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Effects of Various Additives on the Characteristics of Bubbles Originating from the Combustion of Pyrotechnic Mixtures

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Abstract: The bubbling behaviour originating from the combustion of pyrotechnic mixtures of $KClO_4$/Mg-50%Al alloy, and with additives such as nitrocellulose (NC) and urotropine, were studied by high speed photography. The results revealed that with the addition of the additives the combustion pressure and the gas flow rates increased in the order $KClO_4$/Mg-50%Al/NC (**3**) > $KClO_4$/Mg-50%Al/urotropine (**2**) > $KClO_4$/Mg-50%Al (**1**). Additionally, it is confirmed that the bubbling phenomena can be classified into various stages, *i.e.* single bubbling, pairing and single coalescence, double coalescence and so on.

Keywords: additives, pyrotechnic mixtures, bubble, underwater combustion

1 Introduction

In the past, explosives have been used to create underwater sound for ocean acoustics and seismic experiments. Although explosives are an excellent source of acoustic energy, they can be hazardous to use. Alternatives such as air guns, sparkers, and gas combustive sound sources were developed [1]. Although effective, these devices can be cumbersome and expensive to use at sea. A safe, effective, inexpensive, and reliable low frequency underwater sound source is needed.

Pyrotechnic compositions are usually a combination of several mixed substances, such as an oxidizer, a combustible agent, adhesives *etc*. [2]. They can be ignited under water even without air being involved. In 1995, the French defence company Lacroix Pyrotechnic Group developed a "pyrotechnic-acoustic transmitter" acoustic decoy which can generate massive noise to cope with passive acoustic self-guided equipment, or to interfere with torpedo mechanisms by interrupting the self-motivated device signal [3]. Ouyang Di-hua *et al*. have carried out initial research relevant to this subject; their results showed that bubble oscillation and breakdown are the main acoustic radiation sources; the turbulent noise of combustion is supplementary [4, 5].

One major property of pyrotechnic systems is the quantity of gas released. In this research we have initiated work aimed towards understanding how additives affect gas production, and the bubble characteristics of the combustion of standard pyrotechnic mixtures of potassium perchlorate with magnesium-aluminum alloy. For this initial study we have chosen additive substances that are familiar to those working in the pyrotechnics area. These substances have characteristics that can supplement the production of gaseous products.

In the present work, urotropine (1,3,5,7-tetraazatricyclo decane, $C_6H_{12}N_4$) and nitrocellulose (NC) were used as additives. The bubbling behaviour of the underwater combustion of $KClO_4$/Mg-50%Al alloy with these additives has been studied experimentally using high speed photography. This was done in order to examine the influence of the additives on the bubble characteristics resulting from the underwater combustion of $KClO_4$/Mg-50%Al alloy. The results of this work should provide valuable information for selecting mixtures to be used in future studies of additives in the underwater combustion of pyrotechnic mixtures.

2 Experimental

2.1 Materials

The materials used were potassium perchlorate ($KClO_4$, pure, mesh 90) purchased from Richem Company Ltd. (Beijing, China); magnesium-aluminum alloy (Mg-50%Al alloy, Mg-50%, Al-50%, mesh 120) purchased from Northeast Light Alloy Company Ltd. (Harbin, Heilong-jiang, China); urotropine (pure, mesh 90) purchased from Zhengzhou Jinfengda Chemical Products Company Ltd. (Zhengzhou, Henan, China); and nitrocellulose (NC, pure, mesh 90) purchased from Sichuan Nitrocell Corporation (Chengdu, Sichuan China).

2.2 Procedure

2.2.1 Preparation of samples

The pyrotechnic mixtures investigated, containing $KClO_4$/Mg-50%Al, $KClO_4$/Mg-50%Al /urotropine, and $KClO_4$/Mg-50%Al/NC, are shown in Table 1.

