An Oxygen-Exchange Approach to Pyrotechnic Formulation

E. J. Clinger
Sotsyalisticheskaya 65/3, Kharkov 310093, Ukraine
and
Wesley D. Smith
Department of Chemistry, Ricks College, Rexburg, ID 83460-0500, USA

ABSTRACT

An old model of pyrotechnic reactions is presented in such a way that modern pyrotechnists are able to create new formulations using the principles of chemical stoichiometry but without having to know the exact products of the reaction involved. According to the model, pyrotechnic reactions occur in two distinct steps. The oxidizers produce molecular oxygen, then the fuels consume it. How this oxygen (including, in some cases, oxygen from the atmosphere) is distributed among the components of the mixture leads to the coefficients on the reactant side of the corresponding chemical equation. And from them, the composition of the formulation can be calculated. Using the oxygen-exchange approach, one can add or replace ingredients in a given formulation and come up with a stoichiometrically equivalent composition.

Keywords: oxygen exchange, pyrotechnic formulating, oxidizer, fuel, chemistry

Stoichiometry

The ideal way to formulate a pyrotechnic composition is to mix the ingredients according to the stoichiometry of the chemical reaction involved.[1] However, that approach requires a detailed knowledge of the reaction including its balanced chemical equation. Specifying the reactants is easy enough; they are merely the components of the proposed formulation. But the task of predicting all the products of a pyrotechnic reaction is far from simple, even for an experienced chemist. In this paper, we present a method of formulating mixtures using the principles of stoichiometry but without having to know the exact identity of the products.

Introductory Examples

By way of introduction, let us examine the combustion of flash powder. The main reaction is probably

$$3\ KClO_4 + 8\ Al \rightarrow 3\ KCl + 4\ Al_2O_3 \qquad (1)$$

We say “probably” because we have relied only on our chemical intuition here. We have not searched any of the original scientific literature on it. All we know for certain is that we start with potassium perchlorate and aluminum. The products are a matter of assertion. And even if this single equation *does* represent the major chemical change, it would not account for any of the competing side reactions that are always present in a real-world process. Nevertheless, equation 1 tells us to mix our flash powder in the proportion of three moles potassium perchlorate (or 3 mol × 138.55 g/mol = 415.65 g) to eight moles aluminum (or 8 mol × 26.98 g/mol = 215.84 g) for a total weight of (415.65 + 215.84 =) 631.49 g. This theoretical formulation, 65.8% $KClO_4$ (415.65/631.49 × 100%) and 34.2% Al (215.84/631.49 × 100%) by weight, is nearly identical to one of Lancaster’s compositions,[2] which, presumably, has been well-tested.

Unlike ordinary combustibles (e.g., candle flames or campfires), a stoichiometric mixture of potassium perchlorate and aluminum, reacting by equation 1, does not depend on atmospheric oxygen in order to burn. It will deflagrate in the tightly-pasted confinement of a bottom shot or perhaps even in the vacuum of outer space. We say that such a composition has a zero oxygen demand. There is no deficiency of oxidizer in the mix; neither is there an excess.

The commonly-quoted flash formulation, however, is 70.0% $KClO_4$ and 30.0% Al by weight.[2] This corresponds to a mole ratio of

$$\frac{\left(\dfrac{70.0\text{ g KClO}_4}{138.55\text{ g/mol KClO}_4}\right)}{\left(\dfrac{30.0\text{ g Al}}{26.98\text{ g/mol Al}}\right)} = \qquad (2)$$

$$0.4544 = \frac{3.635}{8}$$

In other words, instead of following the stoichiometry of equation 1, the 70:30 formulation comes from a reaction that could be written as

$$3.636\ KClO_4 + 8\ Al \rightarrow \textit{products} \qquad (3)$$

In like manner, Shimizu's Thunder No. 4 formulation[3a] (72.0% $KClO_4$ and 28.0% Al by weight) might be derived from the reaction

$$4.006\ KClO_4 + 8\ Al \rightarrow \textit{products} \qquad (4)$$

Here, the mole ratio of 4.006 to 8 corresponds to the mass ratio of 72 to 28.

Both of these compositions may have an excess of oxidizer, *if* the products are assumed to be the same as those of equation 1. On the other hand, equations 3 and 4 may actually represent new and different reactions from that of equation 1—various oxides of chlorine or potassium might be included as additional products, for instance. For our present purposes, however, we do not have to know.

We can balance the reactant side of the chemical equation for any pyrotechnic reaction if we know the composition of the mixture. We need not know any information about the products. We can always give the left-hand side of the equation whatever coefficients it needs. Different blends of the same components could, in reality, yield different products, or they could simply be non-stoichiometric mixtures that give the same products. But it does not matter as long as we allow ourselves freely to adjust the coefficients of reactants in the balanced chemical equation.

