

Quantification of Visible Aerosols from Pyrotechnics: Metal and Metal Compound Additives

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Abstract: *The effect of metal and metal compounds commonly used in pyrotechnics on visible aerosol development at high relative humidity has been investigated in combustion experiments using a combustion chamber. Ammonium perchlorate/hydroxyl-terminated polybutadiene as oxidant/fuel system allowed aerosols generated from the additives to be observed in the absence of particles generated from the base composite. For magnesium and magnalium and all flame coloring agents except barium nitrate, light extinction measurements at 80% relative humidity were found to be proportional to the mass concentration of hygroscopic metal compound particles which are formed at high temperatures from metal chloride or metal vapors during combustion. Low visible aerosol development under humid conditions was observed for aluminium and titanium which have higher boiling points than magnesium and do not readily vaporize during combustion, as well as for barium nitrate which forms too small hygroscopic barium chloride particles and iron(III) oxide which, because of its low boiling point, forms coarser iron(III) chloride particles at lower temperatures.*

1. Introduction

The use of metal compounds and metal powders is essential for flame coloration and the generation of spark effects in pyrotechnics. Together with combustion products from the pyrotechnic composition base components their reaction products are found in emissions of very fine aerosol (smoke) particles in the range of a few hundred nm.¹⁻³ The particles consist of solid metal chlorides or oxides which can act as condensation nuclei for HCl and H₂O vapor⁴⁻⁶ emitted by the pyrotechnic composition. Though such particles scatter light only weakly at their initial size, they produce visually opaque aerosols^{7,8} when they grow in size, reaching a maximum in light scattering efficiency at around 1 μ m for visible light (~500 nm), if number concentrations are conserved.^{9,10}

Metal powders of various particle size and type find use in gold to silvery-white light, flash, sparkle and tail effects. These light effects are based on continuous spectrum emissions of high temperature particles.¹¹ Practical safety and combustion performance limit the common metal types to aluminium (Al), magnesium (Mg), magnalium (Mg-Al, i.e., ~50% alloy of Mg and Al) and titanium (Ti). For colored flames of green, blue, yellow and red, respectively, as well as their mixtures, only compounds of barium, copper, sodium and strontium are commonly used in pyrotechnic compositions. These metals generally need to form volatile

chlorides during combustion to exhibit colored emission lines.^{11,12} Because chlorides of these metals are hygroscopic, they cannot be directly used as additives in pyrotechnic compositions. Therefore the necessary metals are added as compounds which are decomposed and converted to metal chlorides during combustion. The necessary amount of chloride is generally provided by a dedicated chlorine donor compound or hydrochloric acid produced by the oxidant such as ammonium perchlorate (AP). These metal chloride vapors produce fine aerosol particles at high number concentrations when the exhaust gas is rapidly diluted and cooled to ambient temperatures.

AP, despite its good performance in producing colored flames, is less common in firework compositions. It also corresponds to oxidant/fuel (binder) systems in pyrotechnics due to the recent desire to reduce solid residue fallout. It finds heavy use in propellants and produces virtually no solid ashes or aerosols under dry conditions in contrast to oxidants based on the more common potassium salts.¹¹ Though its relatively high excess of HCl emissions is known to produce visible aerosols under high humidity, combustion chamber experiments have shown in previous work that the effect is limited to relative humidity (RH) higher than 85%.¹³ The effect of additive metals and metal compounds on visible aerosol generation, particularly at high relative humidity conditions, was studied in this work by analyzing aerosol development trends in that combustion chamber.

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Table 1. Formulations of composites based on ammonium perchlorate/polybutadiene

Main formulation			Flame coloring and sparkling effect additives		
HTPB	AP	Curing agent	Compound	Effect	Additive ratio (%)
14.5%	81.9%	3.6%	Ba(NO ₃) ₂	Green	5–20
			CuO	Blue	0.5–20
			Na ₂ C ₂ O ₄	Yellow	1–20
			SrCO ₃	Red	1–10
			Fe ₂ O ₃	Catalyst	2–10
			Al	Sparks, silver flames	10–30
			Mg	Flame modifier	5–20
			Mg–Al	Sparks, white flames	5–30
			Ti	Sparks	5–30

2. Experimental

2.1 Pyrotechnic compositions

As oxidant/fuel system with only negligible visible aerosol over a wide relative humidity (RH) range up to 85% allowing quick laboratory scale production, ammonium perchlorate (AP)/hydroxyl-terminated polybutadiene (HTPB) was chosen. Potassium perchlorate is much more common as an oxidant in pyrotechnics but is known for producing large amounts of solid particles including large fallout particles and fine visible aerosols. Another alternative is potassium nitrate which, as a chlorine-free system, has little visible aerosol output but generates less intense light and large amounts of large particle residue/fallout. The AP/HTPB

system, on the other hand, allows aerosol generation induced and amplified by additive compounds to be observed with little interference from fallout losses or particles generated by the oxidant/fuel system of the base composite. HTPB was treated with a curing agent (polymeric methylene diphenyl diisocyanate) mixed with AP and varying amounts of additives as shown in Table 1. The composites were then rolled out as sheets that could easily be cut to appropriate sample sizes after curing overnight.

