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Analysis of the Influence on Emulsion Sensitization Process for Bulk Emulsion Explosive*

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[**ABSTRACT**] Chemical sensitization is a widely applied, convenient and rapid method in foaming the emulsion matrix. However, compared with physical way, chemical method is more complicated, which were rarely researched systematically. In this study, the relation of various involving factors, which include the amount of $NaNO_2$, pH value, different types of acid, catalysts and temperature, and the emulsion foaming process, were investigated. The following were the findings: the foaming process was accelerated obviously by increasing the concentration of $NaNO_2$ and temperature in matrix to improve the activity of $NaNO_2$; a higher rate of foaming was attained if lowering the pH value of matrix, via applying stronger acid or increasing the concentration of weak acid; low temperature sensitization was achieved through introducing M^{2+} as a positive catalyst; when the concentration of M^{2+} reached 35% mass fraction in the sensitizer, a fastest rate was achieved; higher foaming rate resulted in more NO_x production and the matrix presented yellow color especially under a lower pH of the matrix; too low pH in the dispersed phase leads to a poor quality of emulsion; since big useless bubbles were easily formed under a high rate of foaming, for an optimum sensitizing result, the rate should be controlled.

[**KEYWORDS**] emulsion explosive; foaming; chemical sensitization; catalyst
[**CLASSIFICATION CODE**] TD235.2^{+}1

现场混装乳化炸药化学敏化影响因素分析

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[**摘 要**] 化学敏化是一种广泛采用的、方便快捷的敏化方式,相对物理敏化而言,化学敏化受较多因素影响,但缺乏对影响因素的系统性分析。研究了 $NaNO_2$ 用量、pH、不同强度酸、促进剂、温度等对化学敏化的影响。研究表明,通过提高体系中的 $NaNO_2$ 浓度、温度等,提高 $NaNO_2$ 的活度,能够显著提高发泡速率;采用中强酸酸度调节剂要比添加柠檬酸或醋酸获得更快的发泡速率;降低体系的 pH 能够促进发泡反应进行;采用 M^{2+} 作为敏化促进剂,能够实现低温敏化,其质量分数达到 35% 时,敏化速率最快。研究过程中还发现,发泡速率过快,容易产生较多的 NO_x 气体,乳化基质发黄,酸性较强时情况更为严重;分散相的 pH 过低,乳化基质质量较差,极易破乳。发泡速率过快,非常容易产生无效大气泡,生产时应适当控制发泡速率,以期获得最佳的敏化效果。

[**关键词**] 乳化炸药;发泡;化学敏化;催化剂

Introduction

Generally, manufacture process of emulsion explosive (EE for short) mainly includes emulsification and sensitization[1]. The emulsification will influence stability and shelf life of EE[2-4]. While sensitization will affect the detonation performance, especially for bulk emulsion explosive (BEE for short)[5]. Since BEE was introduced into China in 1980s, chemical foaming has always been an optimal way for sensitization and a widely applied, convenient and rapid method to foam the emulsion matrix comparing with physical sensitization[6]. However, as a chemical reaction,

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chemical method being influenced by much more factors was found in the production process[1,7], such as temperature, concentration, catalyst and so on. It is widely known that the bubble accumulated in emulsion contributes to sensitization and density adjustment. If chemical foaming were not properly controlled, an undesired density or bigger bubbles were more likely to produce, however, adjusting the density could hardly create enough hot spot for better detonation and even result in misfire. Thus it's significant for EE manufacturing to investigate chemical foaming process systemically.

1 Test

BEE was selected as a subject in this study. The formula of emulsion matrix was listed in Table 1. At first, 775 g ammonium nitrate (AN) is dissolved into 180 g water, stirring the solution and heating it to 85-95 ℃; secondly, dissolve 15 g emulsifier into 40 g diesel oil in the 2 L container and it is heated to 30-55 ℃; set up an agitator onto the bench drill, turn it up to 700-1 000 r/min to stir the mixture; then stop the bench drill1min later and pour the emulsion matrix into enamel cup. Acid is introduced into dispersed phase, and the pH or different strength acid affecting foaming was studied.