Oxygen-Exchange Reactions

The point of adjusting coefficients, however, is not to write chemical equations for existing compositions but to create new ones. In order to provide this procedure with some practical predictive power, we need a chemical starting point. If somehow we had to know the finished formulation beforehand, we would be running around in circles. Thus, we must first come up with some chemically-plausible products for the pyrotechnic reaction of interest and use them as a point of departure. These reactions, with both reactants and products, can be tabulated.

Since nearly all pyrotechnic reactions involve the element oxygen, we can make reaction tables quite conveniently by following the century-old method of Tsytovich.[4] We imagine the reaction as proceeding in two steps. First, the oxidizer decomposes into molecular oxygen. Second, the fuel reacts with that molecular oxygen. These two steps are then combined so that the molecular oxygen balances. That is, the two intermediate reactions are adjusted (including, in some cases, certain amounts of outside, atmospheric oxygen) so that the same amount of oxygen is involved in both. The overall reaction then retains all the stoichiometric information of the direct reaction.

For example, to obtain equation 1, we first decompose the $KClO_4$ to produce O_2 and then consume that O_2 with the Al

$$\begin{array}{c} 3\ (KClO_4 \rightarrow KCl + 2\ O_2) \\ \underline{2\ (3\ O_2 + 4\ Al \rightarrow 2\ Al_2O_3)} \\ 3\ KClO_4 + 8\ Al \rightarrow \textit{products} \end{array} \qquad (5)$$

We balance the equation by making sure the same number of oxygen molecules—in this case, 6—are both produced by the oxidizer and consumed by the fuel. No atmospheric oxygen is involved here.

Table 1. The Decomposition of Some Common Pyrotechnic Oxidizers To Produce Molecular Oxygen. The Factor n_o Is the Number of O_2 Molecules Produced Divided by the Number of Oxidizer Molecules Consumed.

Oxidizer	Formula	For. Wt.	Decomposition Reaction	n_o
Ammonium perchlorate	NH_4ClO_4	117.49	$4\ NH_4ClO_4 \rightarrow 2\ N_2 + 6\ H_2O + 4\ HCl + 5\ O_2$	1.25
Barium nitrate	$Ba(NO_3)_2$	261.34	$2\ Ba(NO_3)_2 \rightarrow 2\ BaO + 2\ N_2 + 5\ O_2$	2.50
Strontium nitrate	$Sr(NO_3)_2$	211.63	$2\ Sr(NO_3)_2 \rightarrow 2\ SrO + 2\ N_2 + 5\ O_2$	2.50
Potassium chlorate	$KClO_3$	122.55	$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$	1.50
Potassium nitrate	KNO_3	101.10	$4\ KNO_3 \rightarrow 2\ K_2O + 2\ N_2 + 5\ O_2$	1.25
Potassium perchlorate	$KClO_4$	138.55	$KClO_4 \rightarrow KCl + 2\ O_2$	2.00

The advantage of employing oxygen as an intermediate is that it is much easier to write chemical equations for how the combustion of individual fuels consume O_2, and for how lone oxidizers decompose to produce it, rather than predicting the complicated exchanges of electrons in the fuel/oxidizer mixtures themselves. Further, a plausible equation for the reaction between or among any number of oxidizers and fuels can be created from the information on just two tables. Table 1 gives the oxygen-producing reactions for common pyrotechnic oxidizers. Table 2 shows how common pyrotechnic fuels consume oxygen.

Table 2. The Oxidation of Some Common Pyrotechnic Fuels in the Presence of Abundant Molecular Oxygen. The Factor n_f Is the Number of O_2 Molecules Consumed by Each of the Fuel "Molecules". Substances Marked with an Asterisk Have Empirical Formulas (Which Only Reflect their Elemental Composition) Rather Than Molecular Formulas (Which Indicate the Structure of Specific Molecules).

