

Hazardous Chemical Combinations: A Discussion

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ABSTRACT

All pyrotechnic compositions present some hazard due to their ability to produce energy. However, some compositions pose an added hazard because of the combination of incompatible materials. The use of such compositions may result in more frequent accidental ignitions during processing or spontaneous ignitions during storage. Other compositions pose an added hazard because of their ability to produce especially large amounts of energy with rapid reaction rates. The use of such compositions is likely to result in especially powerful explosions in the event of an accidental ignition.

This article attempts an organized examination of some combinations of commonly used pyrotechnic chemicals that are believed to have significantly increased hazard potentials.

Keywords: accidental ignition, spontaneous ignition, hazardous combinations, chemicals, compatibility, incompatibility

Introduction

By their very nature, all pyrotechnic compositions could be considered hazardous because of their potential for producing energy (occasionally at inopportune times). However, some combinations of materials present a special hazard, either because of an added potential for unintentional ignition or because of the potential for producing a powerful explosion upon ignition. Note that there are other hazards, such as health hazards, which may be associated with

certain chemical combinations; however, that is beyond the scope of the present article.

A pyrotechnic chemical reaction characteristically produces heat energy. This so called "Heat of Reaction" may be useful directly as thermal energy, or more usually as light, sound, or kinetic energy to achieve the desired effect. However, a pyrochemical reaction must not begin to proceed as soon as the pyrotechnic composition is mixed, for then the composition could not be safely prepared. Such spontaneity is prevented by another characteristic of pyrotechnic compositions, a so-called "Activation Energy" barrier.

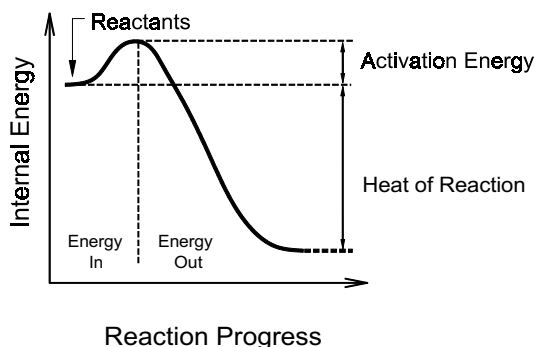


Figure 1. An illustration of the internal energy relationships in a pyrochemical reaction.

The internal energy associated with a pyrochemical reaction is depicted in Figure 1. Note that initially as the reaction begins, the internal energy of the system increases. This corresponds to the ignition process, when the composition is being supplied energy, such as by an externally applied flame. This requirement, to first input

Table 1. Some Hazardous Chemical Combinations Encountered in Pyrotechnics.

Species		Chlorates	Perchlorates	Aluminum	Magnesium	Zinc
Chlorate	ClO_3^-	0	—	X	X	X
Perchlorate	ClO_4^-	—	0	?	?	—
Aluminum	Al	X	?	0	—	—
Magnesium	Mg	X	?	—	0	—
Zinc	Zn	X	—	—	—	0
Acids	H^+	X	—	—	X	X
Ammonium	NH_4^+	X	—	—	X	X
Water	H_2O	—	—	?	X	?
Copper(II)	Cu^{2+}	?	—	?	X	X
Sulfur	S	X	X	—	X	X
Sulfide	S^{2-}	X	X	—	—	—

X = Generally a significantly hazardous combination.

? = Can be significantly hazardous depending on circumstances.

— = Ordinarily, little if any added hazard.

0 = Place filler.

activation energy to the composition, is what prevents its spontaneous ignition. If the activation energy barrier is high, much energy is required for ignition and accidental ignitions will be unlikely. If the activation energy barrier is low, less energy is required for ignition. When this is the case, accidental ignition will be more likely because a relatively small amount of mechanical, thermal or electrostatic energy can cause ignition of the composition. After ignition has been accomplished, internal energy falls as energy is released from the composition. (See reference 1 for a somewhat more complete discussion of activation energy and heat of reaction.)

Over the years, pyrotechnists have tested many substances that seemed promising for use in fireworks. It turned out that some of these, such as potassium permanganate and phosphorus, have such low activation energies in pyrotechnic compositions that they invariably create a significant hazard. Because their unsafe nature in compositions is ubiquitous, it is easy to eliminate such substances from use. A much more difficult problem is the particular combinations of materials that lead to a low activation energy, even though the same materials in other combinations do not pose that hazard. Many of these hazardous chemical combinations are

mentioned in the pyrotechnic literature (e.g., reference 2) but usually without complete explanatory comments. This paper attempts to present somewhat more complete information and explanations. However, this task is often complicated by the lack of solid experimental data reported in the literature. As a result, in some cases the authors will only be able to offer conjecture and anecdotal evidence. While this is not ideal, until more studies are conducted and reported, it is the best that can be done, and it is preferable to not providing any information for these combinations.