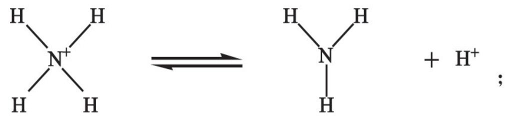
Tab. 1 Formula of emulsion matrix %

Materials	H_2O	AN	diesel	emulsifier
mass fraction	17.0	77.5	4.0	1.5

5%-10% (mass fraction) $NaNO_2$ aqueous solution was the main sensitizer applied and $M(NO_3)_2$ (M is a alkaliearthmetal) solution with different concentration was used as the accelerant. The main sensitizer mix the accelerant with the matrix sufficiently and homogeneously in the enamel cup, and then pour the mixture into a constant volume container and observe the density change regularly.

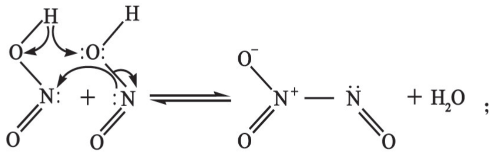
2 Analysis

The mechanism of the reaction between NH_4^+ and NO_2^- catalyzed by acid was proved in this application. NH_3 was generated through the NH_4^+ decomposition reaction; the intermediate, H_2NNO, was formed by the reaction between NH_3 and HNO_2/N_2O_3, and then it decomposed soon and produced N_2. The mechanism could be listed as the below Equation (1) - Equation (7). Generally speaking, Equation (1) - Equation (2) could be the first step and Equation (3) - Equation (7) could be the second step[8-9].



(1)

(2)



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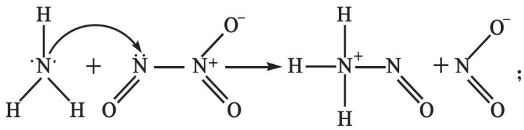

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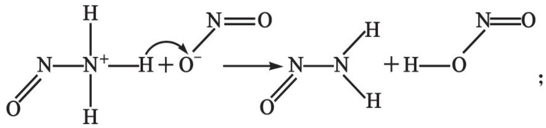

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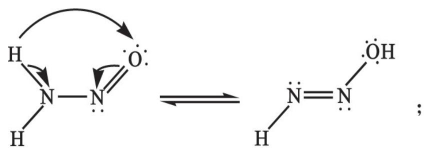

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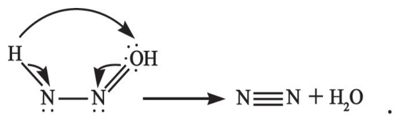

(7)

Chemical foaming process was divided into three distinct stages found in experiment:

1) At the beginning, there was no sufficient amount of NH_3 and HNO_2 generated due to a low reaction rate; and N_2 would be dissolved into internal phase until saturation, so that there were few bubbles and the density scarcely decreased. Thus this stage was called the lag regime.

2) After the lag period, the foaming process began speeding up with a large number of bubbles generated, which resulting in a large decline of the density of emulsion. This stage was also called the kinetic regime.

3) The reactant, after reaction in the kinetic regime, remained a low concentration and thus the foaming rate was low. This stage was called the plateau regime [10].

Several factors affecting the foaming process were investigated here:

1) The amount of $NaNO_2$. 5% (mass fraction) $NaNO_2$ and 10% (mass fraction) $NaNO_2$ solution were applied as sensitizer for foaming. Because of low temperature, the $M(NO_3)_2$ with the same concentration was used as accelerant. The foaming process was presented in Figure 1.

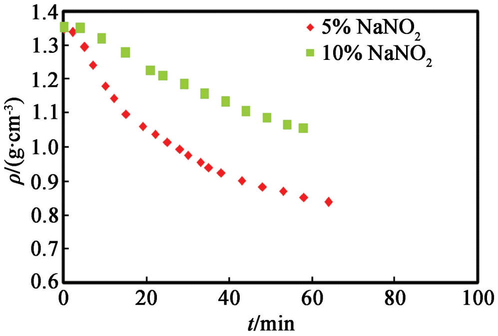

Fig. 1　Foaming process with different amount of $NaNO_2$

From Figure 1, a higher rate of foaming was found due to a higher concentration of NO_2^-, in the meanwhile, the temperature and quantity of $NaNO_2$ were fixed, thus the $NaNO_2$ was significant in foaming process.

