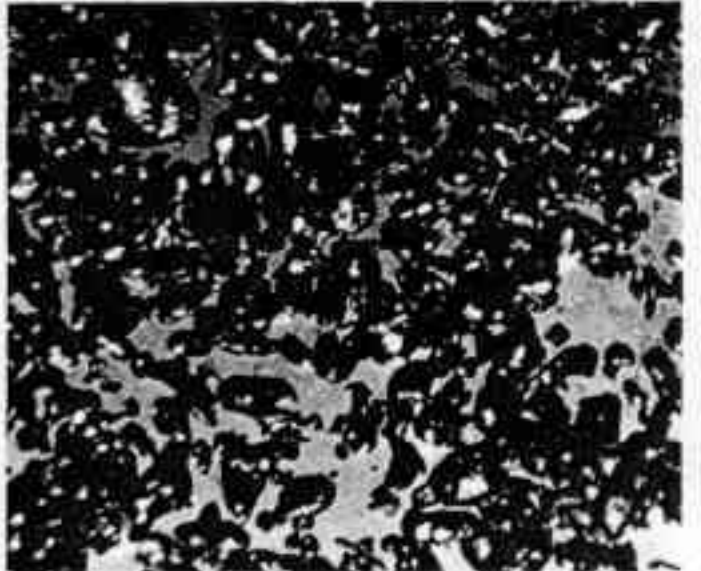
Aluminum; Alcoa 123
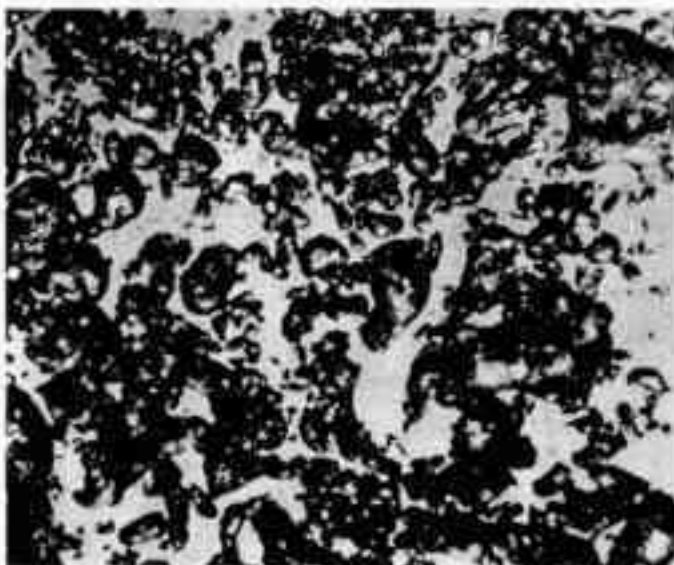
Aluminum; Reynolds 120
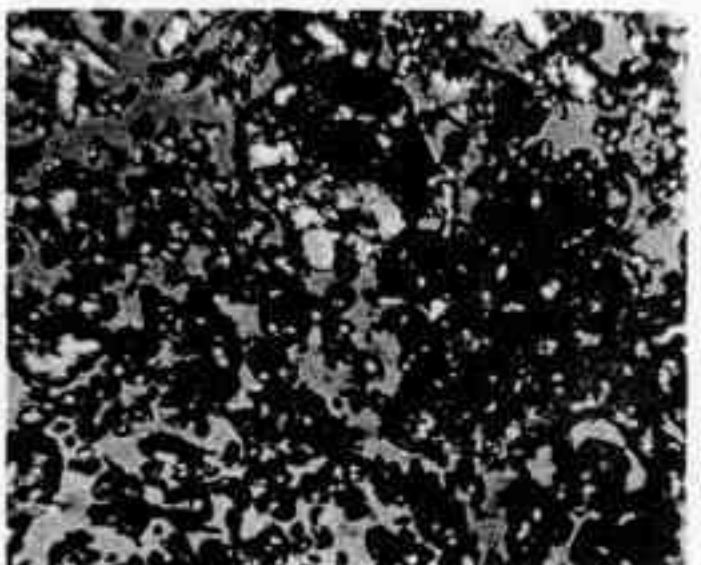
Aluminum; Reynolds 40 atomized

All photomicrographs on this page - 1 mm = 5 microns

Aluminum: Alcoa 101. This product is useful as a source of very large particles when blending aluminums. The first photomicrograph of this aluminum shows the many fines which are too small and too irregular. This aluminum gives poor spritz in most mixes if used alone. (1mm = 5 microns)

Aluminum: Kosanke Services "12 micron". Excellent in short delay; good fines source in blends.
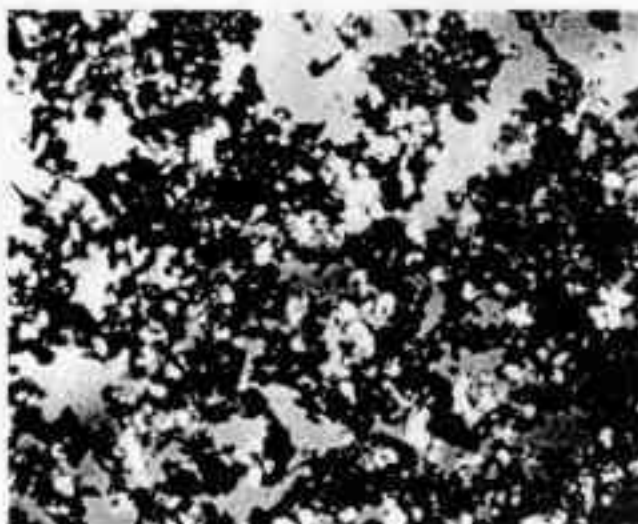
Aluminum: Reynolds 30XD. Best of the "Brights".
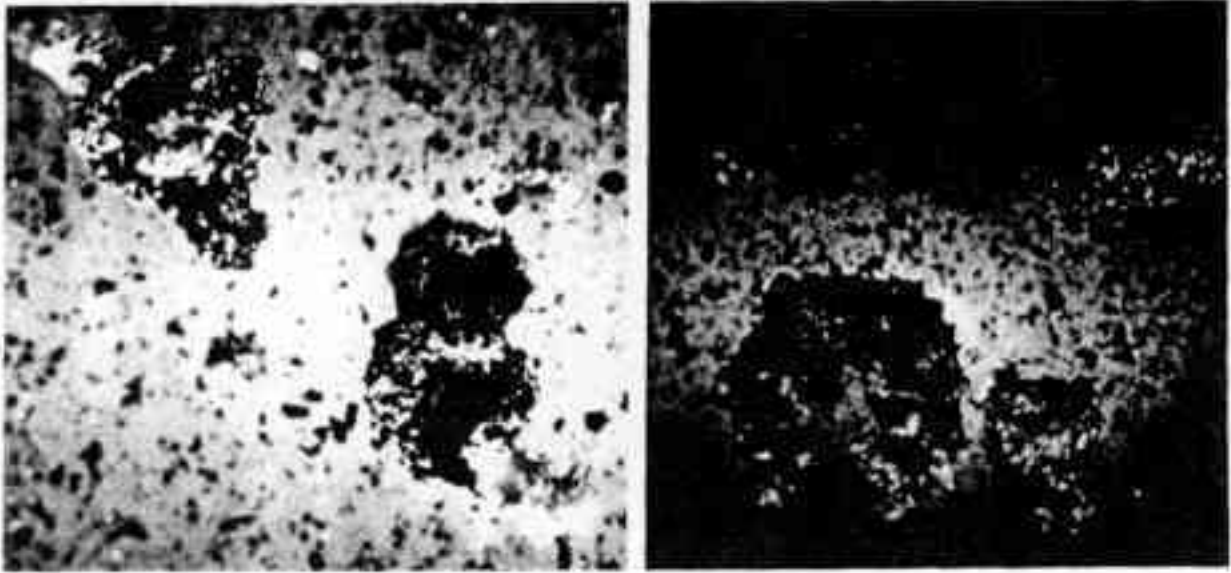
Photomicrographs of spritzels in early formation stages. Note the formation of a spheroidal shell of aluminum aggregate. These spritzels were producing very short spurets. (1 mm = 20 microns)
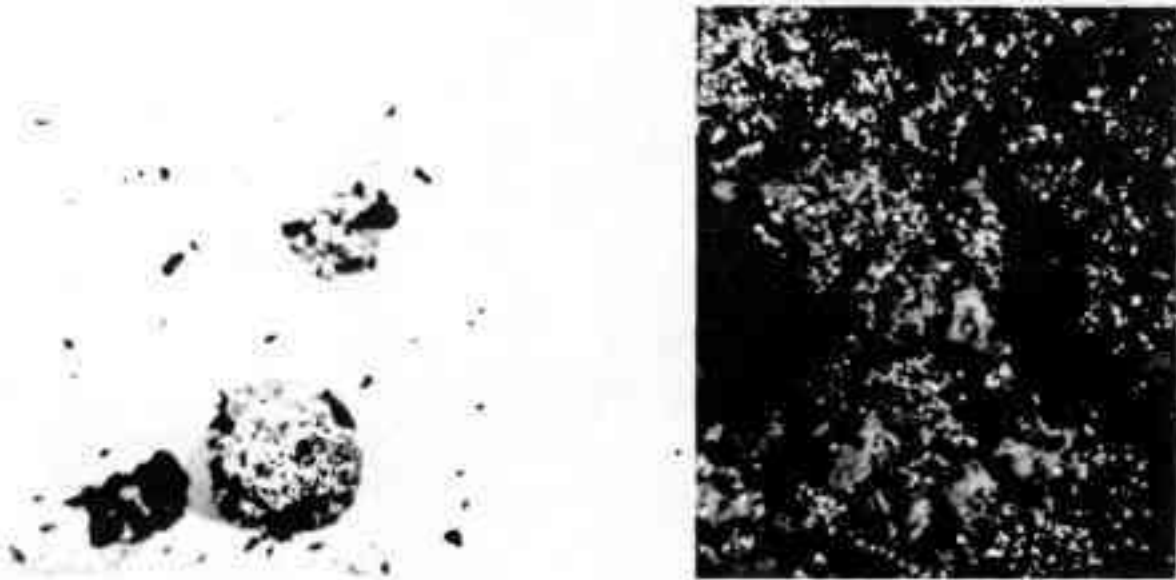
Spritzels of antimony trisulfide compositions. The dark area around the spritzel is splatter indicating a low viscosity fluid. The photomicrograph at the right is literally flowing off the aluminum (1mm = 20 microns)