Some chemical combinations in pyrotechnic mixtures that can be particularly hazardous are listed in Table 1. However, it is important to note that the list is not all-inclusive. Further, on occasion, because of mitigating factors, some listed combinations may not present a high degree of hazard. To better understand why particular combinations of materials can present an increased hazard, each column in Table 1 will be discussed in turn.

Table 2. A Comparison of Ignition Temperatures for Some Common Oxidizers in Stoichiometric Combination with Various Fuels.^[3a]

Oxidizer	Ignition Temperature (°C)				
	Sulfur	Lactose	Charcoal	Magnesium	Aluminum
Potassium chlorate	220	195	335	540	785
Potassium perchlorate	560	315	460	460	765
Potassium nitrate	440	390	415	565	890

[Note that °F = 32 + (9/5) °C.]

Chlorates

Chlorates have the lowest activation energy towards decomposition of any class of oxidizers commonly used in fireworks. Consequently, mixtures containing chlorates tend to be sensitive to all types of accidental ignition. This is evidenced by the especially low ignition temperatures of binary mixtures of potassium chlorate and fuels with low melting point or low decomposition temperature (e.g., see sulfur and lactose in Table 2). One should pay close attention to the materials a chlorate is being mixed with, to be sure that the hazard is not thereby exacerbated. However, by no means is it intended to imply that all chlorate compositions are dangerously unsafe.

With Aluminum:

Aluminum has a highly cohesive and non-porous oxide coating that must be disrupted in order for a reaction with oxidizers to take place. This feature tends to raise the activation energy for ignition, compared with many other pyrotechnic fuels, see again Table 2. However, when assessing degree of hazard, it is necessary to consider both the probability and the consequence of a potential accident.^[4] In this case, the binary mixture of potassium chlorate with a fine particle size aluminum is a classic flash powder, and it has a relatively small critical mass for an unconfined explosion. Therefore, the consequences of such a mixture undergoing accidental ignition are likely to be significantly more severe than for an equivalently small amount of a standard chlorate colored star composition. The mixture is more dangerous be-

cause of the consequence, rather than a greater probability of an accident. Indeed, the probability of accidental ignition is probably less for aluminum than with common chlorate star compositions (except perhaps when the metal powder is so fine that the mixture becomes especially electrostatically sensitive).

The common solution to a hazard of this type, where the consequence is particularly severe, is to attempt to reduce the probability of an accidental ignition by raising the activation energy barrier. Usually this is accomplished by using potassium perchlorate in place of potassium chlorate. One can go further in this direction and raise the activation energy more by using barium nitrate as the oxidizer. However, one should beware of thinking that higher activation energy automatically means “safer”. It also means more difficult ignition and a greater potential for ignition failure (i.e., duds are more likely). Obviously, duds are a safety hazard just as is accidental ignition. In addition, the use of nitrate with aluminum can lead to other problems in the presence of water, as discussed below.

Conventional wisdom for flash powders would suggest using the above approach (i.e., substituting potassium perchlorate or barium nitrate for potassium chlorate). It is certainly possible that such a substitution will indeed make the resulting flash powder more resistant to accidental ignition. Unfortunately, published sensitiveness data does not fully support that. Look again at Table 2; the ignition temperature for potassium nitrate (presumably similar for barium nitrate) and aluminum is the highest of the three oxidizers. However, it is the mixture with potassium perchlorate, and not that with potassium chlorate, that has the lowest ignition temperature.

Table 3. A Comparison of Impact Sensitiveness for Some Common Oxidizers in Stoichiometric Combination with Various Fuels.^[3b]

Oxidizer	Impact Sensitiveness (kg·m/cm ²)				
	Sulfur	Lactose	Charcoal	Magnesium	Aluminum
Potassium chlorate	1.1	1.8	3.2	4.5	4.5
Potassium perchlorate	1.2	2.9	4.2	4.4	5.0
Potassium nitrate	3.6	5.0	5.0	4.6	5.0

Since these ignition temperature data are inconsistent with conventional wisdom, it is worth considering whether ignition temperature is the best indicator of the sensitiveness of mixtures, or even that the published data may be in error. Table 3 presents impact sensitiveness data for the same three oxidizers. Of the mixtures with aluminum, potassium chlorate is most sensitive; however, it is roughly equivalent to that for mixtures with either potassium perchlorate or potassium nitrate. Based on the data in Tables 2 and 3, it is not clear that improved safety results from substituting potassium perchlorate for potassium chlorate in two-component mixes with aluminum.