2.2 Combustion chamber

A chamber already described in previous work¹³ consisting of a cubic steel frame covered with clear acrylic sheets at the top and three sides, a stainless steel floor and a detachable soft PVC sheet at the front side was constructed as shown in Figure 1. Light extinction measurements were provided by laser sensors (a) (Keyence LX-100, $\lambda = 670$ nm) installed in the chamber at distances of 77.5 and 10 cm and a flow of aerosol was transferred to a modified particle size distribution (PSD) analyzer (HORIBA LA-920) through a pipe (12 mm i.d.) of stainless steel serving as sample suction port (c). After initial temperature and humidity conditions were applied with a humidity controllable type air-conditioning unit (Apiste PAU300S-HC) connected through ducts (e), the chamber was sealed. Room temperature was also controlled by air conditioning to match the temperature setting inside the chamber. Aerosol opacity which was previously found to be virtually independent of temperature was set at 20–30 °C. Samples were placed on a combustion platform (b) and ignited electrically using a nichrome wire embedded in a ceramic tube and air in the chamber was mixed using an electric fan (d) so that a sufficiently homogeneous aerosol was yielded within about ten seconds after combustion. A psychrometer composed of two thermocouples was used as robust humidity sensor.¹³

2.3 Theoretical considerations

2.3.1 Chemical equilibrium analysis

Combustion of AP/HTPB composite pyrotechnics can be interpreted as a two-step process. A premixed flame of

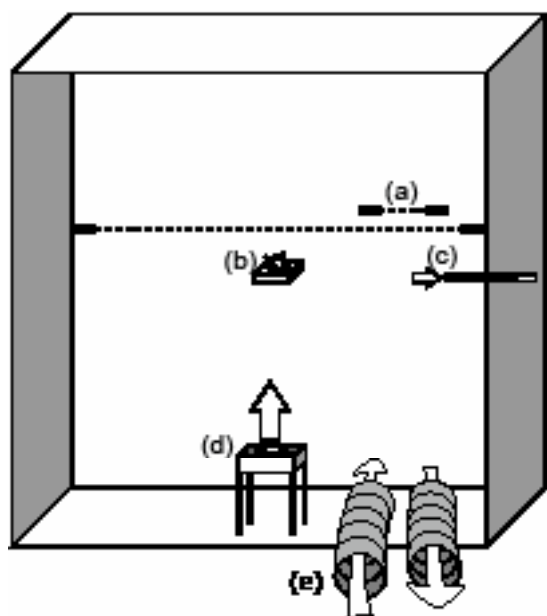


Figure 1. Combustion chamber features (front view). (a) Laser emitter–transmittance sensor assemblies; (b) combustion platform; (c) sample suction port; (d) circulation fan and psychrometer; (e) ducts to humidity control unit.

ammonia with perchloric acid closely coupled with the sublimation and decomposition of AP and HTPB binder provides excess oxidizer to form diffusion flames with fuel fragments released from the binder.¹⁴ Though the kinetics of this process are complex near the surface, especially if additives have to be taken into account, combustion products and flame temperatures can roughly be estimated using chemical equilibrium calculations with the NASA Chemical Equilibrium with Applications (CEA) program package¹⁵ which was extended with thermodynamic data available online.¹⁶ Equilibrium states were analyzed for a dilution series with air for the slightly oxidant-deficient composite. The results were visualized as mass fractions excluding the mass of air additions to track conversion of all species related to the corresponding metals.

2.3.2 Nucleation, coagulation and growth kinetics

Homogeneous and heterogeneous nucleation mechanisms both play important roles in aerosol generation from pyrotechnics. Previous investigations on aerosol size distributions in the range of some hundred nm¹⁻³ strongly support primary particle generation by homogeneous nucleation. Particle nucleation and growth kinetics have however not been extensively studied theoretically for pyrotechnics. Studies on such processes include both experimental measurements and numerical simulations in the vicinity of burning coal particles¹⁷ or in turbulent jets^{18,19} of hot gas. A program for solving particle nucleation and growth problems (Nodal General Dynamic Equation solver; NGDE)²⁰ was extended for calculations of PSDs resulting from condensation of gaseous metal chlorides when they are cooled down by dilution with ambient air. Vaporized metal chloride in hot exhaust from the composite corresponding to a volume of around 2.5 L at standard conditions is diluted to a volume of 1 m³ following an exponential dilution function to imitate the dilution process occurring in the combustion chamber. Particle nucleation, condensation and coagulation are simulated according to the physical properties vapor pressure, surface tension and molecular mass of each of the metal chlorides in liquid state. Trends of mean particle sizes and number concentrations for different concentrations and dilution speeds were analyzed.