Illustration of photomicrographic technique to render a material nearly transparent. The almost invisible crystals in the center are potassium sulfate; the other crystals are potassium carbonate. The two photomicrographs to the right are spritzels with (upper) and without (lower) the benefit of this technique. The potassium sulfate can be seen covering the aluminum in the lower photograph. The upper photograph shows the aluminum covered with potassium sulfate but the coating is now invisible. (1mm = 20 microns)

Left: Spritzels with antimony trisulfide halo, trapped at one-half spritz range. The antimony compounds in the spritzel are light in color. (1mm = 20 microns)

Right: Spritzels with sulfur halo from potassium disulfide and aluminum composition. Spritzels were trapped at one-quarter spritz range. (1mm = 20 microns)

This is a very lucky shot. More than 300 slides and nearly that many photomicrographs were made for this study. Here are two spritzels in the spritz stage. The spritzel to the left has nearly finished exploding; note the spherical particles of burning aluminum that were trapped as they were moving away from the exploding mass. The spritzel on the right has melted down prior to exploding as the aluminum begins to react and the explosion has begun. Notice the aluminum particles leaving at the lower right edge. (1 mm = 20 microns)

Antimony metal dendrites frozen from the gases of the "BaS*(Sb)" mix given in the Cheat Sheet. Sublimed from a gerb flame. (1 mm = 20 microns)

Equation Two (left)

Equation One (below)
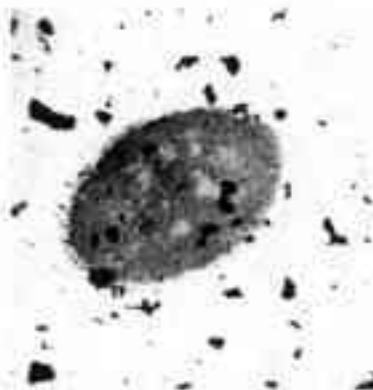
Trapped spritzels or sparks from Equation Two (Sienko Hanabi) and Equation One mix. Notice that the Equation Two mix residues have charcoal submerged in the melt. The Equation One mix residues are sometimes blue. The transient blue which fades out in seconds is probably due to traces of the trisulfide ion. The more persistent blue is due to fine carbon particles. Note the charcoal on the surface of the Equation One spritzel, and that there is no carbon below the surface of the melt. (1mm = 20 microns)

Spritzel of antimony trisulfide.
(1mm = 20 microns)
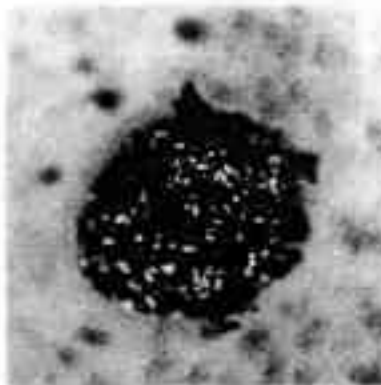
Spritzel of "all sulfur" delay.
(1mm = 20 microns)

In the photomicrographs above, the layer of potassium sulfate has been rendered transparent to allow observation of the aluminum aggregates and their structure.

PART II

Maximizing the Effect

Now that most of the important details have been covered regarding the ingredients, we will proceed to discuss the important physical-chemical alterations which may be made in the mixes themselves to control and maximize the effects of the stars. Any one formula, if it is reasonably in the range of the proper stoichiometry with respect to the equations given, can be made to produce a variety of effects. As an example we can use the formula I call Streaker. This is in some of its modifications the glitter formula which requires priming for use in hard breaking shells and is the formula normally used for producing streaks of glitter spritzels of long delay twinkler effects in the author's shells.

Streaker:	Potassium nitrate	41%
	Barium nitrate	16%
	Sulfur	9%
	Antimony sulfide	8%
	Aluminum	13%
	Charcoal	13%

Dextrin or starch binder is normally used and the aluminum is often #120, supplied by Service Chemical Inc. of Pennsylvania.

EFFECTS OF CHARCOAL

The effects may be varied. An effect similar to the pearl mix, small spritzels and very numerous with spritz occurring approximately 18 inches from the stars burning surface, is achieved by ball mixing of the ingredients before adding the aluminum, and using a very fast reacting charcoal such as willow. By using commercial air float charcoal and ball milling as above, a similar effect is achieved with larger spritzels and fewer producing slightly greater delay, but again nearly uniform delay. These effects are simply explained. Uniform mixing produces stars of nearly homogenous burning rate, and spritzels which are nearly identical in their chemical constitution, so that the spritzel chemistry of delay is nearly identical from one spritz to another. The willow charcoal is made from a wood, the fibers of which are nearly identical throughout and have no concentrations of pitch, tannins, or lignins to produce disconformity in the charcoal. The burning rate is high so the gas velocity of the onboard combustion products is high. The spritzels are blown off the surface of the star while quite small. The great uniformity of the star mix produces spritzels of uniform size.