If it is true, that substituting potassium perchlorate for potassium chlorate does not significantly decrease the sensitiveness of binary mixes with aluminum, then one is left to ponder why conventional wisdom suggests that it does. Could it be a result of experience with flash powders that are not simple binary mixtures, but rather with mixtures including sulfur or antimony sulfide? Tables 2 and 3 do not include data for antimony sulfide but do have data for mixtures with sulfur. The impact sensitiveness data suggests that a sulfur-containing chlorate flash powder would be a little (but not much) more impact sensitive than that with potassium perchlorate. However, the ignition temperature data suggests that the chlorate flash powder would be considerably more sensitive.

The foregoing discussion is far from definitive in answering the question of relative flash powder sensitiveness. However, it is obvious, for safety, that sulfur (and almost certainly antimony sulfide) should not be present in flash powder using either potassium chlorate or perchlorate. In addition, in the absence of more data (e.g., friction and electrostatic sensitiveness), it would be prudent to abide with conven-

tional wisdom regarding the preference for choosing potassium perchlorate or barium nitrate over potassium chlorate.

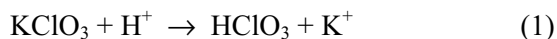
With Magnesium and Zinc:

Like aluminum, magnesium and zinc form energetic mixtures with chlorates, and similar considerations apply. However, because of the lack of a cohesive oxide coating on these metals, the activation energy for their ignition is significantly lower than it is for aluminum. The combination of both the fuel and oxidizer contributing to low activation energy provides these mixtures the potential to be particularly dangerous.

With Acids:

The predecessor of the modern match was a wooden splint tipped with a chlorate pyrotechnic composition. This was ignited by allowing the composition to come in contact with concentrated sulfuric acid^[5] (which was sometimes absorbed on asbestos wool for relative safety). Use outside the home obliged one to carry a vial of sulfuric acid in one's pocket! Also, Alfred Nobel apparently invented a mine for use in naval warfare based on this principle. A ship hitting the mine would break a glass tube of sulfuric acid, which then triggered the potassium chlorate and sugar igniter.

The high ignition sensitiveness of chlorate compositions in the presence of acids is thought to involve the formation of chloric acid.^[6,7]



Ignition may occur because chloric acid is capable of spontaneous ignition of organic fuels, or through its decomposition into highly reactive and unstable chlorine dioxide.^[8-10]

One can therefore appreciate the necessity for keeping acidic materials away from chlorate

compositions. However, if the acid is sufficiently weak, such as stearic acid, it is probably incapable of displacing sufficient chloric acid from the chlorate to induce spontaneous ignition. Moreover, the greasy nature of stearic acid helps lubricate the composition, thereby reducing its friction sensitiveness.

With Ammonium Salts:

Ammonium ions are capable of acting as an acid (proton donor).



Accordingly, most ammonium salts, such as ammonium perchlorate, are acidic in aqueous solution and potentially lead to the problems discussed above.

In addition, a mixture of a chlorate oxidizer and an ammonium salt may form ammonium chlorate through a double decomposition reaction.^[11]



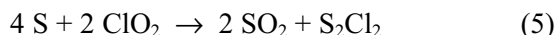
This is problematic because ammonium chlorate is a substance that explosively decomposes at 102 °C and is probably capable of undergoing a true detonation.^[9,12a]

With Copper(II) [Cupric] Salts:

Like the ammonium ion, the cupric ion (Cu^{2+}) has an acidic reaction in aqueous solution. In addition, in common with other transition metals, copper ions catalyze the decomposition of some oxidizers by lowering their activation energy. For these reasons soluble copper(II) salts with an acidic reaction, such as the sulfate, should not be used with chlorates. In practice, experience has shown that such potential problems can be overcome by using a copper(II) compound that is insoluble and/or has a counter anion with a basic reaction (e.g., carbonate, oxide, etc.). Note also that copper(I) [cuprous] salts (Cu^+) do not have an acidic reaction and therefore engender a relatively minor increase in sensitiveness, unless they contain sulfur, such as copper(I) thiocyanate (CuCNS).

With Sulfur:

The combination of sulfur with chlorates is historically the most famous cause of accidental ignitions in pyrotechnics due to “incompatible” chemicals.^[13,14] Such mixtures have long since been banned in some countries (e.g., England). One possible mechanism for the high sensitiveness of such mixtures may begin with the formation of polythionic acids on the surface of sulfur grains, and ultimately producing sulfuric acid^[6,7] (see comments above about acids). To some extent, during mechanical action sulfur reacts with oxygen in the air to form sulfur dioxide.^[13] It is thought that a chain reaction involving the gases sulfur dioxide and chlorine dioxide may be implicated in cases of spontaneous ignition of potassium chlorate and sulfur mixtures.^[6,7]



It can be seen from the equations that one molecule of sulfur dioxide ends up generating two molecules of sulfur dioxide, and the cycle potentially repeats at twice the rate; and so forth until the ignition temperature may be reached. Further, sunlight is thought to exacerbate this problem as well as the use of sublimed sulfur (flowers of sulfur) rather than sulfur flour.^[7,16]