Results and discussion

3.1 Analysis of humidity characteristics

Fine aerosol particles are generated at high number concentrations from metal chloride or metal vapors during combustion and act as condensation nuclei for H₂O and HCl vapors when cooled to ambient temperatures. At high relative humidity conditions, they grow to particle sizes up to diameters of around 1 μm within minutes as can be seen in Figure 2a for an aerosol generated from 2 g of an AP/HTPB composite with 10% of CuO additive at 89% RH. Light scattering and absorption processes on such spherical particles of sizes near the wavelength of light are described in detail by the Mie theory²¹ where the corresponding solutions are obtained from Maxwell's equations. Light extinction has been shown previously¹³ to be proportional to sample-mass and can be normalized as a sample-mass specific scattering or extinction coefficient b^* . In the initial growth phase (Phase I) driven by condensation of H₂O and HCl vapors, particles gain in light scattering efficiency until light extinction reaches its maximum at the point indicated by the dashed line. Although maximum light scattering efficiency for a single aqueous particle should lie at a diameter of 1.3 μm (1.0 μm for $\lambda = 500$ nm¹⁰) according to Mie theory, mode diameters of PSDs have only been observed at around 0.6 μm at the maximum of light extinction in 670 nm laser measurements (Figure 2b). Thereafter growth by coagulation and, if particles grow too large, deposition processes on the chamber surfaces take over and light extinction starts to decrease due to loss in particle number-concentration (Phase II). It was not possible to obtain quantitative data as number concentrations from PSD measurements in the current setup, but the continuing growth in size suggests coagulation as the growth mechanism during Phase II. Compared to the rising slope b^* displays during Phase I, Phase II can be considered as having only a small influence on the maximum value of b^* . At very dry conditions the extinction coefficient even reaches a constant value almost instantly and does not decrease notably within the observed time span. The maximum value of sample-mass specific light extinction b^*_{max} can be extracted for each combustion experiment as a measure of the aerosol's obscuring potential.

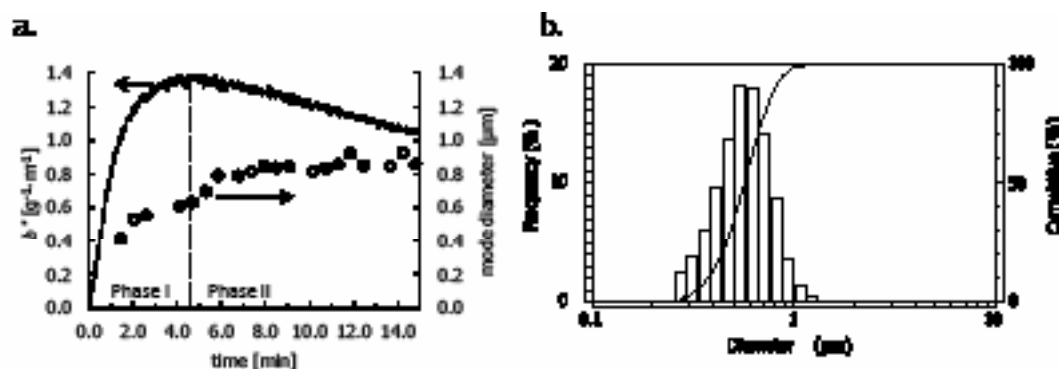


Figure 2. a. Change of sample-mass specific extinction coefficient b^* and mode diameter of aerosol from AP/HTPB composites with 10% CuO additive over time; b. PSD measured at maximum light extinction, 4.7 minutes after ignition.

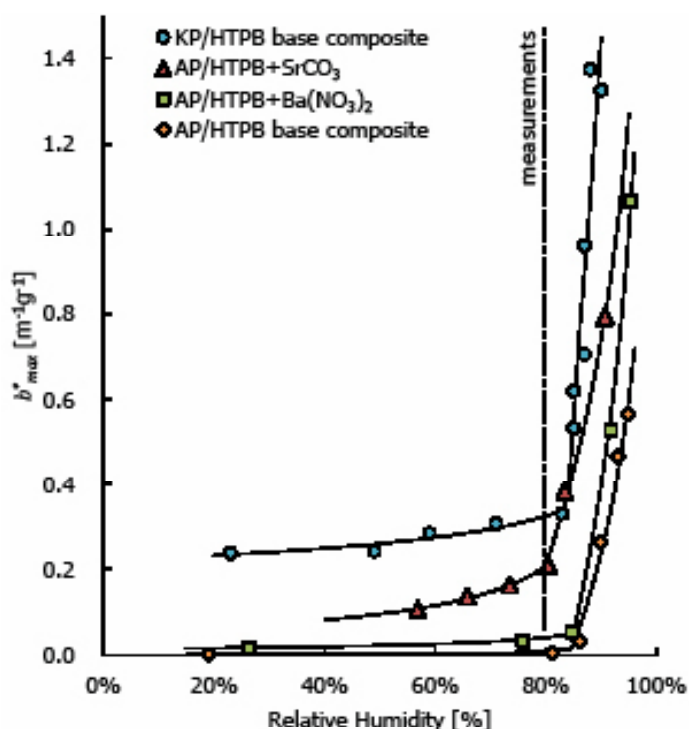


Figure 3. Humidity dependence of maximum sample-mass specific extinction coefficient of KP/HTPB base composite and AP/HTPB composites with 5% of SrCO_3 , $\text{Ba}(\text{NO}_3)_2$ and without additives.