The commercial air float contains charcoal made from wood with a variety of cell wall thickness and therefore the fragments of charcoal are of various thickness, and the thick particles react more slowly. Additionally, the pitch and mineral of the wood varies from spring to summer growth and creates larger differences in burning rate. When this charcoal is ball milled, the thinner spring wood cells break up more readily and a wider range of particle sizes for the charcoal results. Spruce or Fir charcoal would be predicted to give intermediate results, more closely resembling the willow. This has been substantiated experimentally.

The main reason the spritzels show variations in delay is simply the fact that they leave the star at different drop sizes. The variation in charcoal particle sizes results in the spritzels being of different sizes. Large droplets are found to form around the nucleations triggers of large charcoal particles. The larger particles act like nails or pins holding the droplets anchored to the star surface. Experimentally, one can easily test this by making a small amount of bamboo slivers or even toothpicks into charcoal and pumping a ballmilled glitter mix with these long fibers of charcoal mixed with it. If fiber orientation is carefully constrained, stars can be made which on burning, dross up on two sides and not as much on the others. A single fiber through the axis of a cylindrical star makes an interesting experiment. Naturally both of these stars produce an appearance like a snow ball of white fire or a large pearl, when fired from comet tubes or shells.

The next experiment would, logically, be to ball mill all of the ingredients except the aluminum and charcoal. Using air float charcoal and 80 mesh charcoal, we observe a steady progression of the expected changes in effect. Larger differences in spritzel diameter cause larger differences in exposed surface-to-mass to be air oxidized. This larger time difference before the spritz explosive can be formed causes larger differences in delay. Now when the stars are shot from the comet tubes, the long tail associated with the glitter (called tremolante) begins to form with the air float charcoal and is more fully developed with the 80 mesh and below charcoal. Naturally, there is a point of diminishing returns for the trick of using more widely varied charcoal particle size. At eight mesh, the glitter of most mixings is destroyed. 16 to 20 mesh and below are used for twinklers (very long tailed glitter effects).

ADDING FLAKE ALUMINUMS

At this point we can explain a trick used by glitter experts like Bill Withrow and Jerry Taylor. Charcoal is not the only material which can retard spritzel separation from the stars and create nucleation effects for larger spritzel formation. Small quantities of selected large flake aluminum do a better job when spritzels are desired to produce very long delays. Naturally, too much of these aluminums can cause the entire star to become one giant spritzel that never makes a spritz reaction. Best results are obtained in stars where these flakes, if rotated about their centers, would

define a mass of many nearly touching spheres. These spheres are approximately the size of each spritzel which the flakes nucleate. The aluminum flakes are ignited and blasted apart when the spritzel fires, if the composition is otherwise well adjusted.

BASE MIX

These are the principal means used to regulate uniformly mixed glitter stars to create a variety of effects. The theory can predict a further improvement. The chemicals which cause delay reactions can be added in a nonuniform manner to a base mix before it is pumped into stars. Logically, this is best done with a mixture which is sure to produce a spritzel of potassium disulfide. The mixture should contain the aluminum (atomized is best) and whatever other chemicals are to be added to produce the main effect (such as sodium oxalate for yellow) and preferably a little antimony sulfide. These ingredients should be uniformly mixed. Now add to the mixture extra sulfur and/or extra antimony sulfide, and perhaps best at this point, the large flakes of aluminum, fancy charcoal granules etc. This produces a star of variable formula, all of which will glitter and portions of which will have outstandingly long delays. An example is the formula for snowball glitter Weingart gives as a sparkler mix, listing it as a steel sparkler when in fact it contains no steel. It is a long time favorite for glitter stars. The formula in percentages is:

Potassium nitrate	38%
Barium nitrate	18%
Sulfur	10%
Charcoal	9%
Antimony trisulfide	9%
Aluminum	7%
Dextrin	7%

Mix the potassium nitrate and barium nitrate with the stoichiometric amounts of the sulfur and charcoal. Add the aluminum and dextrin. This becomes the base fire.

The stoichiometric amounts for the potassium nitrate may be calculated from the equations. The formulas are easily calculated as a weight formula. For Equation Two we had formula:

Potassium nitrate	67%
Charcoal	12%
Sulfur	21%

This snowball formula has 38% potassium nitrate. To calculate the percentage of charcoal and sulfur required for this percentage:

$$38/67 = 0.567$$

Charcoal: $0.567 \times 12\% = 6.8\%$

Sulfur : $0.567 \times 21\% = 11.9\%$

Since we had only 10% sulfur to begin with, we must use some of the sulfur equivalence in the antimony sulfide. One mole of Sb_2S_3 contains 243.5 grams antimony and 96.192 grams sulfur. (The formula weight of Sb_2S3 is 339.692). $39.692/96.192 = 3.53$, so each percent sulfur that we need will require 3.53% Sb_2S_3 to replace it. We need 1.9% sulfur, so we can substitute approximately 6.7% of antimony sulfide. This leaves only 2.3% antimony to go.

For the reaction of barium nitrate:

$$Ba(NO_3)_2 + 3C + S \longrightarrow BaS + N_2 + 3CO_2$$
$$261.35 \quad 36 \quad 32$$
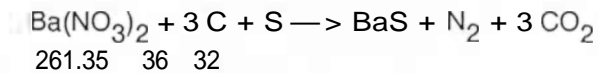
$261.35 \times 100\% / 329.35 = 79.9\%$ or about 79% Barium nitrate

$36 / 329.35 = 10.9\%$ or about 11% Carbon

$32 / 329.35 = 9.7\%$ or about 10% Sulfur

Barium nitrate is 18% of the formula, so we have:

$$18 / 79 = 0.2278.$$

Charcoal: $0.2278 \times 11 = 2.5\%$

Sulfur: $0.2278 \times 10 = 2.3\%$ (Just enough!)

This formula can be improved! Remember that the disulfides are not absolutely necessary for the full equivalence of the metal ions, but delay is increased if they are equivalent. Bob Cardwell gave me an improved formula which Mike Beyer, a PGI man of years gone by, laboriously worked out by empirical trial and error.

Improved Snowball:

Potassium nitrate	35%
Barium nitrate	16%
Sulfur	9%
Antimony sulfide	13%
Charcoal	9%
Aluminum	10%
Dextrin	8%

62

The calculations for the improved formula: potassium nitrate 35% is a disulfide mix 35 / 67 = 0.5223. Sulfur --- x 18 = 4.0; charcoal --- x 10 = 2.2. Total charcoal required is 8.5%. The 9% in the formula is ideal as it allows for ash and water content. Total sulfur requirement is 14.9%, since the formula only has 9 and some of the sulfur in the antimony sulfide must be used to satisfy this. 5.9% x 3.53 = 20%. The formula is short of total disulfide character by 7% antimony or about 2% sulfur, and that is close enough! Remember, the formula was arrived at empirically. Dropping the dextrin to 5% and adding 2% sulfur does improve the formula very slightly.

Now we calculate the base fires as monosulfides.

Potassium nitrate	35%
Barium nitrate	16%
Sulfur	11%
Charcoal	9%
Antimony trisulfide	13%
Aluminum	10%
Dextrin	5%

35/75 = .4666 S, 12% x .4666 = 5.6%   C, 13% x .4666 = 6%

16/79 = .2025 S, 10% x .2025 = 2.0%   C, 11% x .2025 = 2.2%

Total S 7.6%   Total C 8.2%

The formula now contains:

$Ba(NO_3)_2$	16	KNO_3	35
KNO_3	35	$Ba(NO_3)_2$	16
S	7.6	S	11
C	8.2	C	9
Al	10	Al	10
Dextrin	10	Dextrin	5
		Sb_2S_3	5

If we simply use for the base fire, the Al will be protected from oxidation onboard the star.