It is probable that the bad reputation this mixture acquired in the past was due, in part, to impurities in the materials formerly available.^[17] For example, the presence of chlorite in the chlorate, or various sulfur acids in the sulfur, could serve to initiate the chain reaction. Notwithstanding this proviso, it is clear that even with pure materials the sensitiveness of a chlorate and sulfur mixture to friction and impact is too high to justify its use.^[18]

With Sulfides:

Similar considerations apply to mixtures of chlorates with sulfides as for mixtures with sulfur described above. For example, the mixture of arsenic sulfide with potassium chlorate is even more impact sensitive than the mixture of sulfur with potassium chlorate.^[3c] However, different sulfides may vary in the degree and type of hazard involved. While the sulfides of antimony and copper were those most commonly

Table 4. Decomposition Energies for Some Common Oxidizers.^[3d]

Oxidizer	Product	Decomposition Energy (kcal/mole)
Fe ₃ O ₄	Fe	+266
KNO ₃	K ₂ O	+151
Ba(NO ₃) ₂	BaO	+104
Sr(NO ₃) ₂	SrO	+89
KClO ₄	KCl	-1.2
KClO ₃	KCl	-10

Note that the sign convention is that negative values correspond to exothermic decompositions.

used with chlorates in the past, it would be wise to assume that any sulfide so used represents a significant hazard.

Perchlorates

Perchlorates produce substantially less energy upon decomposition than chlorates, see Table 4. Therefore, it can be inferred that any given material is likely to form a “safer” mixture with a perchlorate than with a chlorate. (However, note that ammonium perchlorate is incompatible with many materials because of the ammonium ion.) Perhaps equally important is the observation that, in perchlorate compositions, additives are sometimes specifically used to restore the favorable burning properties present in the corresponding chlorate composition. While it has not been well researched, there is the potential for these additives to increase the hazard, possibly approaching that of the chlorate composition. Thus, one can by no means make a valid generalization, “perchlorate compositions are safer than chlorate compositions”. Much of the advantage of perchlorates lies with less stringent compatibility considerations, rather than its inherent safety.

With Aluminum:

The combination of potassium perchlorate with aluminum has quite a large activation energy and generally causes no problem. However, when the aluminum is a very fine powder, such as in the context of a flash powder, the consequence of accidental ignition is so devastating that such mixtures should be handled with extreme caution and avoided when possible. Mixtures containing relatively small percentages of potassium perchlorate or fine aluminum tend not to be a problem.

With Magnesium:

As with aluminum, there is generally no direct problem with the combination of potassium perchlorate and magnesium. However, as will be discussed below, the presence of water with this mixture is problematic. Further, with fine magnesium powder, the combination of lower activation energy and high energy output do make for a substantial hazard. Small percentages of either potassium perchlorate or fine magnesium in these mixtures do not seem to pose a problem.

Substances Hazardous with Chlorates but not with Perchlorates:

Zinc is not a particular hazard with perchlorates because, despite zinc having a lower activation energy than aluminum, it is not a sufficiently high energy fuel to form a dangerous flash powder with these oxidizers (see Table 5). It is important to note, however, the combination of zinc with ammonium perchlorate is exceptionally hazardous because of its incompatibility with the ammonium ion (discussed below).

Acids (typically encountered in pyrotechnics), ammonium salts, or copper(II) salts present little or no problem with perchlorates for two reasons. First, perchloric acid is a significantly stronger acid than chloric acid and so is less susceptible to displacement from its salts. Second, perchloric acid is a stable acid, in marked contrast with chloric acid, which spontaneously decomposes at 40 °C (104 °F).^[12b]

Table 5. Heats of Reaction for the Complete Combustion of Various Fuels.^[19,20]

Fuel	Heat of Reaction (kcal/mole) ^(a,b)
Aluminum	–200
Titanium	–225
Silicon	–216
Magnesium	–144
Shellac	–131 ^(c)
Stearic Acid	–151 ^(c)
Lactose	–113 ^(c)
Carbon ^(d)	–94
Zinc	–84
Sulfur	–71

- (a) Unless otherwise noted, this is per mole of fuel.
- (b) Note that negative values correspond to exothermic reactions.
- (c) This value is per mole of carbon in the compound.
- (d) Carbon is in the form of graphite.

With Sulfur:

The combination of sulfur with a perchlorate is generally believed to be substantially less hazardous than the combination with a chlorate. However, with respect to impact sensitiveness (see Table 3), the difference is barely worth mentioning. It has been speculated that to some extent the bad reputation of sulfur and chlorate mixes came about because earlier supplies of materials were contaminated.^[17] If this was the case, that might explain the wisdom about perchlorate and sulfur mixtures being substantially less hazardous. That may have been true at one time but not for high purity materials.