A series of b^*_{max} measurements can efficiently describe the humidity characteristics of a test composite. The base composition of AP/HTPB composites used in this work produces only negligible amounts of visible aerosol up to about 80% RH. In Figure 3, b^*_{max} is plotted against initial relative humidity. Usage of potassium perchlorate (KP) would result in a high baseline throughout the whole humidity range with a sharp increase above 85% RH. Metal compound additives like SrCO_3 induce visible aerosol development from AP/HTPB composites even below 80% RH. b^*_{max} increases moderately with rising relative humidity until it shows a steep rise above 80% RH. Hygroscopic aerosol particles already form aqueous solutions by absorbing H_2O vapors at lower RH and efficiently scavenge excess HCl vapors emitted by the composite. The growth of such particles can be considered as being controlled mainly by the HCl/ H_2O system and causes the steep rise in light scattering efficiency above 80% RH. Visible aerosol increase can therefore be best extracted at 80% RH where the effect of metal compound additives is high while aerosol which may originate from the base composition itself is negligible. Also, losses due to coagulation and deposition processes, which would increase with growing particle sizes at higher RH, can be kept within acceptable limits. Results for metal powder additives and flame coloring additives are analyzed separately, because of differences in their combustion behavior and combustion products involved. Further Fe_2O_3 , which is often used as catalyst in pyrotechnics to increase the combustion speed, is discussed together with the coloring agents.

3.2 Metal powders

Sparkling effects in pyrotechnics are produced by burning metal particles which burn at lower combustion rates than the composite itself. The metal particles are ignited but not evaporated in the pyrotechnic flame and continue burning after being ejected into ambient air. The particles' incandescent light emissions depend on particle temperature and combustion times which are influenced by metal type and particle properties such as size and shape. If particles burn long enough, tail or willow-like effects can be produced. For some metals, particles can also burst during combustion (e.g., Ti) and add a crackling effect. Most of the material, however, remains in the condensed phase during the whole process and very low levels of smoke have been observed for composites containing Al and Ti powders compared to samples containing Mg, as a plot of b^*_{max} at 80% RH against amount of added metal shows in Figure 4.

Mg represents an exception to the combustion mechanism observed for other metals. Due to its low boiling point of 1363 K, compared to the other metals (Al: 2743 K; Ti: 3560 K), it evaporates within the flame, unless the metal particles are very large, and can contribute to higher flame temperatures there. Thus AP/HTPB composites containing only Mg powder additive do not emit incandescent light at all, despite the very bright flame burning Mg produces as bulk material. If solid or liquid particles are present in the flame, however, a bright high temperature incandescent flame can be produced (e.g., white stars with $\text{Ba}(\text{NO}_3)_2$ or Mg flash-compositions). As a result Mg produces fine aerosol particles of MgO at high number concentrations by homogeneous nucleation from the gas phase. These hygroscopic particles absorb HCl and H_2O vapor to form aqueous solutions of MgCl_2 and HCl which grow in size, particularly under high RH. The slope for AP/HTPB with Mg flattens at high ratios of Mg in Figure 4, due to reduced emissions of free HCl from a lower proportion of AP/HTPB

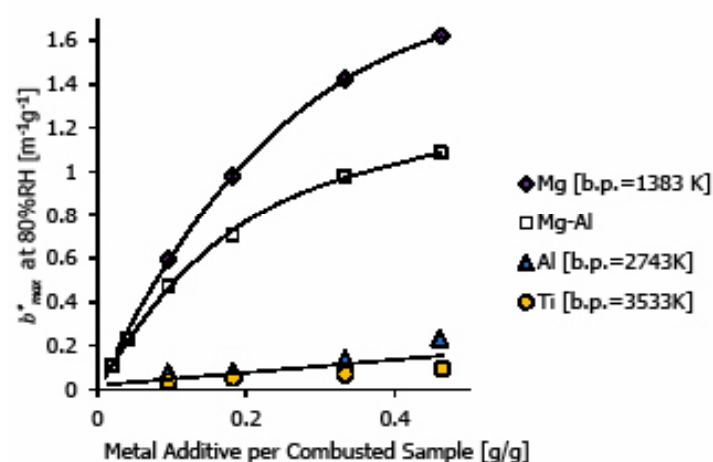


Figure 4. Maximum sample-mass specific extinction coefficient of AP/HTPB composites with Mg, Mg-Al, Al and Ti metal powder additives at 80% RH. Boiling points²² denoted as "b.p.".

base composite (in a 2 g sample) and accelerated coagulation of particles at high aerosol concentrations.

Mg-Al behaves very similar to Mg in respect to visible aerosol formation, but produces bright white sparks. Clearly Al is responsible for the metal particles not evaporating completely during combustion in the composite flame due to its higher boiling point at 2743 K. Some of the Al seems to be evaporated, though, as light extinction measurements suggest. Values of b_{max}^* are significantly higher than would account for half the amount of Mg as would be expected from the proportion of Mg in the alloy. Higher temperatures of metal-particles resulting from better combustion performance of Mg-Al compared to Al also support this. Elemental analysis of aerosol particles should provide insight into the mechanism of this phenomenon.