Table 1. Composition of samples by weight %

No.	$KClO_4$, [wt.%]	Mg-50%Al, [wt.%]	Urotropine, [wt.%]	NC, [wt.%]
1	60	40	0	0
2	54.5	36.4	9.1	0
3	54.5	36.4	0	9.1

The dry chemicals required to prepare 20 g batches of the formulations listed in Table 1 were weighed out and allowed to dry overnight in an oven at 60 °C. The chemicals were then individually sifted through a 90-mesh screen. The sifted chemicals were mixed with the binder (phenolic resin, it was dissolved in acetone before being mixed) and blended by hand for 20 min. After mixing, the formulations were passed through a 40-mesh sieve. The granules were dried in air for 2-3 h at ambient temperature to ensure partial curing before consolidation. The mixtures were divided into two 10 g portions and pressed into pellets using a manual press and tooling die at a consolidation dead load of 3 MPa with a dwell time of 10 s. The pellets had diameter 18 mm, height 22 mm, and weighed 9.95-10.04 g.

Five pellets of each formulation were pressed and initiated with an electric match at an energy of 2 V.

2.2.2 Bubble characteristics measurements

The aim of the experiments was to visualize the effect of additives on the bubble evolution characteristics resulting from the underwater combustion of the pyrotechnic mixtures. The experiments were performed in a transparent laboratory tank, 2 m long, 2 m wide, and 1.5 m deep, filled with fresh water. Bubble generation was recorded with a high-speed video camera (Motion System 8000S, MASD-Red Lake Inc.) at 1000 frames per second. The images were digitized directly from the camera. Illumination was provided by a 450 W halogen lamp which illuminated the rear wall of the tank. The opposite wall was covered with a diffusion screen to avoid, as much as possible, undesired reflections and refractions (see Figure 1).

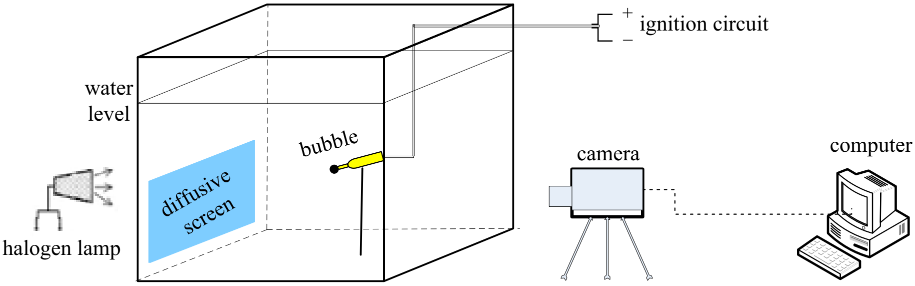


Figure 1. Schematic diagram of experiment set-up.

2.2.3 Combustion characteristics measurements

The combustion pressures of the pyrotechnics in a closed bomb (volume 50 mL) were recorded in air with a pressure transducer (American PCB Company, type M102B, sensitivity 143.96 mV/MPa). The closed bomb was developed according to the verification regulation for closed bomb measuring systems for propellants [6] and was used in [7]. The closed bomb was constructed of refractory steel. The closing bolt and the deaden plug were made of the same steel. The threads were sealed with a polyurethane sealant. The nichrome wires were insulated and sealed in bolt with 502 sealant. Each sample (0.50 g) was weighted into a paper tube (H = 20 mm, R = 5 mm) and consolidated using a ram under hand pressure and placed into the closed bomb. The sample was ignited by electrically heating a coil of nichrome wire buried in the composition at the center of the tube. The schematic diagram of closed bomb apparatus is shown in Figure 2. The burn rate of the pyrotechnic mixtures was measured by target lines at constant pressure. All of the measurements were recorded three times for each composition and then averaged.