Nonetheless, potassium perchlorate and sulfur mixes do have a low activation energy barrier, are quite sensitive to accidental ignition, and must be avoided if possible.

With Sulfides:

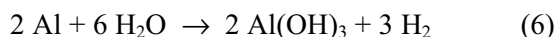
Similar considerations apply to mixtures of perchlorates with sulfides as for mixtures with sulfur.

Aluminum

The burning of aluminum metal produces the greatest amount of energy of the fuels in common use in fireworks, see Table 5. Nonetheless, aluminum can be one of the safest high energy metal fuels because of the cohesive and non-porous oxide coating, which engenders a high activation energy barrier for both combustion (see Tables 2 and 3) and corrosion. However, there are certain circumstances in which the oxide coating may be disrupted, potentially creating a hazard.

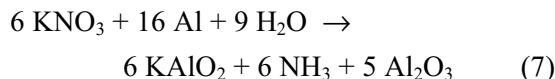
With Water:

Water is widely used to activate binders of pyrotechnic compositions and must therefore be considered a temporary ingredient of such compositions. Any active metal has the capability for a reaction with water to produce hydrogen gas. One example is the simple mixture of aluminum metal powder and pure water.



Because this is an exothermic reaction, there is the potential for generating sufficient heat to reach the ignition temperature of a pyrotechnic composition. (Even if the ignition temperature is not reached, the metal can corrode and the pyrotechnic composition can become useless.) In Figure 2, note the relatively sudden onset of the exothermic reaction after a prolonged latency (see Table 6 for experiment conditions).

The water reactivity of aluminum rises in particular with nitrate compositions, wherein the following exothermic decomposition can take place:



Aluminum oxide is amphoteric, meaning that not only can it dissolve in acids to form aluminum salts, but it can also dissolve in alkalis to form aluminates (such as the potassium aluminate formed in the reaction above). Consequently, the alkaline nature of the ammonia produced in this reaction (equation 7) can enable it to dissolve not only some of the aluminum oxide produced in the reaction, but also some of the oxide coating of the aluminum. The

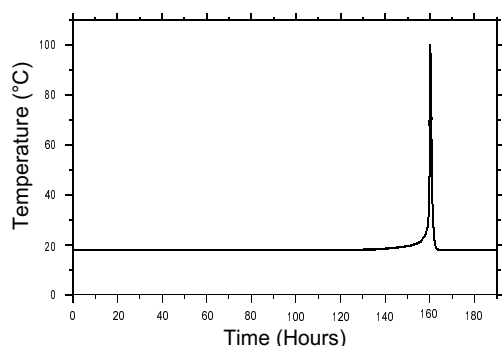


Figure 2. An example of an aluminum and water exothermic reaction.^[21] [See Table 6 for Experiment Conditions.]

aluminum so activated can then go on to react directly with water, generating more heat. Another series of tests similar to that shown in Figure 2 was performed; however, half of the aluminum was replaced with potassium nitrate (see Table 6). In this case, a slightly higher temperature was reached as the water was consumed, and the reaction peaked after only 10 hours. At least one plant explosion, is believed to have been caused by such an aluminum, nitrate, and water reaction, when it occurred in 12 kg (26 lb) of a pyrotechnic mixture left partially submerged in water.^[22]

In practice, many of these water and aluminum reactions do not appear to be a serious problem when atomized or coarse flake aluminum is used. Presumably, this is because the wetted compositions are cut or rolled into relatively small stars, from which heat readily escapes. Also the amount of water present is relatively small and drying is fairly fast.

If for some reason it is desired to use fine aluminum with a nitrate present, or if the anticipated drying time will be prolonged, a small amount of boric acid can be added to counteract the incipient alkalinity and prevent decomposition. This is partly because the protective oxide coating of aluminum is much more resistant to mild acids than it is to alkali. Moreover, aluminum borate, formed^[23] on the surface of the aluminum, is very insoluble and therefore improves the protection offered by the oxide coating. For example, when as little as 0.2% boric acid was added to an aluminum and potassium nitrate mixture, no detectable reaction with wa-

Table 6. Aluminum and Water Reactivity Data at 18 °C (64 °F) unless otherwise stated.^[21]

Conditions for Test ^[a]	Exotherm Time ^(b) (hours)
Aluminum, 2 g Distilled water, 2 g	159
Aluminum, 1 g Potassium nitrate, 1 g Distilled water, 2 g	10
Aluminum, 1 g Potassium nitrate, 1 g Boric Acid, 0.04 g Distilled water, 2 g	>500
Aluminum, 1 g Copper(II) oxide, 1 g Distilled water, 2 g	15
Aluminum, 2 g Distilled water, 2 g Temperature 43 °C (109 °F)	1

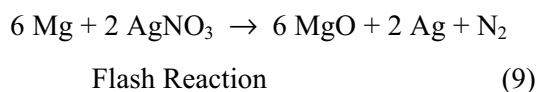
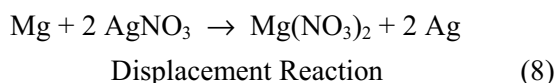
(a) Aluminum was always Alcoa S-10, 12μ atomized.