Fuel	Formula	For. Wt.	Oxidation Reaction	n_f
Aluminum	Al	26.98	$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$	0.75
Antimony trisulfide	Sb_2S_3	339.68	$2\ Sb_2S_3 + 9\ O_2 \rightarrow 2\ Sb_2O_3 + 6\ SO_2$	4.50
Charcoal*	$C_{322}H_{184}NO_{37}$	4659.0	$C_{322}H_{184}NO_{37} + 350O_2 \rightarrow 322CO_2 + 92H_2O + NO$	350
Dextrin*	$C_6H_{10}O_5$	162.14	$2\ C_6H_{10}O_5 + 12\ O_2 \rightarrow 12\ CO_2 + 10\ H_2O$	6.00
Hexamine	$C_6H_{12}N_4$	140.19	$C_6H_{12}N_4 + 9\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + 2\ N_2$	9.00
Iron	Fe	55.85	$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$	0.75
Lampblack	C	12.01	$C + O_2 \rightarrow CO_2$	1.00
Magnesium	Mg	24.305	$2\ Mg + O_2 \rightarrow 2\ MgO$	0.50
Magnalium (50/50)*	Al_9Mg_{10}	485.88	$4\ Al_9Mg_{10} + 47\ O_2 \rightarrow 18\ Al_2O_3 + 40\ MgO$	11.75
Parlon*	$C_5H_6Cl_4$	207.91	$2\ C_5H_6Cl_4 + 13\ O_2 \rightarrow 10\ CO_2 + 6\ H_2O + 4\ Cl_2$	6.50
PVC*	C_2H_3Cl	62.50	$4\ C_2H_3Cl + 11\ O_2 \rightarrow 8\ CO_2 + 6\ H_2O + 2\ Cl_2$	2.75
Red gum*	$C_{31}H_{35}O_{16}$	663.61	$4\ C_{31}H_{35}O_{16} + 127\ O_2 \rightarrow 124\ CO_2 + 70\ H_2O$	31.75
Sulfur*	S	32.06	$S + O_2 \rightarrow SO_2$	1.00
Titanium	Ti	47.88	$Ti + O_2 \rightarrow TiO_2$	1.00

Oxygen-Exchange for a Generalized Reaction

Consider the generalized reaction between one or more oxidizers and one or more fuels. We write the chemical equation as

$$x_0(\text{Oxid}_1 + y_1\text{O}_2 + y_2\text{Oxid}_2 + \cdots) + x_1\text{Fuel}_1 + x_2\text{Fuel}_2 + \cdots \rightarrow \textit{products} \quad (6)$$

Here the x's and y's are the (unknown) coefficients necessary to balance the equation. If there is just one oxidizer, x_0 is its coefficient. As a mathematical convenience, we take the coefficients of the other oxidizers, Oxid$_i$, to be a multiple, y_i, of x_0. Note the explicit participation of atmospheric oxygen, O_2, in the process. Its coefficient is x_0y_1. In flash powders, burst charges, and rocket fuels, for example, y_1 may be zero. But for the open-air burning of stars, comets, gerbs, and the like, significant quantities of outside oxygen (and non-zero y_1's) may be necessary to describe the actual reactions, even though O_2 is never regarded as part of any formulation's recipe.

Now let n_{oi} be the number of O_2 molecules produced by Oxid$_i$, and let n_{fi} be the number of O_2 molecules consumed by Fuel$_i$ according to Tables 1 and 2. For oxygen balance, the number of O_2 molecules consumed by the fuel(s) must be the same as those produced by the oxidizer(s) plus those extracted from the atmosphere. Thus, we have

$$x_0(n_{o1} + y_1 \cdot 1 + y_2 n_{o2} + \cdots) = x_1 n_{f1} + x_2 n_{f2} + \cdots \quad (7)$$

(The number of O_2 molecules involved with each atmospheric oxygen molecule is, of course, 1.) This gives us one mathematical equation with potentially many unknowns. In a balanced *chemical* equation, we can multiply each of the coefficients by the same arbitrary number and still have a balanced equation. So in equation 7 we are free to choose any value we wish for *one* of the coefficients x_i or y_i. (We can let $x_1 = 1$, for example.) Then we solve for x_0.

$$x_0 = \frac{x_1 n_{f1} + x_2 n_{f2} + \cdots}{n_{o1} + y_1 \cdot 1 + y_2 n_{o2} + \cdots} \quad (8)$$

When there is only one oxidizer, one fuel, and no atmospheric oxygen involved, as in the flash examples above, we can obtain x_0 uniquely for each chosen x_1. But if two or more oxidizers, fuels, and/or atmospheric oxygen participate in the mix, an infinite number of sets of x_i and y_i values satisfy equation 8, and they are freely adjustable. Once we have chosen the x_i and y_i values, we can calculate the weight percent w_i of any component in the formulation:

$$\boxed{w_i = \frac{A}{x_0 M_{o1} + x_0 y_2 M_{o2} + \cdots + x_1 M_{f1} + x_2 M_{f2} + \cdots} \times 100\% \quad (9)}$$

where M_{oi} or M_{fi} is the formula weight of component *i*, x_0 is given in equation 8, and A equals x_0M_{o1}, $x_0y_iM_{oi}$ or x_iM_{fi} depending on whether the component is the first oxidizer, another oxidizer, or a fuel, respectively. Notice that the amount of atmospheric oxygen does not appear explicitly in equation 9. It influences the value of x_0, but it does not contribute a separate term to the denominator of equation 9—the total mass of composition. That is to say, oxygen's part in the eventual chemical reaction is accounted for, but O_2 is not a component of the manufactured formulation.