2) pH. Acid was utilized as a catalyst mostly. In the experiment, one type of acid (organic acid) was used to adjust the pH of the aqueous phase. In Figure 2, it showed that when the amount of sensitization composition was fixed, the foaming rate would grow by the increase of the pH value. When the pH = 4.5, the lag period lasted for 15 min. It suggested that H^+ with low concentration couldn't catalyze the intermediate reaction at low temperature. It took a longer time to accumulate reactant to proceed the foaming process. Therefore, reducing the pH appropriately could prompt the rate of sensitization.

3) Different strength acid. In the experiment, C

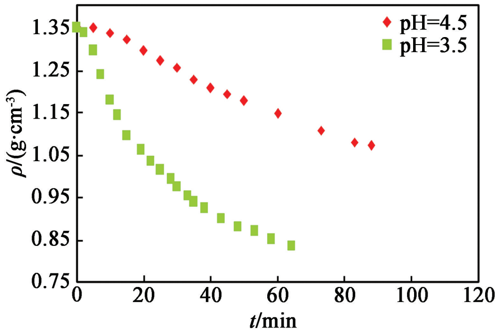

Fig. 2　Foaming process under different pH

acid, B acid and A acid were chosen as the catalyst of sensitization. During the experiment, the same amount of $NaNO_2$ and acid were used to reduce variability at the same temperature. In Figure 3, due to the stronger acid, an increased rate of reaction and a decrease of aftereffect were found in the first stage. Generally speaking, C acid was regarded as a medium-strong acid, B acid and A acid were weak acid, and their pKa (only primary dissociation constant considered) were 2.12, 3.13 and 4.76 respectively. A larger pKa is along with a larger amount of H^+, moreover, C acid and B acid belonged to polybasic acid, using which would increase the foaming process in first two stages compared with A acid. On the other hand, H^+ was consumed too much and thus causing plateau regime coming beforehand. In Figure 3, it showed that when the amount of $NaNO_2$ and acid were fixed, the stronger the acid was, the larger the density was, because stronger acid would result in a higher rate of gassing and a large number of bubbles, a bigger density would consequently created due to a higher rate of bubble escaping, otherwise reaction at low concentration couldn't maintain the reaction.

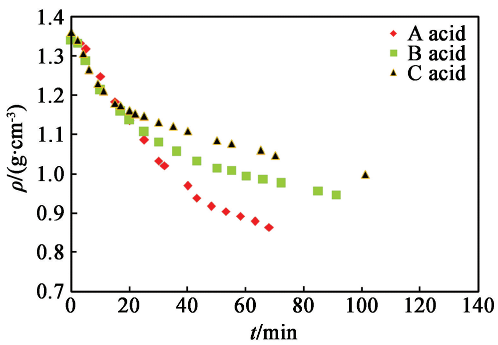

Fig. 3　Foaming process with different acid

In addition, short starting and kinetic regime would lead to big useless bubbles generating easily; stronger acid or low pH could cause more NO_x produced owing to high amount of side reaction product of Equation (2)-Equation(5); Since the acid damaged the emulsifier and decreased the stability of matrix under high temperature, a low pH of aqueous solution caused a high probability of demulsification.

4) M^{2+}. At low temperature, applying $NaNO_2$ and acid wouldn't accelerate the foaming process. In the experiment, the M^{2+} was introduced as accelerant. In Figure 4, when the pH = 4.5, the density of matrix was decreased to 1.15 g/cm^3 over 60 min after adding 35% (mass fraction) M^{2+}, in contrast, it decreased slightly without M^{2+}. It was the reaction mechanism that M^{2+} made compound reaction with NH_3 to reduce the reaction difficulty with NH_3 in the second step and reacting with NO^+ (a variant of N_2O_3) to promote generating N_2. So M^{2+} played a significant role in the foaming process at low temperature. In Figure 5, lag period of two processes wasn't found obvious change in gassing rate. While a lower density in the kinetic regime was found after using a larger amount of M^{2+}, which proved the inference valid.