Also the overall mixing will be almost complete. After wetting down the mix the remaining antimony sulfide is added with moderate mixing, so that it will be marbled throughout the finished stars. In effect, we will have spritzels from a range of formulas in one star, some of these spritzels having very long delay from high an-

timony content. The effect is a tremolante or with the proper techniques given before, the effect can be a twinkler.

OTHER MIXING TECHNIQUES

Other complex mixing techniques which come from an understanding of the chemistry of glitter mechanisms and which are found to produce the predicted effects, derive from techniques I call ricing or granulating. These techniques are used with at least two different mixtures. One is formed into grains by pressing dampened mixture in a putty-like mass through seives of sizes 20 mesh through 4 mesh, and the resulting grains either allowed to dry or blended damp with a second mixture. The second mixture may be applied dry (tumbled with the still damp first mixture so as to coat the grains) or dampened and added to dried grains of the first mixture. By using another technique of the same type, large grains of both mixtures are blended while both are damp, and the entire mass pumped into stars. This later technique can be used to produce a novel effect where very short delay spritzels burn near the star, and intermediate delay very uniform spritzels burn a short distance behind the star. The effect can be a dumbbell-like shape of spritz flash zones, or may be regulated to give a pearl headed twinkler effect. Outstanding tremolante effects can be similarly achieved using three granulated mixtures. It is difficult to produce glitter that gives a clear separation of sodium yellow and white flashes, but interesting effects which have many intermediate intensities of yellow coloration are simply accomplished. Pink effects from lithium oxalate require very low sodium content ingredients, but are outstanding if used with whites of barium nitrate mixtures in shells.

These latter techniques are especially useful for large comets where having one-half the usually required water present aids in drying, and therefore limits wet destruction of the metals. This is very useful with magnalium.

Glitter crossettes and exploding comets are difficult to regulate and almost impossible to make outstanding without the above techniques. The greatest problem with these is the achievement of a well controlled spread at speeds suitable for the mixture. When one mix is first coated by tumbling onto another and this is mixed with damp granules of the third, it can be very useful for crossettes. The third mixture is naturally chosen for its ignition properties.

Outstanding glitter gerbs are easily achieved by ramming hard grains of comps of long delay, with loose or soft grains of a second mixture chosen for its speed and fluidity. Also, three formula gerbs can be very beautiful. The author has used such gerbs designed as strong drivers, with good results for several years, on wheels and other sets.

These techniques can obviously be combined with the previously mentioned marbling with delay reagents, meal powder marbling and the flake aluminum technique to build very complex structures of pyrotechnic utility.

64

One other technique is to simply make two formulas of differing effects, and pump them into stars with a special star pump which has a ram setting for half filling the total cavity, filling with one composition to half the full cavity, resetting the ram and filling the remainder of the cavity with the second composition. I call this type of star pump a stepped star pump. They are easily made from a standard star pump by cutting a step in the depth pin groove of the cylinder.

Except for this last technique, all of the complex mixing techniques given here can be thought of as tests for the glitter theory given here. In fact most of them were conceived by the author for that purpose. For instance, granules of a fast burning short delay pearl type mix, if embedded in a slow drossy long delay mix, should produce an intermediate effect of no special interest. Conversely, if granules of a slow mix are embedded in the fast mix, a pearl followed by a long tall might be expected. Actual tests reveal that the stars burn rather uniformly in both cases and a great deal of dross mixing occurs onboard the star. However, a clear difference in the two arrangements can be seen.

DESIGNING THE EFFECTS

Starting with an understanding of the causes, we can now design the effects. The greatest problem in formulation is to produce the most spritz fire in a pleasing pattern. The aluminum and magnesium content, furnish the fuel for the bright flashes, so it is obvious that formulas which contain the highest total percentages of these fuels produce the best effects for shell stars which will be used at great distance from the audience. Formulas which have around seven or eight percent aluminum are best reserved for small devices.

Viscosity of spritzel fluids cannot be measured by the traditional techniques of physical chemistry. Forensic scientists use blood splatter patterns to assess speed and direction of blood droplets impacting surfaces at the scene of a crime. By studying the splatter patterns of spritzels impacting surfaces at constant angle of incidence and at as nearly matching velocities as possible, some assessment of melt viscosity and surface tension may be made. High viscosity fluids do not splatter as thinly as low viscosity fluids, so thickness and spread of drops at matching velocity of impact will reveal viscosity differences. High surface tension fluids tend to splatter more like mercury than water. Microscopic examination of spritzels will yield semiquantitative surface tension comparisons. Low surface tension droplets have protruding particles and more distorted shapes. Firing a standard size star a set distance above a smooth concrete surface is a simple adequate technique. Supplemental measurements of splatters made on pine boards held at forty-five degrees to the vertical are useful for assessing differences in surface tension. Measurements of splatter will generate data for comparative studies. It is useful to compare mixtures that have no metal fuels with those which contain metal fuels, to observe the apparent change in viscosity.

STUDYING PAST ART

Before attempting to formulate glitter mixtures, an examination of the formulas published in the past is advisable. It is interesting to observe the evolution of such formulas from the mixtures of mealpowder and aluminum with antimony trisulfide to the large array of chemicals in use today. In the tables which follow, the published formulas are grouped by chemical similarities. Formulas which contain the fewest chemicals are considered first, and others in order of increasing complexity. Formulas which contain positive ion sources other than potassium nitrate are calculated to bring the total positive ion equivalence to two equivalents, so as to simplify the comparison with Equation One and Equation Two stoichiometry. Note that where oxalates are used, charcoal equivalence may be dropped and the reduction of the remaining nitrate is all that will be required. Recall that oxalates are carbon monoxide sources and this carbon monoxide is available for nitrate reduction. In the tables, antimony sulfide is calculated as equivalence per sulfide unit, thus its effective molecular weight is one third the formula weight of 339.72 g/mole.

Each formula is assigned a code number to identify it in the tables.

001: Weingart's gold twinkler
002: Degn's #10 twinkler
003: Weingart's white flitter
004: Degn's gold glitter
005: Lancaster's yellow
006: Weingart's second gold twinkler
007: Izzo's #1
008: de Francesco Blanco tremolante
009: Davis's splitter
010: Degn's #16
011: Degn's silver glitter
012: Lancaster's "cheap" white
013: Lancaster's white
014: Weingart's silver comet #1
015: Izzo's #2
016: Degn's #11

All of the formulas Robert Winokur published were previously calculated and tabulated by the author for use in a seminar, and appear in separate tables for that reason. These empirically derived formulas are of varying degrees of excellence in effect. They furnish a large data field of functional formulations. Since the data were derived empirically for each formula, it is probable that a much larger range of for-

66

TABLE #9: WHITE FORMULAS WITH POTASSIUM NITRATE ONLY					
	007	008	014	015	016
POTASSIUM NITRATE	2.00	2.00	2.00	2.00	2.00
SULFUR	0.86	0.84	0.84	0.84	0.84
ANTIMONY TRISULFIDE	0.53	0/64	0.54	0.29	0.28
TOTAL SULFUR	1.39	1.48	1.38	1.13	1.12
CHARCOAL	3.37	3.59	3.36	3.37	3.37
ALUMINUM	0.69	1.06	0.91	1.23	1.19