Stoichiometric Equivalence

One of the most daunting aspects of pyrotechnic formulation by trial-and-error is the sheer number of tests that must be carried out. A Shimizu publication,[5] for instance, documents 152 experiments on triangle diagrams and 82 more in tables just on blue flame compositions alone. However, with the oxygen-exchange approach, we can create, on paper, many formulations which are stoichiometrically equivalent to any given published composition. Such equivalence in no way insures an identical pyrotechnic effect, but the results, in our experience, are often quite similar. It allows us to build on the painstaking work of others without having to be so indefatigable. In a phrase, our formulations can have higher "convenience quotients". The quality of their performance versus the man-hours necessary for their optimization is much greater.

Adding a Component

As an illustration, suppose we wish to add some sulfur to the equation 1 mixture. Proceeding with full knowledge that sulfur will make the mixture more sensitive to accidental ignition, especially by impact,[6] we seek an equivalent combination. To do so with a zero oxygen demand, we must either increase the amount of oxidizer to consume the extra fuel, or we must replace some of the aluminum with sulfur. Either way, the two fuels must share the one oxidizer. We recall from equation 5 that 6 oxygens are produced by the potassium perchlorate. In the absence of outside oxygen, those 6 oxygens must be divided between the aluminum and the sulfur. If they are divided evenly, we have

$$\begin{array}{c} 3\ (\mathrm{KClO_4} \rightarrow \mathrm{KCl} + 2\ \mathrm{O_2}) \\ 3\ \mathrm{O_2} + 4\ \mathrm{Al} \rightarrow 2\ \mathrm{Al_2O_3} \\ 3\ (\mathrm{O_2} + \mathrm{S} \rightarrow \mathrm{SO_2}) \\ \hline 3\ \mathrm{KClO_4} + 4\ \mathrm{Al} + 3\ \mathrm{S} \rightarrow \textit{products} \end{array} \tag{10}$$

This combination, 67.1% $KClO_4$, 17.4% Al, and 15.5% S, is close to another formula[7] (67:17:16) attributed to Lancaster, but it is not the only possibility. Dividing the oxygen between the two fuels in all possible ways gives the formulations along the straight line in the triangle diagram of Figure 1. All these compositions fall into the region where sound accompanies the reaction, except when the amount of aluminum falls below about 5%. The loudest of them, however, are in the immediate neighborhood of equation 10.

One way to obtain the formulations that fall above or below the straight line is to allow atmospheric oxygen to participate. We can give the compositions either a positive or a negative oxygen demand. Shimizu's Thunder No. 3[3a] (64:23:13), for example, lies below the line. It can be viewed as coming from a process in which atmospheric oxygen is a necessary reactant, namely

$$\begin{array}{l} 3\ (\mathrm{KClO_4} + 0.263\ \mathrm{O_2}) + \\ 5.540\ \mathrm{Al} + 2.635\ \mathrm{S} \rightarrow \textit{products} \end{array} \tag{11}$$

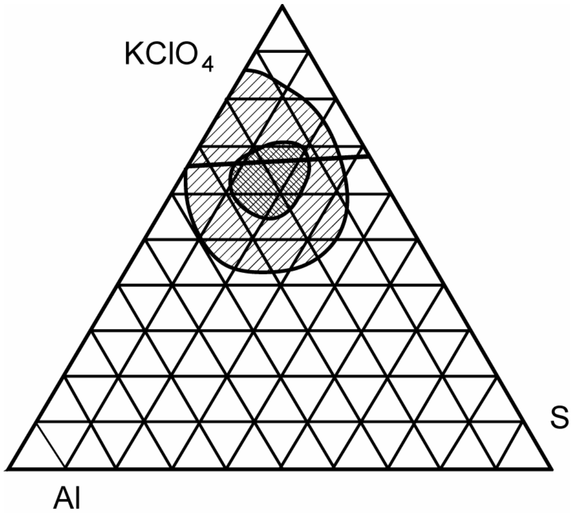

Figure 1. Regions of sound production in flash powder mixtures (reference 2). Those in the darker region produce louder sounds.

Here, oxygen's coefficient, $y_1 = 0.263$, is positive. Thus, this formulation, like all others below the line, has a positive oxygen demand.

We calculated the coefficients of equation 11 as follows: First, we chose one of them at random. We took $x_0 = 3$ so that the equation would have a 3 $KClO_4$ term just like equation 1, but any other choice would have been just as good. Next, we used that coefficient together with the 64% $KClO_4$ of the formulation to calculate the denominator of equation 9. (We could also have used the 23% Al amount—or the 13% S—as the means of determining it.) Knowing the value of the denominator and the other percentages of the formulation, we then solved equation 9 repeatedly for the remaining coefficients. Finally, the value of y_1 came from equation 7.