Particle emissions of aluminium oxides have been reported for combustion plumes of solid rocket motors to have maxima in their PSDs at 0.1 and 2 μm .²³ These particles act as condensation nuclei for H_2O vapor and HCl emissions, which can be observed as thick white rocket trails. Combustion in these propellants, however, follows a different temperature and pressure profile during combustion and uses atomized aluminium, which has combustion characteristics different from the aluminium flakes common in firework pyrotechnics. Aluminium is therefore much more readily vaporized in those propellants than Al and Ti used as spark effect metals in pyrotechnics. In the case of magnalium, Al vapors may be present more abundantly during combustion due to Mg supporting the combustion and evaporation process of the metal particles.

3.3 Flame coloring agents

Flame coloring compounds form volatile metal chlorides

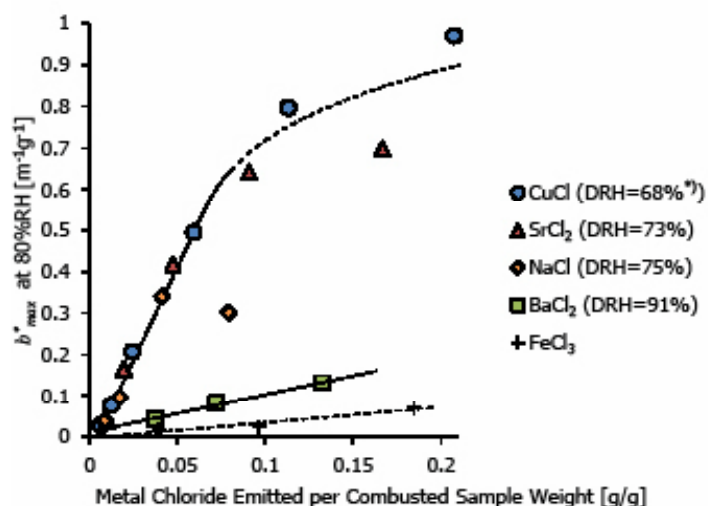


Figure 5. Maximum sample-mass specific extinction coefficient of AP/HTPB composites with CuO , SrCO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Ba(NO}_3)_2$ calculated as chlorides formed during combustion. Deliquescent relative humidity²⁵ annotated as “DRH”. *DRH of CuCl_2 .²⁶

(BaCl_2 , CuCl , NaCl , SrCl_2) during combustion, which produce fine aerosol particles by homogeneous nucleation during rapid cooling of the exhaust gas. Figure 5 shows linear plots of b_{max}^* against metal chloride mass formed per gram of composite during combustion, which flatten out at high additive ratios because combustion performance cannot be sustained by the base composite. Furthermore, all metal chlorides except BaCl_2 show the same slope, which implies that aerosol nucleation and growth processes at high temperatures (boiling points are 1833, 1763, 1686 and 1523 K, respectively²⁴) immediately after combustion result in particle number-concentrations proportional to mass concentrations, even for metal chlorides. Mg from the previous section would also fit the common slope of the colorants if it is considered an analogous nucleation process of MgO from Mg vapor. This suggests that particles produced by rapid condensation at high temperatures have the same average masses rather than diameters or volumes for all compounds. When cooled to ambient temperatures at high RH, these hygroscopic particles grow by uptake of HCl and H_2O and become highly efficient in light scattering.

BaCl_2 , which showed low visible aerosol response, has the highest deliquescence relative humidity value (91% RH at 20 °C)²⁷ among the tested metal compounds (68%, 73%, 75% RH for CuCl_2 , SrCl_2 and NaCl respectively – CuCl is oxidized and converted to CuCl_2 by O_2 and HCl over 50% RH²⁸). HCl vapor therefore does not condense on BaCl_2 particles. Instead, HCl and H_2O vapors are absorbed by heterogeneous nucleation on other hygroscopic particles present in ambient air. This results in the formation of large particles at low number concentration analogous to the base composite without additives. This is observed over the whole humidity range and is also seen in Figure 3, where the values of b_{max}^* of AP/HTPB with 5% of $\text{Ba(NO}_3)_2$ additive only slightly surpass those of the base composite. For $\text{Ba(NO}_3)_2$ additives, PSDs could not be measured in the current setup, because overall scattering efficiencies were too low. Weak forward-scattered light of the transmission lasers has however been observed with the naked eye through the transparent chamber walls at relatively large scattering angles up to around 45°, suggesting particles sized in the range of a few hundred nm.

Fe_2O_3 , which catalyzes decomposition of the HTPB binder during combustion, is converted to gaseous FeCl_3 , and has a much lower boiling point of 553–589 K because of its molecular structure and ability to form dimers. It will therefore stay gaseous longer than chlorides from coloring agents. Although FeCl_3 is very hygroscopic, its presence does not increase light extinction noticeably. In Figure 5, its plot rises only marginally to 0.07 at its maximum addition ratio of 10%. It can be therefore said that FeCl_3 will only form aerosol particles at much lower concentrations than compounds condensing at high temperatures if at all. A plot of b_{max}^* over humidity is practically indistinguishable from plots of aerosol produced by the base composite. Under very high RH of over 90%, aerosol particles grow large enough

for a faint brownish coloration from dissolved FeCl_3 to be observed.