TABLE #10: WHITE GLITTER FORMULAS CONTAINING POSITIVE ION SOURCES OTHER THAN POTASSIUM NITRATE					
	009	010	011	012	013
POTASSIUM NITRATE	1.47	1.44	1.69	1.80	1.69
BARIUM NITRATE	0.53	0.56	-----	-----	-----
STRONTIUM OXALATE	-----	-----	0.31	-----	0.31
BARIUM CARBONATE	-----	-----	-----	0.12	-----
SULFUR	1.15	1.14	0.86	1.25	0.71
ANTIMONY TRISULFIDE	0.32	0.32	0.15	0.66	0.43
TOTAL SULFUR	1.47	1.46	1.01	1.91	1.14
CHARCOAL	3.08	3.03	2.29	2.38	2.84
ALUMINUM	0.76	0.67	1.28	1.16	1.02

TABLE #11: YELLOW OR GOLD SODIUM SPECTRA GLITTER FORMULAS				
	001	004	005	006
POTASSIUM NITRATE	1.65	1.56	1.55	1.50
SODIUM OXALATE	0.35	0.44	0.45	0.50
SULFUR	0.69	0.74	0.65	0.63
ANTIMONY TRISULFIDE	0.82	0.13	0.21	0.22
TOTAL SULFUR	1.51	0.87	0.86	0.85
CHARCOAL	2.78	2.23	2.62	2.53
ALUMINUM	0.82	0.77	0.78	0.93

mulas were tested and found wanting. This larger field of data is lost but the fact that it existed is significant and enhances the validity of conclusions drawn from the data published. If it can be shown that the published known functional formulas make a chemically logical pattern, then the theory given here and the arguments made here are valid enough to be called a theory rather than a hypothesis. We are looking for patterns in the formulas, rules for formulating glitter mixtures. It is expected that the formulas are sufficient in number to represent the boundaries of the possible formulations. We know that the formulas can be shown to be a near continuum of effect variations. The minimal necessities of chemical results for the production of glitter are sought. We expect to find the adjustments of formulas for the differing natures of the charcoal and a frequent adjustment for the fact that charcoal is not pure carbon. We expect to see sulfur in a continuum of concentrations with a definable lower limit and a range that exceeds the stoichiometric requirements for potassium disulfide type ratios, especially the all sulfur delay formulas should show great variation and high equivalence. The antimony sulfide equivalence should show the greatest variation of all the chemicals used for the reasons already given.

Naturally, the formulas which are based on meal powder are first calculated as the amount of the meal powder ingredients the meal powder represents, and then the chemical equivalence of the formulas are calculated. The formulas below are calculated as equivalence of materials present disregarding binders, and setting the positive ion equivalence to two.

FIELD #1: SUBFIELD A						
ALL NITRATE PRESENT AS KNO_3. ALL AMOUNTS ARE IN MOLES.						
	#06	#17	#18	#26*	AVER.	STD.DEV.
KNO_3	2.00	2.00	2.00	2.00	2.00	----
C	4.15	4.66	3.37	3.24	3.86	0.67
S	1.08	1.21	1.89	2.55	1.68	0.68
SB_2S_3	0.18	0.20	0.08	----	0.12	0.09
TOTAL S	1.62	1.62	2.06	2.55	1.96	0.44
					-	----
AL	0.65	----		0.87	---	
MGAL		2.01	2.05			
TOTAL AL & MG	0.65	2.01	2.05	0.87	1.40	0.74

Thus far into our comparison we see that it takes approximately three moles to reduce two moles of nitrate, and if oxalates are used as substitutes for the nitrates it takes correspondingly less charcoal to perform the transition to sulfide melt. Look at the total sulfur. In no instance does it fall below the amount necessary for Equation One stoichiometry. Notice that our empiricists have found that half way to Equation Two from Equation One is a nice zone of compromise between longer delay and forming enough potassium sulfide to use plenty of aluminum. Notice that the aluminum equivalence is very erratic. Aluminum is the least controllable variable. In the early days of glitter, the flake types of aluminum predominated and the equivalence of aluminum used had to be smaller for reasons already discussed. Remember that the spritz reactions derive their energy for light production from the aluminum fuel. The older formulas intended to be used with flake aluminums can be made more effective by using atomized aluminums at maximum effective loading levels. We can now see that formulas are only a guide - a starting place - and the production of the best glitter will depend upon knowledgeable adjustments.

FIELD #1: SUBFIELD B					
ALL NITRATE PRESENT AS KNO_3. CONTAINS SrC_2O_4 OR $SrCO_3$. ALL AMOUNTS ARE IN MOLES.					
	#03	#04	#12	AVER.	STD. DEV.
KNO_3	2.00	2.00	2.00	2.00	----
C	2.69	2.69	3.37	2.92	0.39
S	1.14	1.14	0.92	1.07	0.13
Sb_2S_3	0.12	0.12	0.05	0.10	0.04
TOTAL S	1.38	1.38	1.02	1.26	0.21
AL	----		1.91	----	----
MgAl	1.89	1.89	----	----	----
TOTAL AL & Mg	1.89	1.89	1.91	1.90	0.01
SrC_2O_4		0.14			
$SrCO_3$	0.16	----	0.07		

SPECIAL COMPARISONS					
ALL AMOUNTS ARE IN MOLES. AVERAGE AND STANDARD DEVIATION ARE CALCULATED ONLY ON FORMULA WHICH CONTAIN THAT COMPOUND.					
	HIGH	Low	# OF FORMULAS	AVER.	STD. DEV.
TOTAL NO_3-	2.00	2.00	39	2.00	
KNO_3	2.00	1.38	39		

FIELD #1: SUBFIELD C

ALL NITRATE PRESENT AS KNO_3. CONTAINS $NaHCO_3$.

	#13	#14	#15	#16	#19	#20	AVER	STD.DEV.
KNO_3	2.00	2.00	2.00	2.00	2.00	2.00	2.00	----
C	3.03	3.36	3.16	3.86	3.36	3.51	3.38	0.29
S	1.14	1.39	1.18	1.18	2.52	2.23	1.61	0.61
SB_2S_3	0.12	0.06	0.12	0.11	----	----	0.07	0.06
TOTAL S	1.50	1.57	1.54	1.51	2.52*	2.23*	1.81	0.45
AL	1.12	1.50	1.09	1.09	0.75	0.94	1.08	0.25
MG	0.25	0.33	1.21	1.04	0.83	1.04	0.78	0.40
TTL AL & MG	1.37	1.83	2.30	2.13	1.58	1.98	1.86	0.35
$NaHCO_3$	0.43	0.24	0.35	0.35	0.29	0.25	0.32	0.07

*NOTICE THAT WHEN THERE IS NO SB2S3 THAT THE TOTAL S IS HIGHER.

FIELD #1: SUBFIELD D

ALL NITRATE PRESENT AS KNO_3. CONTAINS $NaHCO_3$. DOES NOT CONTAIN MAGNALIUM.
ALL AMOUNTS ARE IN MOLES.

	#21	#22	#23	#27	#28	#29	#30	AVER.	STD.DEV.
KNO_3	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	----
C	3.23	3.37	3.37	3.03	3.03	3.37	3.03	3.20	0.17
S	1.82	2.27	2.52	1.14	1.14	1.89	1.14	1.70	0.58
SB_2S_3	0.07	0.05	----	0.12	0.12	0.18	0.12	0.09	0.06
TOTAL S	2.03	2.42	2.52	1.50	1.50	2.43	1.50	1.99	0.48
AL	0.87	1.20	1.20	1.35	1.35	1.20	1.20	1.20	0.16
$NaHCO_3$	0.28	0.29	0.39	0.43	0.43	0.34	0.29	0.35	0.07

FIELD #3: SPECIAL CASE

#24 IS A POOR GLITTER AND CONTAINS NACL.
#39 USES ONLY SB_2S_3 FOR S. ALL AMOUNTS ARE IN MOLES.