(b) (b) Average time to exotherm for three tests. (See Figure 2.)

ter occurred even after 500 hours, see Table 6. (Note that using 0.5% boric acid would provide a more reliable safety margin.)

With Copper(II) [Cupric] Salts:

A metal will react with the salt of a more electronegative (less reactive) metal in what is called a displacement reaction. Such a reaction is exothermic and has the potential of producing enough heat to raise a pyrotechnic composition to its ignition temperature. A classic example of this is the silver nitrate and magnesium flash powder that is initiated by a mist of water droplets:^[8]



The activation energy of the displacement reaction is lowered so much by the presence of water that the reaction proceeds at ambient temperature, generating sufficient heat to initiate the pyrotechnic flash reaction.

Displacement reactions can occur with copper salts and aluminum, but in practice, this is seldom a problem because of the large activation energy engendered by the oxide layer on aluminum. However, problems can arise when the copper salt is significantly soluble. Although most copper salts used in pyrotechnics are not very soluble, it should be borne in mind that the presence of ammonia substantially enhances the solubility of the copper salts.^[24] Consequently, situations with the potential for generating ammonia, such as described in the previous section (equation 7), can be exacerbated by the presence of a copper compound.

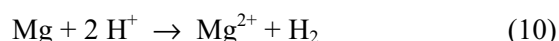
As part of the testing of aluminum's reactivity with water (Table 6), a series of tests were conducted wherein a mixture of atomized aluminum and copper(II) oxide were used. Despite the low solubility of copper(II) oxide, a reaction similar to that shown in Figure 2 occurred. The time interval before the peak (exotherm) was 15 hours, nearly as fast as it occurred when testing aluminum with potassium nitrate.

Magnesium

The activation energy for the reaction of magnesium is substantially less than for aluminum. As a result, the associated chemical reactivity problems are generally similar in kind but much greater in degree.

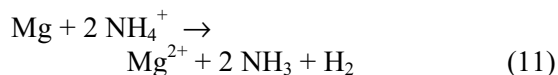
With Acids:

Magnesium is extraordinarily reactive toward acids, thus even mild acids, such as boric acid, must be avoided.



With Ammonium Salts:

The ammonium ion is sufficiently acidic to react with magnesium:



The only effective way of preventing this reaction is by conversion coating the metal. Traditionally, the only effective coating was obtained by treatment with a dichromate.^[25,26] This, however, may be considered an extreme solution because of the carcinogenicity of dichromates. Recently, a conversion coating that may be superior to that of dichromate was reported.^[27] That coating is based on treatment with a low toxicity ammonium metamolybdate and ammonium dihydrogen phosphate solution.

With Water:

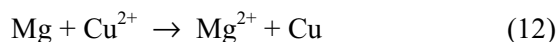
The reactivity of magnesium with water is so great that aqueous binding is generally considered to be incompatible with the presence of magnesium. In fact, reactions occur with unprotected magnesium and many (most?) salts in the wet state. For example, Shimizu^[25] reports that active or violent reactions occur between magnesium and the wet salts listed in Table 7.

Table 7. Some Wet Salts Invoking Active or Violent Reactions with Magnesium.^[25]

Barium nitrate	Potassium chlorate
Potassium nitrate	Potassium perchlorate
Sodium oxalate	Sodium chloride
Sodium bicarbonate	Sodium carbonate
Strontium nitrate	

With Copper Salts:

The reactivity of magnesium with copper salts (both cupric and cuprous) is so great that such mixtures are generally considered to be incompatible. This is because of an exothermic displacement reaction.



Copper metal or copper(II) oxide should be used when combinations with magnesium are desired. Copper metal works because both it and magnesium metal are in the same oxidation state, zero or neutral, thus displacement is not possible. However, because of magnesium's intrinsic water reactivity and because copper and magnesium metals form an electrochemical

couple, non-aqueous binding is essential. When drying times are fairly short, copper(II) oxide seems to be acceptable because of its low solubility. However, there may be problems similar to that when mixed with aluminum (see above and Table 6).

With Sulfur:

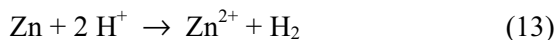
Sulfur can act as an oxidizer for active metal fuels. A metal associated with low activation energies, such as magnesium, can react spontaneously with sulfur leading at least to corrosion, and perhaps to ignition under some circumstances. Even aluminum and sulfur mixtures can present a problem under rare circumstances. For example, it has been reported that when a mixture of aluminum and sulfur was ball milled, an explosion resulted.^[28] Presumably this was partly the result of physical abrasion removing enough of the protective aluminum oxide layer to lower the activation energy to unsafe levels for ball milling.