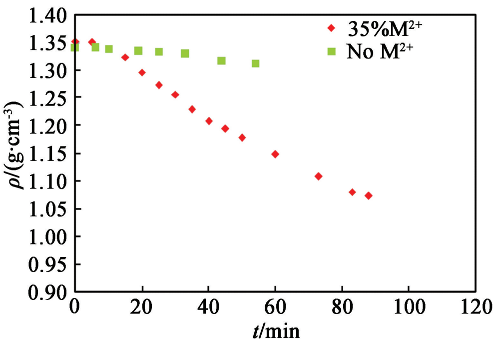

Fig. 4 Application of M^{2+} in low temperature foaming process

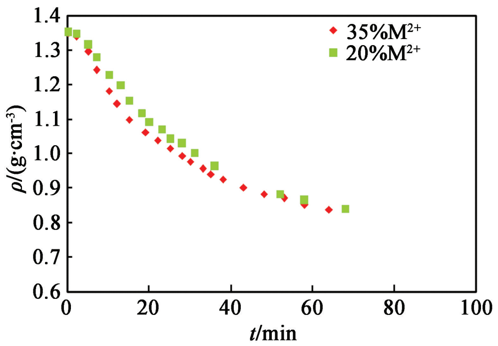

Fig. 5 Foaming process with different mass fraction of M^{2+}

5) T. T, as a catalyzer, was used in bulk emulsion and packing products for decades[1]. Adding a few amount of T, emulsion could create a high foaming rate and the reaction mechanism was showed as Equation (8)- Equation (9)[10]. NO^+ combining with T reacted much easier with NH_3 than NO^+.

$$NO^+ + T \longrightarrow NO^+T; \tag{8}$$

$$NO^+T + NH_3 \longrightarrow N_2\uparrow + H_2O + T + H^+. \tag{9}$$

It's important to note that it's easy to generate useless big bubbles which would be harmful for initiation when, T was applied. Therefore, T should be controlled in a reasonable amount during test or practice.

T was added with 0, 0.05%, 0.10% and 0.15% (mass fraction) into emulsion at 60 ℃, and the rate of reaction was showed in Figure 6. When the amount of T was 0.15%, a lot of big useless bubbles generating and sound of collapse of bubble were observed.

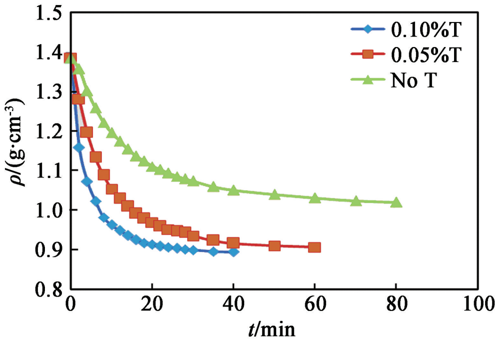

Fig. 6 Gassing process with different concentration of T

6) Temperature. In the experiment, the new made matrix was cooled to 40 ℃ and 50 ℃ respectively and then 10% (mass fraction) $NaNO_2$ solution was introduced to sensitize. The foaming process was showed in Figure 7. In Figure 7, a higher rate of foaming was found when the temperature was 50 ℃ in the lag period and kinetic regime, and a lower top density was tested in the plateau regime.

3 Conclusion

The amount of $NaNO_2$, pH, different strength acids, catalysts and temperature, which influence the foaming process of emulsion were investigated in this paper. In the industrial production process, many other factors were found, such as device, sensitization

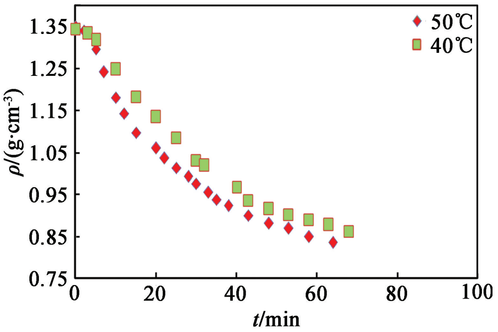

Fig. 7 foaming process at different temperature

mode and emulsification mode. In the test, homogeneous and tiny bubbles were found in lowering the rate of foaming. As a result, we should consider those factors in a comprehensive way and reduce the rate in a proper range to gain a good sensitizing result. Thus, a comprehensive method was set up for better understanding. Besides, through test analysis, trend data could be acquired in directing to solve problems in manufacture process, and further it would improve production control level.

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