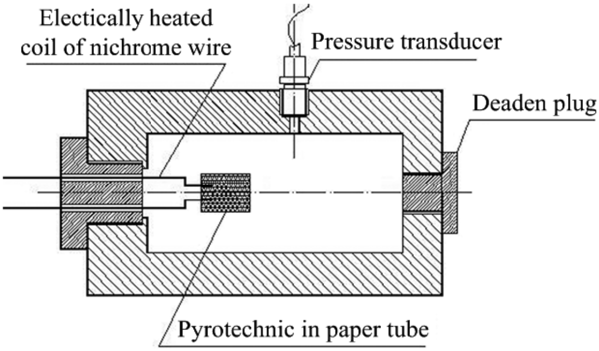
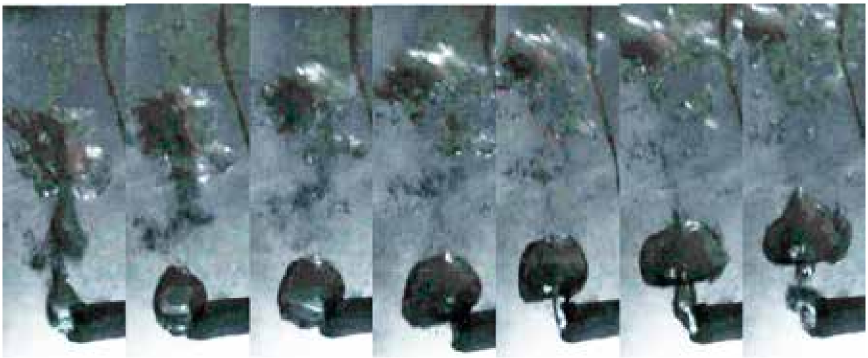


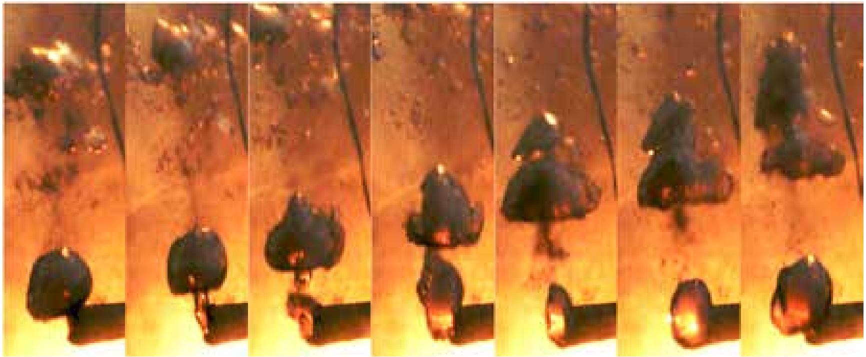
Figure 2. Structural diagram of closed bomb testing.

3 Results and Discussion

A pyrotechnic composition has the ability to produce oxygen for constant combustion. High temperature and high pressure gases as well as some residue, are also produced during this process. When the high temperature and high pressure gases are suddenly injected into water, the pressure will decrease rapidly to the ambient water pressure, which will form a kind of overheated state. Thus the flash vaporization of water will turn into bubbles as shown in Figure 3.



(a) $KClO_4$/ Mg-50%Al alloy



(b) $KClO_4$/ Mg-50%Al alloy/urotropine

(c) $KClO_4$/ Mg-50%Al alloy/NC

Figure 3. Behavior of the bubbles originating from the underwater combustion of the pyrotechnic mixtures (t = 10 ms, film speed 1000 frames per second).

Figure 3 shows bubble formation for the $KClO_4$/Mg-50%Al alloy mixture alone and with various additives. Bubble formation for the $KClO_4$/Mg-50%Al alloy mixture is shown in Figure 3a. The single bubbles are formed strictly periodically, and after their detachment from the nozzle, they move upwards as single bubbles deforming irregularly. The photographs are presented sequentially during the formation of a single bubble at the nozzle. The bubble, just after detachment from the nozzle is almost spherical in shape. Subsequently, it moves upwards as a single bubble and deforms irregularly.

Figure 3b shows bubble formation for the $KClO_4$/Mg-50%Al alloy/urotropine mixture. We can see that two successive bubbles, after their detachment from the nozzle, move upwards as either a coalesced pair or remain as a non-coalesced pair (both possibilities exist). The coalescence between the two bubbles of the pair is termed here as single coalescence and the resulting bubble as double bubble.

Figure 3c shows bubble formation for the $KClO_4$/Mg-50%Al alloy/NC mixture. The coalescence of an already formed double bubble with the consecutive single bubble is characterized here as triple bubble formation, *i.e.* it consists of three coalesced bubbles. We can also see that the double bubble coalesces with the following single bubble at a distance from the nozzle exit, forming a triple bubble, which is moving upwards. As can be seen in Figure 3c, the third bubble, during its formation at the nozzle, elongates in the vertical direction. The elongation of the third bubble is caused by the strong wake formed by the upwards movement of the double bubble.

