Dragon's Egg/Crackle Compositions

Part 1

Introduction

Crackling compositions, containing lead oxides and magnalium, appear to have been discovered and introduced by the Chinese at some time in the nineteen eighties. The characteristics of micro-stars made from these mixtures appear to be that of a delay, followed by one or more explosions and are based on the oxidation/reduction thermite reaction between a metal and a metal oxide. As far as I am aware, there are no published formulae for the Chinese compositions. There are indications that present day Chinese crackling stars may use quite different formulations and, in particular, that they probably use a resin binder.

The first reported Western composition of the metal oxide/magnalium type seems to be one by Michael S. Swisher, in 1988. He used a stoichiometric[1] mixture of 89% lead tetroxide (Pb_3O_4) and 11% 100 mesh magnalium (50:50), bound either with starch and water or with nitrocellulose lacquer. In 1990, Shimizu published a study of a variety of mixtures of lead oxides with magnesium, aluminium or magnalium, in an attempt to determine the mechanism. He believed that the process was a two-stage reaction, similar to his explanation of strobe compositions. According to him, there is a 'smoulder' or 'dark' stage, where the magnesium burns in the oxygen released, for example, by the decomposition of the lead tetroxide into lead (II) oxide (PbO), followed by an explosion, when the aluminium reacts with the remaining lead (II) oxide, reducing it to metallic lead. It has been alleged that the heavy lead atoms enhance the explosion by providing a degree of self-confinement.

Around this time, a number of workers introduced varying amounts of copper (II) oxide (CuO) into the mixes, presumably with the intention of making them more 'lively' (the reaction between CuO and Mg or Al is fast and energetic). Somewhat later, because of concerns over the toxicity of lead compounds, lead oxides tended to be replaced by other, less poisonous heavy metal compounds that were found to be effective – such as bismuth trioxide (Bi_2O_3), bismuth subcarbonate ($Bi_2O_2CO_3$) or even antimony trioxide (Sb_2O_3). Interestingly, Bi_2O_3 contains a percentage of oxygen (10.3%) that is very close to that of Pb_3O_4 (9.3%) so can, at least in that respect, be used as a near-direct weight-for-weight replacement. I believe the first such formula was discovered and published by Clive Jennings-White in 1992:

Bi_2O_3	75
Mg/Al (60 mesh)	15
CuO	10

Since then, a wide variety of mixtures have been developed. In a very cursory search I discovered more than twenty different formulae, with greatly varying proportions of the three main ingredients

[1] In the exact proportions by weight as indicated by the chemical equation that represents the reaction.

(heavy metal oxidant, magnalium and copper (II) oxide), with widely different recommendations for the magnalium particle size and with many different additives.

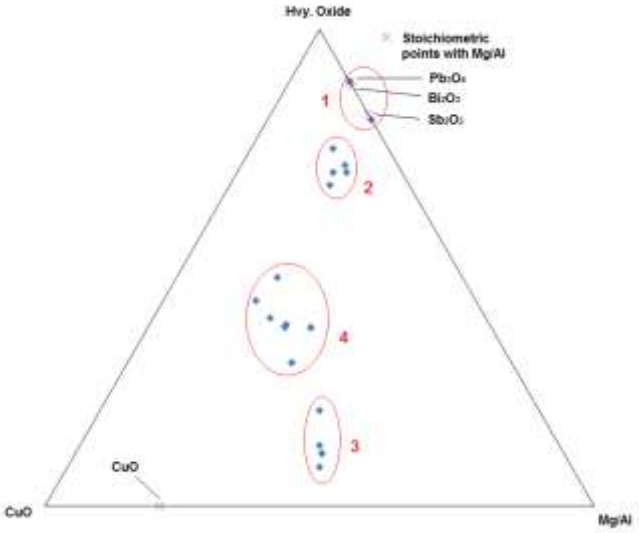
The purpose of an additive such as titanium sponge seems to be simply to add sparks to an explosion and, presumably, has little other effect on the reactions taking place. Others, such as potassium nitrate, sulphur or antimony sulphide are likely to influence the ease of ignition and/or the nature of the delay and subsequent explosion(s).

It is worth noting that there are two interpretations of what makes a good crackling micro-star. One school of thought, deriving mainly from the USA, is that a granule should produce a single report, preferably as loud as possible. The other, which has mainly European adherents, is that each micro-star should give multiple explosions, with loudness being of somewhat lesser importance. I feel that the wide divergence of the formulae is likely, to some degree, to be a consequence of this difference of opinion.

Initial Analysis

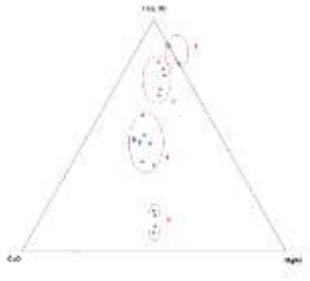
In order to try and make some sense out of the apparent chaos, I started by plotting the mixtures on a triangle diagram. To do so, I ignored all the additives, even if present in reasonably large amounts; the diagram shows only the relative percentages of the three common ingredients. I also made no distinction between the various heavy metal compounds, classifying them all simply as 'heavy metal oxides'. Ignoring these differences causes one or two formulae to become closely similar, or even identical to one or more of the others. In consequence, the diagram is possibly an oversimplification, but still shows some interesting relationships.

Firstly, despite the wide differences in the formulae, the points are not distributed randomly, but are restricted to relatively small portions of the diagram. Furthermore, they seem to be distributed in a number of separate groups, as indicated. To a first approximation, all the points lie not too far away from the vertical bisector of the diagram, which implies that the greatest difference between them is the proportion of heavy metal oxide that they contain and that the variation in the relative proportions of magnalium and copper oxide is of secondary significance.