Zinc

Despite being a substantially less energetic fuel than magnesium (see again Table 5), zinc also has a somewhat low activation energy barrier, and so generally shares similar compatibility concerns.

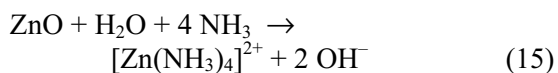
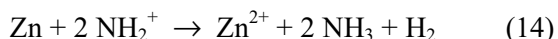
With Acids:

Zinc reacts readily with acids, and the combination is best avoided.



With Ammonium Salts:

Like magnesium, zinc is incompatible with ammonium salts. The reaction is exacerbated in this case because zinc oxide is dissolved by aqueous ammonia.



Thus, the ammonia formed in the first reaction is able to solubilize the partly protective zinc oxide layer on the zinc particles, thereby accel-

erating its decomposition. A classic demonstration of spontaneous combustion is a mixture of zinc and ammonium nitrate that is initiated with a drop of water. Under conditions of high humidity, the presence of hygroscopic ammonium nitrate will cause the mixture to spontaneously heat up.

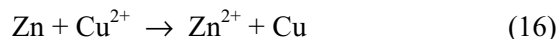
With Water:

In its behavior with water, zinc more closely resembles aluminum than magnesium. Usually there is no problem, even with nitrates present. However, on occasion, such mixtures have been known to heat up. Ammonia, the water reaction product of nitrates and zinc (see equation 7 for a similar reaction) dissolves the protective zinc oxide layer, leading to a self-accelerating reaction.

With zinc metal, because of its acid sensitivity, anything but a neutral pH composition must be avoided. Thus, in practice, nitrate and zinc mixtures can generally be used with aqueous binding only if there are no acidic or alkaline ingredients present to initiate its decomposition. However, it is well to be aware of this potential problem.

With Copper Salts:

Like magnesium, zinc is incompatible with copper salts due to exothermic displacement reactions as discussed above.



With Sulfur:

The mixture of zinc and sulfur is a traditional model rocket fuel.



However, it is not generally recognized that this mixture has a quite low activation energy for ignition and is significantly sensitive to both friction and impact. According to Partington^[29] "... the mixture may detonate on percussion." As with magnesium, this combination is best avoided, even though it probably is not capable of a true detonation.^[30]

Addendum for Magnalium

In general, the properties of an alloy are somewhat intermediate between those of its constituent metals. However, this is not necessarily the case. For example, the hardness of magnalium (magnesium/aluminum alloy) is significantly greater than that of either of its constituent metals. Nevertheless, its chemical sensitivity is more often intermediate than resembling a mixture containing particles of the individual metals.^[25] Of particular interest are hazardous combinations that are not exactly predictable from the properties of the constituent metals. (For the purpose of this discussion, magnalium refers specifically to the 50:50 alloy. Other magnalium alloys may be expected to have properties more or less intermediate between this alloy and the major constituent metal.)

With Chlorates and Perchlorates:

It is not expected for there to be a significant deviation from intermediate properties here; namely significantly hazardous with chlorates, less so with perchlorates. (See below for ammonium perchlorate.)

With Acids:

Here again the properties are intermediate. Magnalium is more acid sensitive than aluminum, but less so than magnesium. However, it is still sufficiently acid sensitive so as to preclude its use even with mild acids such as boric acid.^[25,31] There are a number of published formulations that combine boric acid with magnalium, or even with magnesium. However, such compositions are almost always used with non-aqueous binding, which minimizes the danger. If similar formulations are developed for use with aqueous binding, the boric acid content should be deleted in the interest of safety.

With Ammonium Salts:

Magnalium is more reactive than aluminum, but less reactive than magnesium, towards moist ammonium perchlorate.^[25] Boric acid does not prevent this reactivity and should not be used because of magnalium's reaction with acids. In

practice, the problem can be avoided with the use of non-aqueous binding.

With Water:

Magnalium does not usually present any problem with aqueous binding. However, the potential for decomposition exists and it is well to be aware of this possibility when developing formulations. Certain substances seem able to trigger the reactivity of magnalium towards water. Examples are lampblack and alkali metal oxalates.^[25,32] The reasons are not obvious and do not necessarily depend on any acidic or alkaline reaction. For example, aqueous lithium oxalate has a pH of 7 (neutral), yet is able to trigger such exothermic decomposition of magnalium.