	#24	#39
KNO_3	2.00	2.00
C	3.24	3.96
S	2.55	----
SB_2S_3	----	0.14
TOTAL S	2.55	0.42
AL	0.87	1.18
NACL	0.40	----
$BaCO_3$	----	0.13

FIELD #2: SUBFIELD A							
MIXED NITRATES. NITRATES PRESENT AS KNO_3 AND $Ba(NO_3)_2$.							
ALL AMOUNTS ARE IN MOLES.							

	#31	#38	#33	#32	#37	#08	#35	#36
TOTAL NO_3-	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
KNO_3	1.71	1.58	1.60	1.53	1.55	1.52	1.48	1.50
$Ba(NO_3)_2$	0.15	0.20	0.19	0.22	0.21	0.24	0.26	0.24
C	3.20	4.00	3.14	3.40	3.27	3.47	3.47	3.33
S	1.20	1.50	1.18	1.66	1.35	1.95	1.69	1.25
Sb_2S_3	----	----	----	----	----	----	----	----
TOTAL S	1.20	1.50	1.18	1.66	1.35	1.95	1.69	1.25
AL	1.71	1.78	1.82	1.82	1.74	----	1.85	1.78
MgAl	----	----	----	----	----	2.11	----	----
TOTAL AL & MG	1.71	1.78	1.82	1.82	1.74	2.11	1.85	1.78
Fe_2O_3	0.10	0.18	0.17	0.20	0.17	0.16	0.21	0.25
TOTAL FE, AL,MG	1.91	2.14	2.16	2.22	2.08	2.43	2.27	2.28
$BaCO_3$	0.10	----	----	----	0.50	----	----	----
$SrCO_3$	----	----	----	----	----	----	----	----
$Na_2C_2O_4$	----	----	----	----	----	----	----	----

	#34	#07	#09	#10	# 11	AVER	STD.DEV.
TOTAL NO_3-	2.00	2.00	2.00	2.00	2.00	2.00	----
KNO_3	1.52	1.38	1.38	1.38	1.44	1.51	0.10
$Ba(NO_3)_2$	0.24	0.31	0.31	0.31	0.28	0.24	0.05
C	3.84	3.33	3.33	3.33	3.03	3.40	0.27
S	1.20	1.75	1.25	2.12	1.13	1.48	0.33
Sb_2S_3	----	----	0.11	----	----	----	----
TOTAL S	1.20	1.75	1.58	----	1.13	1.50	0.32
AL	1.71	1.33	----	2.08	1.89	1.50	0.69
MgAl	----	----	1.87	----	----	----	----
TOTAL AL & MG	1.71	1.33	1.87	2.08	1.89	1.81	0.19
Fe_2O_3	----	----	----	----	0.02	----	----
TOTAL AL, FE,MG	1.71	1.33	1.87	2.08	1.95	2.03	----
$BaCO_3$	----	----	----	----	----	----	——
$Na_2C_2O_4$	----	0.29	----	----	----	----	----
$SrCO_3$	----	----	----	0.03	----	----	----

Plotting a few interesting factors as bar graphs will make some of the relationships more obvious.
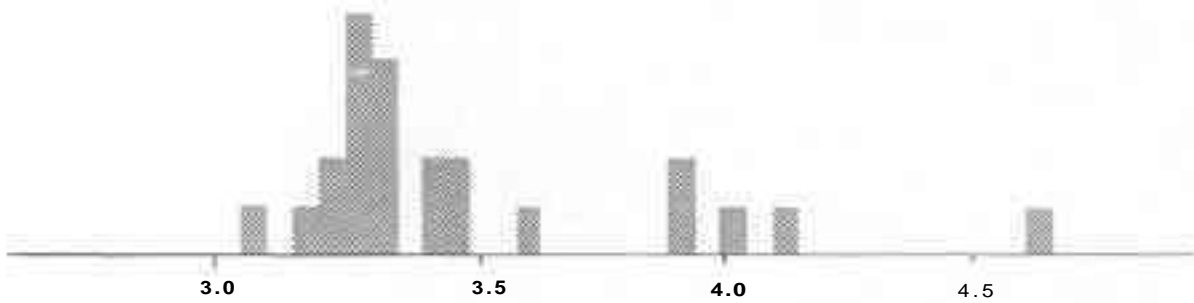
As indicated in Equation One and Equation Two, three equivalents are required, and since the charcoal is not pure carbon a little extra is needed, about ten percent.
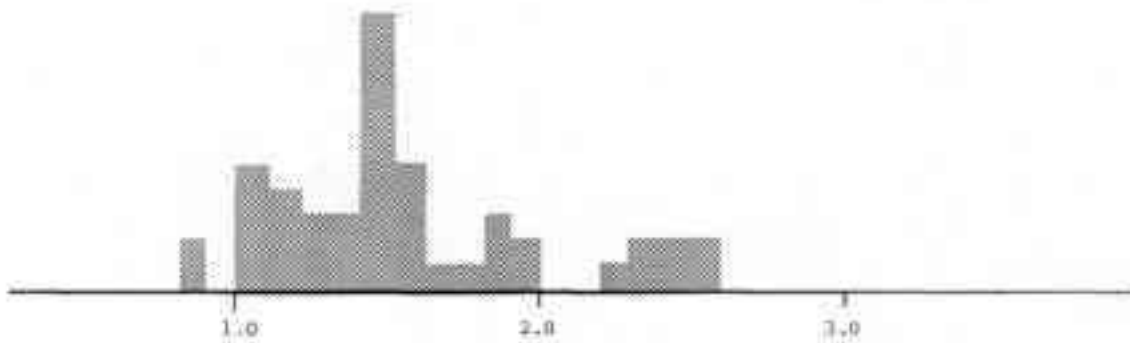
Most of the formulas in the right hand block are all sulfur delay types, the group around 2.0 are famous for long delay, the two below 1.0 are all sulfur as antimony sulfide flukes of theoretical interest only. Perhaps our empiricists are on to Mother Nature's chemical ways. Plotting other equivalence fields or ratios of the fields may be useful if you are not convinced.

72

FORMULATING THE MIXES

The formulas which follow constitute a crib sheet for the simplification of formulation procedures. The formulas which appear in quotations do not necessarily produce the chemical species indicated but are rather stoichiometric ratios that may be found convenient in creating a glitter effect. Some are only of theoretical value. As long as a formula lies in the range of the stoichiometry of Equation One to Equation Two, glitter effects are possible. If formulas are desired to go above the Equation Two range, the additional sulfur for delay is best added as antimony sulfide.

The steps to formulate a glitter mixture are:

1) Decide how much delay is desired for artistic purposes;

2) Decide how many of the glitter additives, and which ones, are desirable;

3) Choose the levels at which the additives will be used. *(In general, the additives should not be more than one-third of the mixture; in practice, only barium nitrate works well above the 15% level);*

4) Add up the components and express as a percentage or parts formulation. *(This establishes the base fire for the glitter);*

5) Add atomized aluminum or magnalium until the mixture fails to perform well with the particular aluminum used; back up to the maximized range of aluminum for that base fire.

For example: *Yellow glitter is desired.* Sodium oxalate is used at low concentration to give a bright yellow rather than the common deep golden yellow. Magnesium carbonate will be used to enhance spritzel size and delay. *Tremolante to twinkler range delay is desired.* From the cheat sheet find the ratio of sulfur to sodium oxalate for creation of the disulfide. Next, the same information for magnesium carbonate. Using the ranges of utility given, choose two percent sodium oxalate and three percent magnesium carbonate. Now since the stoichiometry should be about midway between Equation One and Equation Two, find the simple average of those two formulas. After the mathematical maneuvers, the base fire is ready for the aluminum trials. Make a large experimental batch of the base fire and add various aluminums at different percentages in about two percent increments. Form stars of ten gram batches and test fire. Having mixtures already made up of the various stoichiometries already adjusted for the charcoal in use will considerably speed the laboratory work. The entire range of stoichiometries in ten percent increments can

be tested in a day or so with any new metal fuel batches. Remember that the manufacturers of metal fuels are inconsistent in batch to batch properties. ALWAYS test each new batch for the optimal loading in a formula. Magnalium is an exception. Reade Mfg. of Lakehurst produces well controlled narrow distribution lots of magnalium powders seldom requiring recalibration of formulas.