When excessive amounts of additive are used, combustion performance (combustion speed) of the composite is degraded and aerosol opacity does not further increase linearly, because reduction of particle number-concentrations by coagulation effects is accelerated and energy output of the base composite is not sufficient to support complete reaction and vaporization of the metal compounds or even stable combustion. For $\text{Na}_2\text{C}_2\text{O}_4$ the negative effect of its endothermic decomposition reaction appears most distinctly at additions as low as 10% (0.08 as NaCl in Figure 5), while for the same amounts of SrCO_3 (0.09 as SrCl_2) and CuO (0.11 as CuCl) b^*_{max} at 80% RH deviates only slightly from the linear trend. Also, color quality can be reduced by continuous spectrum emissions (condensed phase) or emission spectra (vapors) of interfering by-products, if too much additive is used. Additive ratios for a pyrotechnic composite therefore have to be optimized for each additive.

3.4 Chemical equilibrium and particle nucleation calculations

All metal compounds used as coloring agents are transformed to their metal chlorides according to chemical equilibrium calculations and exist only in the gas phase at adiabatic combustion temperatures. Figure 6 shows the main species containing the respective metal in the case of SrCO_3 as additive. Dilution with ambient air first causes further increase in temperature, because combustion of the oxygen deficient composite can progress. Further dilution, however, cools the mixture and at around 1100 °C after 5-fold dilution the first condensed-phase species of liquid $\text{SrCl}_2(\text{L})$ appears, which subsequently transforms to solid phases of $\text{SrCl}_2(\text{b})$ and $\text{SrCl}_2(\text{a})$ representing high-temperature superionic and low-temperature phases²⁹ of a cubic fluorite crystal-structure, respectively. Analogous formation of condensed phase metal chlorides from their vapors has been obtained as a result for all coloring agents. Only CuO shows the peculiarity of forming Cu metal vapor (which in experiments

can be condensed as metal on cold surfaces held into the flame) before condensation as CuCl . Rapid cooling of those gaseous species by turbulent mixing lead to supersaturated conditions at high temperatures of over 1000 °C under which particles are formed by a homogeneous nucleation process.

Except Mg which at least partly forms metal Mg and MgCl_2 vapors before condensing as MgO , metals used for spark effects only form their oxides in liquid state. Mg follows the same scheme as the coloring agents with the difference of MgO forming from Mg or MgCl_2 vapor. When plotted against MgO mass the slope of b^*_{max} also concurs with the metal chlorides. Other metals' actual combustion processes may not be sufficiently reproduced with chemical equilibrium calculations, but results showing only little aerosol formation support a combustion mechanism with minimal nucleation from the gas phase.

Particle nucleation, growth by condensation of monomers and coagulation processes of vaporized metal chlorides could be described by solving the General Dynamic Equation with the available software.²⁰ The model results in smaller particles and higher number concentrations at higher dilution (and consequently cooling) rates. Dilution rates were chosen so that exponential dilution of exhaust gas from the combustion to the chamber volume of 1 m³ would be complete in 0.0008 to 8 seconds. For all calculations an increase in metal chloride concentration formed from the additive compound would form significantly larger particles as Figure 7 shows for the case of SrCO_3 . Number concentrations show therefore a decreasing trend with mass concentration of introduced metal chloride. This contradicts the trends observed for light extinction properties of the aerosol, which would suggest equally sized particles regardless of concentration. It is an indication of too many assumptions having been made in this application of the simple model beginning at the dilution rates and also including the particle growth and coagulation model itself, which assumes liquid particles, although temperatures approach or even fall below the melting points during the particle growth processes.

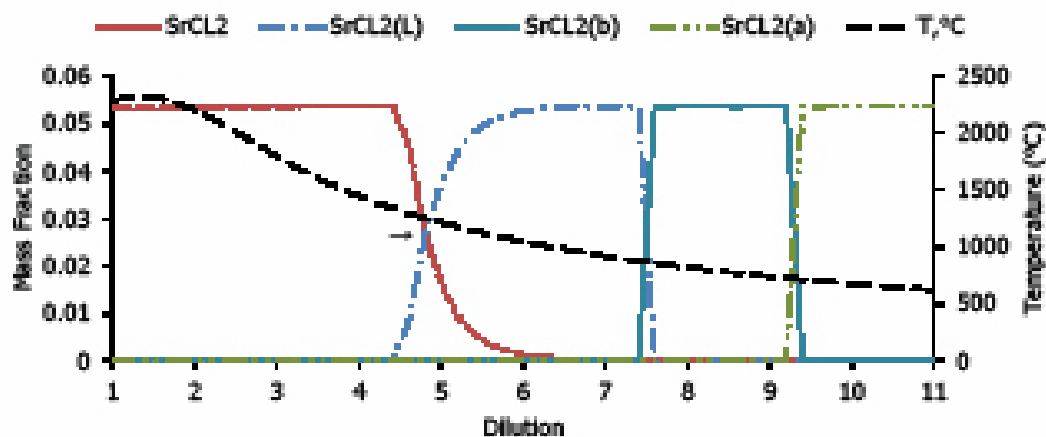


Figure 6. Equilibrium calculation results for AP/HTPB with 5% SrCO_3 additive and dilution with air. Mass fractions exclude mass added by dilution air.