In general, magnalium is more stable in an alkaline rather than an acidic environment, in contrast with aluminum. Thus, lithium carbonate, with an alkaline reaction, presents no problem with magnalium, although it is incompatible with aluminum.^[32]

With Copper Salts:

Copper salts, both copper(I) and copper(II), should be avoided with magnalium unless the counter anion has a basic reaction. Fortunately many of the copper salts used in pyrotechnics, such as the carbonate or benzoate, fall into the latter category and normally present no problem. A danger can arise when conditions allow the production of ammonia, which has the ability to solubilize otherwise poorly soluble copper compounds.^[24] Ammonium perchlorate in combination with alkaline materials, such as hexamine, can produce sufficient ammonia to cause a solubilization effect with certain copper salts.^[33] Thus, the fourfold combination of ammonium perchlorate, hexamine, copper(II) carbonate, and magnalium is incompatible despite the fact that any of the binary combinations cause no problem.^[34] Certain copper compounds, such as copper(II) benzoate, seem to be less problematic for unknown reasons.^[34,35]

With Sulfur:

Magnalium does not cause any particular problems with sulfur and resembles aluminum in this respect.

Exercise for the Reader

As a self test, the reader is invited to consider all of the combination hazards associated with the hypothetical blue star formulation in Table 8. Any experimentation with this composition is definitely not advised.

Table 8. Hypothetical Blue Star Formulation.

(Consider what is wrong with this blue star formulation!)	
Ammonium perchlorate	30
Potassium chlorate	30
Sulfur	20
Copper(II) sulfate	10
Zinc	10
(Dampen with water)	

Closing Remarks

The discussion of some particularly hazardous combinations and the listings in Table 1 should not be interpreted too rigidly. They should serve only as guidelines. Some combinations listed as generally hazardous can be used by knowledgeable and skilled pyrotechnists in certain circumstances with reasonable safety, provided appropriate precautions are taken. Conversely, the list is not all inclusive, with other hazardous combinations existing.

Knowledge of hazardous combinations has been acquired through more than a century of observations by pyrotechnists. The explanations given in this article should be seen as post facto rationalizations rather than as theoretical predictions. Consequently, formulation development should be guided by cautious experimentation. For example, it is not obvious that titanium is compatible with ammonium salts whereas manganese is not, despite the two metals having almost identical electronegativities.

New star compositions containing active metal fuels should be dampened with water (if at all) only as a small sample. Such stars should be checked periodically for the occurrence of an exothermic reaction or other indication of an

adverse reaction (e.g., an ammonia or a hydrogen sulfide odor).

Great care must be taken when working with new formulations, especially if there is any known potential for an adverse reaction. It is always appropriate to start working with very small quantities and to store these materials separate from other pyrotechnic materials and in a manner such that an accidental ignition would be less than disastrous.

Only after small batches have been successfully prepared, should larger batches be attempted. However, it must be recognized that since small batches did not experience adverse reactions, is not a guarantee that problems will not appear when batch sizes are scaled up. Mostly this is because increasing temperature generally has a powerful effect on the rate of chemical reactions. As an example, consider the two experiments with aluminum and water reactions in Table 6. Note that while at 18 °C the reaction peaked only after 159 hours, the same reaction at 43 °C peaked in only 1 hour. When large batches are prepared, any heat produced will generally escape more slowly (i.e., the temperature will rise to higher levels). This in turn accelerates chemical reaction rates and the rate of heat production. Such a thermal run-away may well lead to a catastrophe for a large batch while a small batch may show no signs of a problem.

In the event an adverse reaction is detected, it may be necessary to take more or less immediate safety measures. If the reaction is mild, the amount of material is small and it is in an isolated location, it may be possible to monitor the situation and hopefully wait it out. Actual ignitions of compositions undergoing adverse reactions are not common; nonetheless, disposal is probably the best way to terminate the potential problem.

The only certain way to eliminate a pyrotechnic hazard is to consume the material, generally by burning. While such disposal may constitute unlicensed hazardous waste disposal, it may also be a safety imperative. Great care must be taken when materials under going adverse reactions are handled or moved, such as in preparation for disposal by burning. Consideration must always be given to the possibility that

the material may enflame at any time. If the temperature of the composition has risen (as will almost always be the case), combustion of the material will probably be especially violent and could be explosive. When burning pyrotechnic materials, always be extremely careful. Even under the best of conditions, unexpectedly large or violent output is possible. Some limited guidance on the subject that may be useful can be found in references 36 and 37. In cases where immediate disposal by burning is not possible and when the amount of material is relatively small, it will generally be possible to limit the buildup of heat in the materials by their immersion in a large amount of water. This will preclude the ignition of the material, but often will not terminate the adverse reactions such as the production of flammable (potentially explosive) hydrogen gas. If such treatment is necessary, as soon as possible the pyrotechnic composition should be separated from the water and disposed of by burning. Obviously, the best course of action is studiously to avoid those potentially hazardous combinations that might lead to adverse chemical reactions!

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