In the calculations which follow, the equivalence of the additives, magnesium carbonate and sodium oxalate, as part of the overall equivalence of the base fire, is small and may be ignored. The simplest way to perform the adjustment exactly, would be to blend the mixtures of the additives and sulfur of the percentage composition given in the cheat sheet. In practice, this is rarely necessary, as so many other factors are used to vary the effect that small variations in stoichiometry are of small impact on the effect the star will produce. With this simplification the calculations for the mix become:

2% sodium oxalate will require sulfur at the rate of 0.48 parts per part to be converted to the disulfide. The total material added to the mixture for this is:

2 x 0.48 S = 0.96% sulfur and 2% sodium oxalate.

3% magnesium carbonate will require:

3 x 0.76 S = 2.28% sulfur

The remainder of the composition will have a formula that is the average of the Equation One and Equation Two mixtures.

Potassium nitrate:	(75% + 67%) / 2 = 71.0%
Sulfur:	(12% + 21%) / 2 = 16.5%
Charcoal:	(13% + 12%) / 2 = 12.5%

Magnesium carbonate	3.00%
Sodium oxalate	2.00%
Sulfur	3.24%

The sum of the above 8.24%

The remaining portion of the mix must have the percentage composition which was determined by averaging the Equation One and Equation Two mixes.

Subtracting, we find the remainder of the mix is 91.76% of the formula, multiplying by the percentages found above:

$$91.76\% \times .71 = 65.15\% \text{ Potassium nitrate}$$
$$91.76\% \times .165 = 15.14\% \text{ Sulfur}$$
$$91.76\% \times .125 = 11.47\% \text{ Charcoal}$$

Before we add up the formula the adjustment for charcoal impurities should be kept in mind.

The formula becomes:

Potassium nitrate:	64%
Sodium oxalate:	2%
Magnesium carbonate:	3%
Sulfur:	18%
Charcoal:	13%

This is the base fire. It is an all sulfur delay formula. The actual mix is made and tested with various lots of aluminum at various ratios, as is advisable with any formula. It will probably be worth the testing involved. After the aluminum loading is established, the nonhomogenous mixing techniques are tried, and the full utility of the mix is established. This is best done one technique at a time. After each technique is evaluated individually, combinations of the most effective techniques for this mix are tested.

The possibilities are myriad and with the theoretical guidance of the cheat sheet, the success rate of experimentation is very good. With practice, the pyrotechnist will begin to formulate a special mixture for each artistic effect desired. The author makes use of very few standard formulas, creating new formulas as desired for a particular application. This seems to be a great deal of trouble at first, but with practice it becomes trivial and the rewards are well worth the effort. In practice, the cheat sheet is worth a thousand formulas. The understanding of the ingredients and their reactions will help in controlling other fireworks effects; after all, they are chemical devices too.

CHEAT SHEET TABLE ONE: RATIOS OF GLITTER ADDITIVES TO SULFUR		
	SULFIDE	DISULFIDE
LITHIUM OXALATE	1 : 0.24S	1 : 0.39S
SODIUM OXALATE	1 : 0.24S	1 : 0.48S
STRONTIUM OXALATE	1 : 0.18S	1 : 0.36S
BARIUM OXALATE	1 : 0.14S	1 : 0.28S
MAGNESIUM CARBONATE	1 : 0.38S	1 : 0.76S
STRONTIUM CARBONATE	1 : 0.22S	1 : 0.43S
BARIUM CARBONATE	1 : 0.16S	1 : 0.32S

Maximum and recommended ranges: Antimony trisulfide is effective from three percent to a maximum of over fifty percent in formulas of theoretical interest only. It is most economically used at six to eight percent, and up to twenty eight percent in stars can be seen to make a usable difference. Lithium oxalate is not well studied but makes perceptible differences in spritz flash color at four percent and has been used at twelve percent with good results. About eight percent of lithium oxalate is recommended. Sodium oxalate is useful from one percent to about fourteen percent. Best range is two to ten percent. Strontium oxalate is useful from a two percent to fifteen percent range. Best results are seen around eight to ten percent. Barium oxalate is about the same as strontium oxalate. Magnesium carbonate is useful from one percent to about twelve percent and is commonly used at about three to six percent. Strontium carbonate ranges are somewhat smaller than the oxalate. Barium carbonate is not well studied but seems useful in less than ten percent range and best in less than five percent range.

The oxides of iron consume charcoal in the reduction to the metal. A simple assumption of stoichiometry to the metal and carbon monoxide gives the following ratios which may be of use.

Red iron oxide : assume formula Fe_2O_3 1 : 0.23C
Black iron oxide: assume formula Fe_3O_4 1 : 0.21C

CHEAT SHEET TABLE Two: PERCENTAGES OF GLITTER ADDITIVES AND SULFUR FOR PREMIXED STOICHIOMETRIES OF SULFIDE AND DISULFIDE.		
	SULFIDE	DISULFIDE
SULFUR LITHIUM OXALATE	24% 76%	39% 61%
SULFUR SODIUM OXALATE	19% 81%	32% 68%
SULFUR MAGNESIUM CARBONATE	28% 72%	43% 57%
SULFUR STRONTIUM CARBONATE	18% 82%	30% 70%
SULFUR BARIUM OXALATE	3% 87%	22% 78%
SULFUR BARIUM CARBONATE	14% 86%	25% 73%
SULFUR STRONTIUM OXALATE	15% 85%	27% 73%

CHEAT SHEET TABLE THREE: STOICHIOMETRIC FORMULATIONS TO PRODUCE THE COMPOUNDS INDICATED OR MELTS OF THOSE STOICHIOMETRIES TO AN APPROXIMATION (CHARCOAL CALCULATED AS PURE CARBON)

	K_2S	K_2S_2	"K_2S_3"	"K_2S_4"
POTASSIUM NITRATE	75	67	60	55
SULFUR	12	21	29	35
CHARCOAL	13	12	11	10

	"K_3SbS_3"	$K_2S*(Sb)$	$K_2S_2*(Sb)$
POTASSIUM NITRATE	48	57	44
SULFUR	4	--	--
ANTIMONY TRISULFIDE	39	32	48
CHARCOAL	9	11	8

	BaS	"BaS_2"	"BaS (Sb)"
BARIUM NITRATE	79	72	64
SULFUR	10	18	--
ANTIMONY TRISULFIDE	--	--	27
CHARCOAL	11	10	9

Many of the above formulations do not produce the chemicals implied by the formulas. In no case is the indicated chemical produced as a pure chemical. Most of the formulas that do not have quotation marks around the formula do produce residues that are primarily the indicated compound after cooling the melt to room temperature. Conversions to the indicated compounds may run as high as 96% depending on conditions, and as low as 48%. Other ratios have theoretical interest and some of the above have theoretical interest only. It is recommended that the reader make up each formula and burn it in different configurations, observing the types of chemicals volatilized and the viscosity of the dross produced. Each mixture should be burned as stars from comet guns and the burning behavior noted. All of the experiments in the experimental section should be tried with the all sulfur mixtures.