Figures 3a, 3b and 3c also indicate that the additive determines the various stages of bubble formation and coalescence. This may be attributed to the mixtures with additives having different combustion pressures (gas production), resulting in different gas flow rates.

As shown in Figure 4, we observed that the combustion pressures of all of the $KClO_4$/Mg-50%Al alloy mixtures increased after adding the different additives. For the mixture of the $KClO_4$/Mg-50%Al (**1**) alone the maximum combustion pressure (P_{max}) was 4.58 MPa. The result of the closed bomb experiment for the $KClO_4$/Mg-50%Al/NC (**3**) mixture shows that this mixture had a maximum pressure of 6.10 MPa. For the second mixture, $KClO_4$/Mg-50%Al/urotropine (**2**), P_{max} was 5.23 MPa. The maximum pressure was lower for the urotropine mixture because the quantity of gas produced is less than that for the same weight of NC.

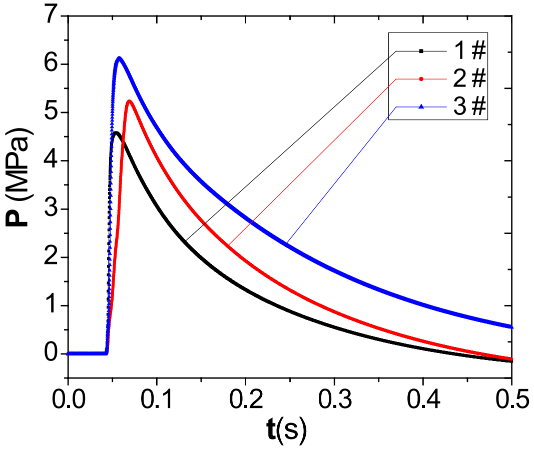


Figure 4. Pressure *vs*. time curves (0.50 g).

Additionally, we can see that the addition of the additives, causes the burning rate and the mass burning rate to be increased, as shown in Table 2. This means that the larger mass burning rate causes a greater gas flow rate at the nozzle exit, and consequently faster bubble growth.

Table 2. Combustion characteristics of samples **1-3**

No.	Mass [g]	Height [mm]	Burning rate [mm/s]	Mass burning rate, [g/s]
1	10.02	19.8	2.60	1.32
2	9.82	21.0	3.52	1.65
3	9.84	20.8	5.62	2.66

For a low gas flow rate (**1**), each bubble forms at the nozzle exit in a strictly periodic manner and rises individually in the liquid, becoming irregular in shape. In the "transition" region, the bubbles start to rise in pairs. For an even higher gas flow rate (**3**), the members of a bubble pair interact with each other forming a "doublet" [8, 9].

N. K. Kyriakides *et al*. [10] has concluded that the nozzle Reynolds number (*Re*) is tentatively the controlling parameter for the bubbling phenomena. The Reynolds number of these mixtures can be compared according to Equation (1), where u is the gas flow rate at the nozzle exit (m/s), ρ_g is the gas density (kg/m^3), d is the nozzle orifice diameter (m), and μ_g is the gas dynamic viscosity (kg/m·s).

$$Re = \frac{u \cdot d \cdot \rho_g}{\mu_g} \tag{1}$$

Equation (1) indicates that with increasing u, Re increases under the same conditions, *i.e.* Re is directly related to u. In another words, the gas flow rate (u) is tentatively the controlling parameter for the bubbling phenomena.

4 Conclusions

The bubbling phenomena of pyrotechnic mixtures of $KClO_4$/Mg-50%Al alloy, alone and with the different additives, were studied by high speed photography. The results revealed (see Figure 3) that the bubbling phenomena can be classified into various stages, *i.e.* single bubbling, pairing and single coalescence, double coalescence and so on. The addition of additives causes gas production (combustion pressure, see Figure 4) and gas flow rate to be increased in the order $KClO_4$/Mg-50%Al/NC (**3**) > $KClO_4$/Mg-50%Al/urotropine (**2**) > $KClO_4$/Mg-50%Al (**1**), and this leads to the above changes in bubbling phenomena. It was concluded that gas flow rate is one of the most important controlling parameters for the onset of each stage.

Acknowledgements

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