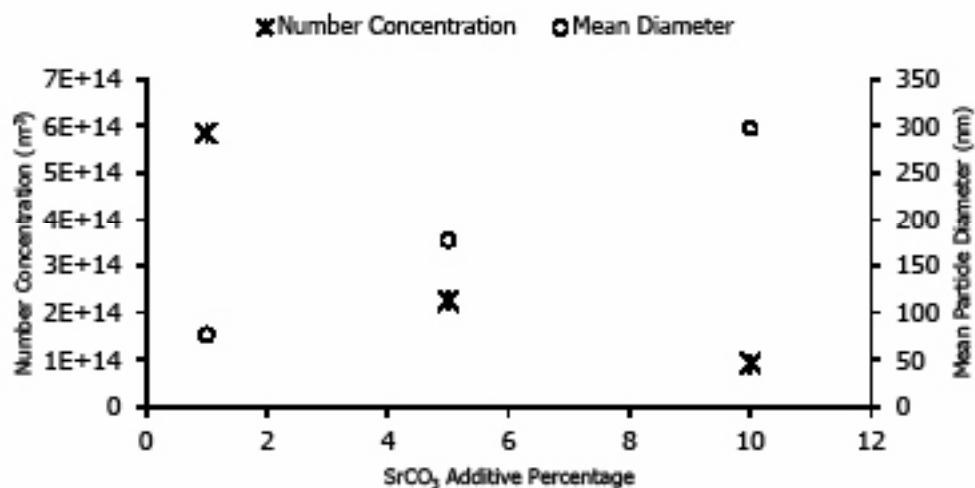


Figure 7. Simulation results modeling particle nucleation, growth and coagulation during dilution of vaporized SrCl_2 with ambient air within about 0.08 seconds.

Conclusion

Promotion of visible aerosol development by common additive metals (Mg, Al, magnalium, Ti) and flame coloring metal compounds ($\text{Na}_2\text{C}_2\text{O}_4$, CuO, SrCO_3 , $\text{Ba}(\text{NO}_3)_2$) after combustion of pyrotechnic compositions based on the low-smoke oxidant/fuel system of ammonium perchlorate/hydroxyl-terminated polybutadiene has been confirmed at high relative humidity above around 80%. With the exception of Al and Ti metal powders for sparkling effects and $\text{Ba}(\text{NO}_3)_2$ for green flames, which produce only minimal visible aerosols, light extinction has been found to increase proportionally with the mass concentration of the corresponding metal chloride (CuCl , NaCl , SrCl_2) or metal oxide (MgO) emissions. Fine aerosol particles are produced through homogeneous nucleation during the combustion process and act as condensation nuclei for HCl produced during combustion and H_2O vapors present in ambient air after dilution. Growth of these particles to highly opaque aerosols occurs distinctly at relative humidity above 80%. For low smoke pyrotechnics producing only little visible smoke even under high relative humidity, Al and Ti are found to be effective spark-generating metals, while from the available coloring agents only Ba (green) is found to be unaffected by humidity. Under RH above 80%, use of Mg and magnalium should be avoided and replaced by Al and Ti as much as possible. Use of flame-coloring compounds of Cu (blue), Na (yellow) and Sr (red) produce thickening smoke at high humidity and needs to be minimized contrary to Ba (green) which does not increase smoke production.

References

- 1 B. Wehner, A. Wiedensohler and J. Heintzenberg, "Submicrometer aerosol size distributions and mass concentration of the millennium fireworks 2000 in Leipzig, Germany," *Journal of Aerosol Science*, vol. 31, no. 12, pp. 1489–1493, 2000.
- 2 A. Dutschke, C. Lohrer, L. Kurth, S. Seeger, M. Barthel and U. Panne, "Aerosol Emissions from Outdoor Firework Displays," *Chemical Engineering & Technology*, vol. 34, no. 12, pp. 2044–2050, 2011.
- 3 A. Dutschke, C. Lohrer, S. Seeger and L. Kurth, "Gasförmige und feste Reaktionsprodukte beim Abbrand von Indoor-Feuerwerk," *Chemie Ingenieur Technik*, vol. 81, no. 1–2, pp. 167–176, 2009.
- 4 A. T. Cocks and R. P. Fernando, "The rates of formation of hydrogen chloride/water aerosols by homogeneous nucleation," *Atmospheric Environment*, vol. 15, no. 7, pp. 1293–1299, 1981.
- 5 N. Kubota, "Propellant Chemistry," in *Pyrotechnic Chemistry*, Whitewater, Journal of Pyrotechnics Inc., 2004, pp. 7–11.
- 6 A. Schenkel and K. Schaber, "Growth of salt and acid aerosol particles in humid air," *Journal of Aerosol Science*, vol. 26, no. 7, pp. 1029–1039, 1995.
- 7 J. A. Conkling, "Smoke and Sound," in *Chemistry of Pyrotechnics*, New York, Marcel Dekker Inc., 1985, pp. 167–179.
- 8 J. T. Hanley and E. J. Mack, "A laboratory investigation of aerosol and extinction characteristics for Salty Dog, NWC 29 and NWC 78 pyrotechnics," Calspan Report No 6665-M-1, Department of the Navy Naval Air Systems Command, Washington DC, 1980. <http://oai.dtic.mil/oai/oai?verb=getRecord&metadataPrefix=html&identifier=ADA093098>
- 9 C. Bohren and D. R. Huffman, *Absorption and scattering of light by small particles*, Weinheim, Wiley-VCH Verlag GmbH & Co. KGaA, 2004.
- 10 M. Z. Jacobson, "Absorption and scattering by gases and particles," in *Fundamentals of Atmospheric Modelling*, Second Edition, New York, Cambridge University Press, 2005, pp. 301–312.
- 11 T. Shimizu, *Fireworks: The Art Science and Technique*, third edn, Austin, Pyrotechnica