For compositions above the straight line, like equations 3 and 4, oxygen can also take part, but with a *negative* coefficient. A negative coefficient in a chemical equation simply means that the substance belongs on the opposite side of the arrow. In these above-the-line formulations, the potassium perchlorate can be regarded as present in excess of its stoichiometric necessity. As such, it would produce more oxygen than is needed to consume the fuel(s), and that extra oxygen would appear among the products.

Table 3. Percent Compositions of Fish's "Excellent" Formulations for Green Flame (reference 8) and for Three Magnalium Compositions Derived from the Magnesium Formula by Oxygen Exchange.

Component	Fish's Formulations		Derived Formulations		
Barium sulfate	40.5	42.5	41.5	40.8	42.3
Magnesium	17.0	—	—	—	—
Magnalium	—	13.0	14.9	15.4	14.3
Parlon	18.5	19.5	19.0	19.6	18.3
Potassium perchlorate	24.0	25.0	24.6	24.2	25.1
Hexamine	+10.0	+10.0	+10.0	+10.0	+10.0
Boric acid	+3.0	+2.0	+3.0	+3.0	+3.0
Red gum	+3.0	+3.0	+3.0	+3.0	+3.0
Oxygen Demand	2.856	—	2.856	3.142	2.570

It would be interesting to test whether molecular oxygen *literally* participates pyrotechnically in these ways. But, as we have said, the oxygen-exchange approach would work regardless of the experiments' outcome. Balancing the intermediate oxygen—be it real or imaginary—is nothing more than a self-consistent method of tracking reaction stoichiometry.

Substituting Ingredients: Green Flame

Fish,[8a] after a thorough study of colored-flame compositions containing metal fuels and Parlon, came up with two formulations for green flame which he labeled as "excellent". These are quoted in Table 3.

Suppose that we knew one of these two formulations but not the other. Could we create an "excellent" magnalium formulation if we knew only the magnesium composition, or vice versa, without resorting to brute-force trial-and-error? The oxygen-exchange technique gives us a good chance.

Following the procedure of the previous section, we obtain the chemical equation corresponding to Fish's magnesium formulation.

$$2.477(\mathrm{KClO_4} + 1.002\ \mathrm{BaSO_4} + 2.856\ \mathrm{O_2}) + 10\ \mathrm{Mg} + 1.272\ \mathrm{Parlon} \rightarrow \textit{products} \qquad (12)$$

Here, the coefficient of Mg was chosen arbitrarily, and the stoichiometric contributions of hexamine, boric acid, and red gum were ignored, since they would retain their constant percentages in any derived formulations. The data for barium sulfate is from Table 4.

Our next objective is to create a stoichiometrically equivalent equation that contains magnalium instead of magnesium. Consulting Table 2, we determine that the magnesium in equation 12 consumes 10 (0.50) = 5 molecules of O_2. Since each formula unit of magnalium consumes 11.75 oxygens, Al_9Mg_{10} (the empirical formula for 50/50 magnalium) needs a coefficient of 5/11.75 = 0.4255 to use the identical amount of molecular oxygen. Substituting magnalium, with this coefficient, into equation 12, we obtain[9] the formulation in the third column of Table 3. This has the same y_1 oxygen-demand coefficient as the magnesium composition in the first column. If we increase y_1 by 10% or decrease it by 10%, we get the formulations the fourth and fifth columns, respectively.

Now we have three new formulations to evaluate—not the three dozen or three hundred of an exhaustive test. Since none of them matches Fish's result exactly, we cannot tell *a priori* whether any would also be judged "excellent", but the chances are good one or more of them will measure up. Each will produce at

Table 4. The Decomposition of Selected Oxidizers Not Listed in Table 1. The Factor n_o Is the Number of O_2 Molecules Produced Divided by the Number of Oxidizer Molecules Consumed.

Oxidizer	Formula	For. Wt.	Decomposition Reaction	n_o
Barium sulfate	$BaSO_4$	233.39	$2\ BaSO_4 \rightarrow 2\ BaO + 2\ SO_2 + O_2$	0.50
Bismuth(III) oxide	Bi_2O_3	417.96	$2\ Bi_2O_3 \rightarrow 4\ Bi + 3\ O_2$	1.50
Copper(II) oxide	CuO	79.545	$2\ CuO \rightarrow 2\ Cu + O_2$	0.50
Lead tetroxide	Pb_3O_4	685.0	$Pb_3O_4 \rightarrow 3\ Pb + 2\ O_2$	2.00

least a "good" green flame because the latitude of effectiveness for such mixtures is rather large.[8b] And all three are very close to the recommended composition. The third one, in fact, has almost the identical percentages of oxidizers (but it may be weak in its amount of chlorine donor). The second has the same amount of Parlon (but it has lower percentages of barium sulfate and potassium perchlorate). Regardless of the differences or similarities among them, however, their "convenience quotients" will certainly be high.