For interest, I have also included, as purple crosses, the points representing the stoichiometric binary mixtures of magnalium with each of Pb_3O_4, Bi_2O_3, Sb_2O_3, and CuO. Note the nearness of the points for Pb_3O_4 and Bi_2O_3, reflecting the close similarity of their oxygen content – as noted earlier in this document.

As a check on whether my ignoring the differences between the various heavy metal oxides might be distorting the results, I plotted a second triangle diagram. In each formula I replaced the relevant metal oxide with the equivalent weight (same number of molecules) of Pb_3O_4 and recalculated the percentages. The result of this (admittedly still somewhat crude) 'correction' is shown in the second diagram; the groupings are a little more diffuse, but are still clearly present. I therefore decided that there was likely to be some real, physical significance to the existence of the groups and that they would be worthy of further study.



Group 1: The mixtures in this group contain only Pb_3O_4 and magnalium (with one variant that contains an additional few percent of atomised aluminium). One member is the original formula reported by Swisher and the other seems to be a minor modification. From what little description I have of their behaviour, they appear to be mixtures that produce one, or a small number of explosions from each micro-star. They are generally consolidated with nitrocellulose lacquer, although Swisher reports some success using starch and water.

Group 2: These are characterised by a high proportion of heavy metal oxide, in the region of 75%; they seem to be based on the Jennings-White Bi_2O_3 formula quoted earlier. Again, as far as I can tell, they appear to be mixtures that produce multiple crackles and are largely devoid of additional substances, other than the occasional addition of aluminium. The recommended binder is nitrocellulose lacquer.

Group 3: All these mixtures contain a low proportion of heavy metal oxide (between 8 and 20 percent) and roughly equal quantities of Mg/Al and CuO. None of the formulae contain any additional substances. Most are American in origin and appear to be of the type that produces a single, very loud explosion. All are bound with nitrocellulose lacquer; the greater the amount of lacquer, the louder the explosion.

Group 4: This group is by far the most complex and diverse. They all contain moderate amounts (around 30 to 50%) heavy metal oxide and the majority contain additional ingredients – atomised aluminium, potassium nitrate and sulphur, potassium perchlorate and red gum, or antimony sulphide and titanium. Of those mixtures that come with a description of the effect, there appears to be a range of behaviours from a quiet crackle to a single loud explosion. Most are bound with nitrocellulose lacquer, but those containing red gum are intended to be wetted with alcohol.

Another point of interest to be taken from the triangle diagram is to note that all the plotted points lie on, or to the right of a line joining the Cu/Magnalium and Pb_3O_4/Magnalium stoichiometric points. The line itself represents all possible mixtures of the two stoichiometric combinations of the oxides with the magnalium fuel; all these mixtures must also, therefore, be stoichiometric.

That the points lie to the right of this line indicates that they all contain, to a greater or lesser degree, an excess of the magnalium fuel. In principle, therefore, each of the 3-component mixtures considered in this survey could be derived from an appropriate stoichiometric combination by the addition of a further quantity of magnalium.

If we also make the assumption (which may or may not be justified) that the plotted points form a representative population of the whole of the region(s) in the triangle diagram that produce viable crackle compositions, we can take this observation a little further. Noting that the points near the bottom of the diagram are further from the line of stoichiometry than those near the top leads to the following hypothesis; a mixture with a lower percentage of Pb_3O_4 (or Bi_2O_3) requires a greater excess of magnalium.

In any case, it seems to me that it would be well worth investigating the properties of mixtures lying along the line of stoichiometry.

Stoichiometric Tests

I decided to start with Pb_3O_4 as the heavy metal oxide. I made batches of the two stoichiometric mixtures: 89% Pb_3O_4 plus 11% magnalium, and 79.1% CuO plus 20.9% magnalium. The magnalium I used was 50:50 Mg:Al and of 275 mesh. There was no particular reason for choosing this mesh size, other than that I wanted to use a reasonably fine powder to aid thorough and uniform mixing, and this one was the first suitable sample to come to hand when I assembled the ingredients.

I then combined the two mixtures in various proportions, as shown in the following table, to generate a number of compositions that all lie on the line of stoichiometry. I tested each mixture as a micro-star, consolidated with nitrocellulose lacquer. Because of the relatively small samples, it was difficult to ensure that the same amount of NC lacquer was used for each. Samples 2, 3 and 8 ended up with rather more than the others, with sample 8 probably receiving (as a result of a bit of finger trouble) almost double the average dose. The micro-stars were cut approximately 5 mm square and 2 to 3 mm thick, each weighing around 0.2 to 0.25 grams.

Sample	Ratio	%Pb_3O_4	%CuO	%Mg/Al	Delay (s)	No. Crackles	Loudness
1	1:0	89.0	0.0	11.0	0.6	2	Moderate
2	7:1	77.9	9.9	12.2	2.2	3	Moderate
3	3:1	66.7	19.8	13.5	2.6	1	Loud
4	5:3	55.6	29.7	14.7	2.0	1	Loud
5	1:1	44.5	39.5	16.0	6.3	1	Very Loud
6	3:5	33.4	49.4	17.2	12.2	1	Moderate
7	1:3	22.3	59.3	18.4	12.4	3	Moderate
8	1:7	11.1	69.2	19.7	6.7	14	Quiet
9	0:1	0.0	79.1	20.9	3.5	9	Quiet

The results show some interesting trends in the delay, the number of crackles and their (subjectively assessed) loudness.

I had hoped to put some numbers to the loudness measurements but, so far, I've been defeated by the software I use. It seems to insist on scaling all sound files to a peak amplitude of ±1.0, making comparisons valueless. I'll keep looking for a solution/work-around.