- Publications, 1981.
- 12 K. L. Kosanke and B. J. Kosanke, "The Chemistry of Colored Flame," in *Pyrotechnic Chemistry*, Whitewater, Journal of Pyrotechnics Inc., 2004, pp. 25–49.
- 13 R. Y. Abe, Y. Akutsu, A. Shimada and T. Matsunaga, "Quantification of Visible Aerosols from Pyrotechnics: The Effect of Relative Humidity," *Journal of Pyrotechnics*, in press, 2014, preceding paper.
- 14 N. Kubota, "Combustion of Composite Propellants," in *Propellants and Explosives*, second edn, Weinheim, Wiley-VCH, 2007, pp. 181–233.
- 15 M. J. Zehe, "Chemical Equilibrium with Applications," NASA, 2010. <http://www.grc.nasa.gov/WWW/CEAWeb/>
- 16 "NIST-JANAF Thermochemical Tables," National Institute of Science and Technology, 2013. <http://kinetics.nist.gov/janaf/>
- 17 C. L. Senior and R. C. Flagan, "Ash Vaporization and Condensation During Combustion of a Suspended Coal Particle," *Aerosol Science and Technology*, vol. 1, no. 4, pp. 371–383, 1982.
- 18 K. Zhou and T. L. Chan, "Simulation of Homogeneous Particle Nucleation in a Free Turbulent Jet," *Aerosol Science and Technology*, vol. 45, pp. 973–987, 2011.
- 19 T. K. Lesniewski and S. K. Friedlander, "Particle nucleation and growth in a free turbulent jet," *Proceedings of the Royal Society of London A*, vol. 454, pp. 2477–2504, 1998.
- 20 A. Prakash, A. P. Bapat and M. R. Zachariah, "NGDE: Software for Solution of Nucleation, Surface Growth and Coagulation Problems," Departments of Mechanical Engineering and Chemistry, University of Minnesota, 2003. <http://www.me.umn.edu/~mrz/software.htm>
- 21 G. Mie, "Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen," *Annalen der Physik*, ser. IV, vol. 25, no. 3, pp. 377–445, 1908.
- 22 Y. Zhang, "Corrected Values for Boiling Points and Enthalpies of Vaporization of Elements in Handbooks," *Journal of Chemical Engineering*, vol. 56, pp. 328–337, 2011.
- 23 M. N. Ross, P. D. Whitefield, D. G. Hagen and A. R. Hopkins, "In Situ Measurement of the Aerosol Size Distribution in Stratospheric Solid Rocket Motor Exhaust Plumes," *Geophysical Research Letters*, vol. 26, no. 7, pp. 819–822, 1999.
- 24 D. L. Perry, *Handbook of Inorganic Compounds*, Second Edition, Boca Raton, Taylor & Francis Group, 2011.
- 25 L. Greenspan, "Humidity Fixed Points of Binary Saturated Aqueous Solutions," *Journal of Research for the National Bureau of Standards – A. Physics and Chemistry*, vol. 81A, no. 1, pp. 89–96, 1977.
- 26 L. B. Rockland, "Saturated Salt Solutions for Static Control of Relative Humidity between 5° and 40° C," *Analytical Chemistry*, vol. 32, no. 10, pp. 1375–1376, 1960.
- 27 World Meteorological Organization, "Measurement of Humidity," in *Guide to Meteorological Instruments and Methods of Observation*, 2008, p. I.4.
- 28 H. W. Richardson, "The Manufacture of Copper Compounds," in *Handbook of copper compounds and applications*, New York, Marcel Dekker, Inc., 1997, pp. 53–92.
- 29 S. Hull, S. T. Norberg, I. Ahmed, S. G. Eriksson and C. E. Mohn, "High temperature crystal structures and superionic properties of SrCl₂, SrBr₂, BaCl₂ and BaBr₂," *Journal of Solid State Chemistry*, vol. 184, pp. 2925–2935, 2011.