Substituting Ingredients: Crackle

With crackling microstars, the Chinese have developed a truly exciting effect. Their compositions, however, usually contain lead oxides which are highly toxic. A typical formulation, attributed to Swisher,[10] is given in Table 5. It is a mixture of lead tetroxide and magnalium. In an effort to defeat the toxicity problem, Jennings-White[11a] came up with a lead-free crackle composition by replacing the lead oxidizer with a blend of bismuth(III) oxide and copper(II) oxide. He then did many laboratory tests to arrive at an optimal result—which remains as the only sure way to do so, this paper notwithstanding. But formulations like his can be predicted theoretically with the oxygen-exchange approach.

Choosing the coefficient of magnalium as 1, we obtain the corresponding chemical equation for Swisher's crackle:

$$\begin{aligned}&5.739\ (Pb_3O_4 + 0.0474\ O_2) + \\ &1\ Al_9Mg_{10} \rightarrow \textit{products}\end{aligned} \tag{13}$$

Since the one formula unit of magnalium consumes 11.75 oxygens, the lead tetroxide must produce an equal amount, minus that which is supplied by atmospheric oxygen. Thus, the contribution of the lead oxidizer is 11.75 − 5.739(0.0474) = 11.48 oxygens. For a stoichiometrically equivalent formulation, any substitute combination of bismuth(III) oxide and copper(II) oxide must also produce 11.48 oxygens. All possible mixtures of Bi_2O_3, CuO, and magnalium that meet these criteria are represented by the line on the triangle diagram in Figure 2. (Mixtures to the right of the line have greater oxygen demands; those to the left have lesser.) However, from Shimizu's study[10] on lead microstars, we find that whenever his compositions contained CuO, it was present only in the 5-17% range. If CuO is included in these proportions in our derived lead-free formulations, the results fall on that part of the line inside the region of effectiveness. As one example, if we fix the CuO percentage at 10%, we get the first

Table 5. The Percent Compositions of Various Formulations for Crackling Microstars.

Component	Swisher	Jennings-White	Derived Formulations	
Lead tetroxide	89.0	—	—	—
Bismuth(III) oxide	—	75.0	75.8	75.0
Copper(II) oxide	—	10.0	10.0	10.7
Magnalium	11.0	15.0	14.2	14.3
Oxygen Demand	0.0474	—	0.0474	0.0474

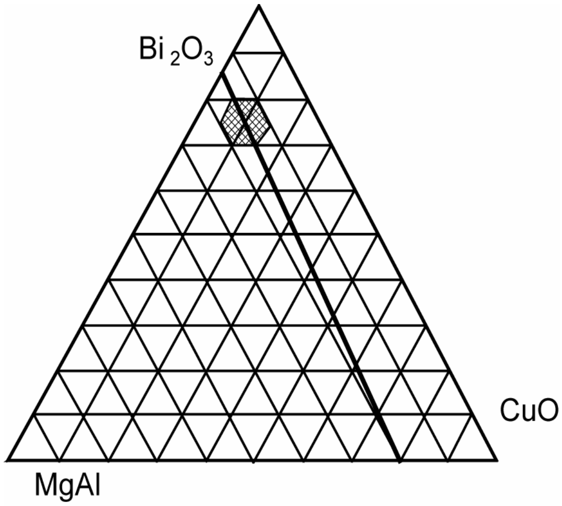

Figure 2. Region of effectiveness of lead-free crackling microstars (reference 11).

derived formulation in Table 5. As another, if we cause four-fifths of the 11.48 oxygens to come from Bi_2O_3 and one-fifth to come from CuO, we get the other tabulated composition. These correspond to the reactions,

$$6.204(Bi_2O_3 + 0.693\ CuO + 0.474\ O_2) + 1\ Al_9Mg_{10} \rightarrow \textit{products}$$

$$6.112(Bi_2O_3 + 0.750\ CuO + 0.474\ O_2) + 1\ Al_9Mg_{10} \rightarrow \textit{products} \qquad (14)$$

respectively. Both of them fit well within those “adjacent formulations in the triangle diagrams at a 5% level of resolution” that Jennings-White[11b] says should “function fairly well”.

Formulating from Scratch

The quest for new and better fireworks effects is the driving force of pyrotechnic research. Blindly testing multitudinous formulations whose compositions are chosen at random is one way to go about it. But that approach is neither efficient nor artful. If we first peruse as many published formulations[7] as we can, however, we can make some broad generalizations. These are found in Table 6. These rough figures are meant to be used only as first approximations. Exceptions can be found in many compositions, even among the examples in this paper. But if we start within these ranges, we are more likely to be in the ballpark. To achieve these initial proportions, and as we proceed toward the final formula, we repeatedly adjust the coefficients in the appropriate chemical equation. We do this and the accompanying calculations, rather than just adjust the parts-by-weight in the mixture directly, because the oxygen-exchange method continually keeps the components in stoichiometric balance.