※

Example of chemical instability of combustion products. Spritzel oil covered in less than two seconds is here evolving gas in less than thirty seconds. Note bubbles of gases. (1mm = 5 microns)

APPENDIX I

Suggested Analysis Procedure and Experiments

A typical reaction series with spritzels may be determined as follows. The spritzel is trapped and instantly frozen by impingement on a glass slide. A drop of 1 molar copper acetate is allowed to fall on a selected spritzel. This is best observed using a five to ten power binocular microscope. Instant formation of black CuS at the surface of the spritzel, slowly growing to about 0.1 mm diameter, is observed. Beyond this, red-brown crystals of CuS2 slowly form. After the ring of CuS_2 is several millimeters in diameter, a cloudy precipitate of blue copper hydroxide forms beyond the red-brown ring.

Conclusions: Spritzel contained K_2S, K_2S_2, K_2O_2. By working with known mixtures, semiquantitative results may be obtained. Note that the presence of potassium oxides is not proven by the above test and requires substantiation by the tests which follow. In the above experiment, potassium hydroxide in the spritzels would have behaved very similarly.

An interesting series of subjects for microchemical examination is given here for the reader to try himself with the above techniques, and develop further understanding of the reactions typical of sulfide melt chemistry.

The stoichiometric mix for Equation One (K_2S) mix is prepared as a fine powder and well mixed.

Potassium nitrate:	74%
Charcoal:	14%
Sulfur:	12%

The dry mix is burned 1 centimeter below a slide. About half of a .22 caliber rimfire case of the mix is required for each burn. CAUTION: The slide may shatter, especially if larger charges are used. A red hot iron wire is a convenient igniter for this series of experiments. If the wire is quickly quenched in water after use the residues will be eliminated and cross contamination will be avoided.

To one such slide, a tissue dampened with 0.1 N HCl, 2% starch and 10% potassium iodide solution (made fresh daily) is applied. A weak color reaction, which is much stronger at the locations of charcoal flecks and any white droplets are potassium oxides and carbonate. A tissue overlay of hexamethylene rosaniline hydrochloride (crystal violet) is applied to another fresh slide. Bleaching and pH effects are observed. Other pH indicators and other peroxide sensitive solutions should be applied. The author finds that thickening the reagents with carbohydrate and polyvinyl alcohol to slow diffusion rates is advisable in some cases.

Acetates of lead, copper and mercury as simple aqueous solutions, in 1 N acetic acid and as amine complexes, are applied to similar slides. Barium acetate, in neutral and acidic solutions for sulfate and other oxy-thio ions, and other reagents which dissolve sulfur, such as carbon disulfide, may be tried. These require an understanding of their reactions with all substances which may be present or be formed by reactions of such chemicals as are present, to be of diagnostic use. The reader should consult the chemical literature.

The next series of tests for this mixture should be made with slightly dampened powder. Observe that larger and more frequent spritzels are found. Potassium hydroxide predominates over oxides, and also observe more carbonates and much more sulfides are formed than with the dry mix.

Micro-gerbs are made conveniently by funnel and wire ramming of .22 rimfire brass or similar size paper tubes. Observe increase in spritzel count and size, less oxide products, and more carbonates and sulfides.

To the loose powder add 5% dextrin. Burn in the same manner as with damp powder. Dextrin decomposes by the following equation:

$$C_6H_{10}O_5 \longrightarrow 6\,C + 5\,H_2O$$
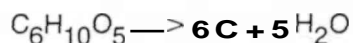
Next observe micro gerbs of the powder with dextrin. Notice how similar the chemistry is to the wet powder tests.

Pump and dry stars of straight powder mix and again with dextrin added. Prepare slides and compare with previous experiments.

Add 10% of a glitter producing aluminum to the straight mix. Compare with above. Add similarly to the powder with dextrin and make micro gerbs and stars. Observe that the aluminum acts as nucleation material for the spray of material produced by the burning comp. Glitter-like and flitter spritzels are found. Collect spritzels at various distances from the source and test.

Perform the entire series with the K_2S_2 mix.

Potassium nitrate:	67%
Carbon:	12%
Sulfur:	21%

Further experiments with other simple sulfide mixtures are good illustrations of the simple chemistry in fireworks effects regulation. Notice that some mixes evolve sulfur as monoatomic gas, which does not condense easily, and others evolve S_2 gas, which does condense easily. Notice that spritzels evolving monoatomic sulfur quickly float charcoal and aluminum to the outer surface of the spritzel and quickly blow particles of charcoal off the surface of the spritzel. The spritzels which evolve

S_2, wet and submerge the particles of charcoal and aluminum. Try putting blue, red or brown glass in the mix. This difference in the violence with which gas is evolved from the mix where sulfur is present in odd numbered stoichiometry should be studied to learn regulation of delay.

Experiments with compositions which contain antimony sulfide must be done in very well ventilated areas. The spritzels must be kept and handled in a chemical hood or outdoors where the breeze is constant and away from the experimenter. Antimony is a very poisonous material and many of the reaction products of comps containing antimony evolve poisonous gases during chemical examinations. The author does not wish to tempt amateurs into performing dangerous experiments that they may be ill trained for, and the professional chemist can find his own techniques. Photomicrographs of the more interesting results of experiments in this area are given to avoid the need of actual experiments. Fireworks containing antimony and arsenic sulfides have been used safely for centuries, with only a very few poisoning cases. Most of these were spent tubes containing residues of spent fireworks which were ingested by infants of careless parents. Experienced chemists have died or been made seriously ill while working with arsenic and antimony compounds. There is a great difference in hazard level of the different arsenic and antimony compounds.

The yellow-orange form of antimony sulfide is condensed on cool surfaces near spritzels which evolve antimony sulfide constituents as a gas. Gas phase spectra are not available to determine the atomic species atoms or compounds present in such sublimates. See the photomicrograph of an antimony sulfide sublimate.

Antimony metal is evolved as a gas by homogeneous mixtures of monosulfide stoichiometry and spritzels of that stoichiometry. See the photomicrograph of antimony regulus sublimed from a microgerb of the mix:

Barium nitrate	:	64%
Carbon:		9%
Antimony sulfide:		27%

Tripotassium antimony disulfide (K_3SbS_2) forms very characteristic crystals and is sparingly soluble in water. See photomicrograph.

It should be observed that mixtures which evolve sulfur as diatomic gas often show large spritzels with the blue flame typical of burning sulfur. Conversely, mixtures which tend to evolve sulfur as monoatomic gas often show no visible flame, but SO_2 can be detected a few inches from the burning material as monoatomic sulfur combines with atmospheric oxygen. Burning the comps which produce monoatomic sulfur in quartz tubes with inert atmosphere, the sulfur will be recovered as the element. The barium nitrate formulation produces only BaS and is energetic enough to produce monoatomic sulfur.

A few test tube experiments can be done to illustrate the chemistry of glitter.

81

One inch test tubes and charges of .05 gram are relatively safe. The test tubes must be borosilicate glass, Vycor glass, or quartz. Some of the experiments require temperatures near the melting point of the borosilicate type glass. A propane torch is required. Remote testing in fixed or clamped apparatus is advised.

Potassium or sodium sulfide is dried and melted in a test tube. After cooling, aluminum, preferably German dark pyro, is added. The air in the tube is replaced with an inert gas, such as nitrogen, helium, argon, etc. Carbon dioxide is too reactive for these experiments. Regardless of heating, no reaction is observed.

Potassium or sodium sulfate is mixed with aluminum and heated. The mix reacts near the melting point of the sulfate to produce an exothermic reaction which glows but does not explode.

Potassium sulfide or sodium sulfide is melted with aluminum as above, and no reaction is observed. To the cooled tube, dry potassium or sodium sulfate is added and upon reheating a glitter-like flash or explosion occurs. Ergo: a spritzel must contain sulfide to flash.