To illustrate, let us create a gerb mix with ammonium perchlorate as the oxidizer and iron metal as the fuel and the source of sparks. If we choose a zero oxygen demand, we have a two-component system, and we can calculate its stoichiometry without adjusting any coefficients. From the reaction

$$3\ NH_4ClO_4 + 5\ Fe \rightarrow \textit{products} \qquad (15)$$

Table 6. Approximate Ranges of Content for Selected Components in Typical Pyrotechnic Mixtures.

Component	Example	Percent
Oxidizers	$KClO_4$	77–84
	KNO_3	58–75
	$KClO_3$	35–45
Color Oxidizers	$Sr(NO_3)_2$ or $Ba(NO_3)_2$	56–66
Metal Fuels	Mg	11–30
	Magnalium	11–30
	Al	5–45
	Ti	0–20
Chlorine Donors	Parlon, PVC, etc.	6–20
Binders	Dextrin, Starch, etc.	1–14

Table 7. Sets of Stoichiometrically Equivalent Formulations Illustrating the Development of a Gerb Mix by the Oxygen-Exchange Technique.

Component	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
NH_4ClO_4	55.8	71.7	74.8	49.4	53.3	39.0	41.8
KNO_3	—	—	—	—	—	14.5	15.6
Hexamine	—	4.0	6.2	7.1	11.5	6.5	10.5
Red Gum	—	5.3	4.2	9.5	7.7	8.8	7.0
Iron	44.2	19.0	14.8	34.0	27.5	31.2	25.1
Oxygen Demand	0	0	0	2	2	2	2

we obtain the preliminary Mix 1 in Table 7. However, for several reasons, we sense that this formulation needs improvement. First, the percent of metal fuel is on the high side, according to the guidelines in Table 6. We should do something to decrease it. Second, we want the mixture to ignite easily and remain lit. With iron as the only fuel, we know that these aims will be notoriously difficult to achieve; therefore, we should include one or more additional fuels. Finally, we want the particles of carbon, dissolved in the molten iron, to reach their ignition temperature and explode in the atmosphere as sparks.[3b] Thus, we should give the mixture a positive oxygen demand.

As part of the improvement, we add hexamine as a more energetic fuel and red gum as an auxiliary fuel and binder. But in what proportions should they be mixed? Intuition tells us that perhaps we should give slight emphasis to the hexamine. But lacking any concrete motivation, we choose first to give the three fuels about equal thirds of the available oxygen and second, for intuition sake, to give them a 50:25:25 oxygen ratio in favor of hexamine. The three moles of ammonium perchlorate in equation 15 each give 1.25 moles of molecular oxygen for a total of 3.75 oxygens. Giving each fuel 3.75/3 = 1.25 oxygens, we obtain Mix 2. Mix 3 comes from our assigning 1.875 oxygens to the hexamine and 0.9375 oxygens each to the red gum and the iron. Because the n_f values for these fuels—the number of oxygens consumed per mole—are quite different from each other, so are their coefficients in the chemical equations

$$\begin{aligned}
&3\ \mathrm{NH_4ClO_4} + 0.139\ \mathrm{Hex} + 0.0394\ \mathrm{Gum} + 1.67\ \mathrm{Fe} \rightarrow \textit{products}\\
&3\ \mathrm{NH_4ClO_4} + 0.208\ \mathrm{Hex} + 0.0294\ \mathrm{Gum} + 1.25\ \mathrm{Fe} \rightarrow \textit{products}
\end{aligned} \qquad (16)$$

and so are their percentages by weight in the formulation in Table 7. It is not obvious, without the oxygen-exchange approach, to see how those percentages are related.

Now we allow atmospheric oxygen to participate in these equations, with $y_1 = 2$. And this changes the percentages in more non-obvious ways. Mix 4 is the modification of Mix 2, and Mix 5 comes from Mix 3. The chemical equations become

$$\begin{aligned}
&1.15\ \left(\mathrm{NH_4ClO_4} + 2\ \mathrm{O_2}\right) + 0.139\ \mathrm{Hex} + 0.0394\ \mathrm{Gum} + 1.67\ \mathrm{Fe} \rightarrow \textit{products}\\
&1.15\ \left(\mathrm{NH_4ClO_4} + 2\ \mathrm{O_2}\right) + 0.208\ \mathrm{Hex} + 0.0294\ \mathrm{Gum} + 1.25\ \mathrm{Fe} \rightarrow \textit{products}
\end{aligned} \qquad (17)$$

As a final modification, we replace some of the ammonium perchlorate with potassium nitrate. This milder oxidizer will slow the burn rate of the composition to a pace more appropriate for gerbs. As with the fuel mixture, the relative amounts of oxidizers are arbitrary. But the beauty of this technique is that it provides such a wide range of viable choices. By this point, we have zeroed in on the formulation well enough that large differences in the distribution of oxygens have small effects on the resulting percentages. We choose here to have the nitrate supply about 30% of the oxygens that the perchlorate produced in the previous formulations. But choosing, say, 20% or 40% would have changed the outcome here and there only by a percent or two. The "final" equations, for Mix 6 and Mix 7, are

$$\begin{aligned}&1.15\ \left(\mathrm{NH_4ClO_4} + 2\ \mathrm{O_2} + 0.433\ \mathrm{KNO_3}\right) + 0.139\ \mathrm{Hex} + 0.0394\ \mathrm{Gum} + 1.67\ \mathrm{Fe}\ \rightarrow \textit{products}\\ &1.15\ \left(\mathrm{NH_4ClO_4} + 2\ \mathrm{O_2} + 0.433\ \mathrm{KNO_3}\right) + 0.250\ \mathrm{Hex} + 0.0294\ \mathrm{Gum} + 1.25\ \mathrm{Fe}\ \rightarrow \textit{products}\end{aligned} \tag{18}$$

Mix 7 is quite similar to a formulation that one of us (EJC) developed and put into commercial production in the Ukraine. (It uses the Russian-manufactured binder *iditol* in place of the red gum.) This product, a gerb called "Cold Fountain", shoots a plume of brilliant sparks over two meters high. Remarkably, for most of that height, the plume is benign enough that it will not burn bare skin—hence the name.

Conclusions

A pyrotechnic formulation is a combination of oxidizers and fuels. Starting with a reasonable set of decomposition reactions for the oxidizers and a set of plausible combustion reactions for the fuels, we can form a preliminary chemical equation for the formulation's eventual reaction. We balance it by balancing the oxygens involved—including as much atmospheric oxygen as we please. This equation will then have standardized products that come from the tabulated oxygen reactions. There is nothing mystical about these products. Anyone may alter them into a different self-consistent set. Whatever their identities, they may or may not be present in the actual reaction, and it does not matter. We focus only on the coefficients of the reactants. With proper adjustment, we transform the preliminary coefficients into those for the equation that corresponds to the optimized pyrotechnic formulation.

Of course, for any new composition, we do not know the optimized formula. The only way that can be discovered is by extensive testing. So the "proper adjustment" of the coefficients involves a certain art. We start either with a published formulation or with a bare-boned mixture of one oxidizer and one fuel. Then we make additions or substitutions as dictated by our experience, education, or intuition. All during this creative process, we rely on the model that molecular oxygen is the currency of exchange in the reaction. The oxidizers jointly produce oxygens, we say, and, together, the fuels consume those same oxygens. When we control (on paper) the distribution of these oxygens by means of adjusting coefficients, we are also specifying the composition of the mixture. And all the while, we are keeping the proportions stoichiometrically consistent.

The oxygen-exchange approach does not eliminate the need for experimentation. It has no built-in method of evaluating a formulation. It cannot specify the ideal mesh size of a component or the identity of the solvent most useful in binding. Nor does it account for kinetic or thermodynamic differences in reactions. But it can be a powerful means of narrowing the experimentation to a few theoretically-promising candidates, and thereby it can increase the "convenience quotients" of new formulations.

References

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2) R. Lancaster *et al.*, *Fireworks: Principles and Practice*, Chemical Publishing Co., New York, 1972, p 120.
3) T. Shimizu, *Fireworks: The Art, Science and Technique*, Pyrotechnica Publications, Austin, TX, 1981; (a) p 230; (b) p 75.
4) A. A. Shidlovskiy, *Principles of Pyrotechnics*, Mashinostryeniye Press, Moscow, 1964, p 52.
5) T. Shimizu, "Studies on Blue and Purple Flame Compositions Made with Potassium

Perchlorate”, *Pyrotechnica* VI, 1980, pp 5–21.

6) C. Jennings-White and K. Kosanke, “Hazardous Chemical Combinations: A Discussion”, *Journal of Pyrotechnics*, Issue 2, 1995.

7) An excellent and ever-growing database of pyrotechnic formulations is maintained by Andrew Krywonizka on the Internet: http://www.pangea.ca/~gryphon ,1998.

8) Troy Fish, “Green and Other Colored Flame Metal Fuel Compositions Using Parlon”, *Pyrotechnica* VII, 1981; (a) pp 25–37; (b) p 30.

9) Spreadsheet programs that perform these calculations are easily written. Two examples, one for Corel Quattro Pro and one for Microsoft Excel, are available on the Journal of Pyrotechnics Web Site:http://www.98.net/jop, 1998.

10) T. Shimizu, “Studies on Mixtures of Lead Oxides with Metals (Magnalium, Aluminum, or Magnesium)”, *Pyrotechnica* XIII, 1990, pp 10–18.

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