Guide for stability evaluation of ammonium nitrate-based emulsions

Amanda Rie Funaki[1,2]
https://orcid.org/0000-0002-6780-309X
Marcelo Kaminski Lenzi[1,3]
https://orcid.org/0000-0002-0103-9017
Alexandre Ferreira Santos[1,4]
https://orcid.org/0000-0001-5885-3637

[1]Universidade Federal do Paraná – UFPR, Departamento de Engenharia Química, Curitiba – Paraná – Brasil.

E-mails: [2]riefunaki@yahoo.com.br, [3]lenzi@ufpr.br, [4]alexfsantos@ufpr.br

Abstract

This article aims to compile stability measurement tests for explosive emulsions (EE), which were developed and used in the last decades. So, it could serve as a stability guide for EEs. The main methodologies to evaluate the condition of the emulsion's matrix is through microscopy, DLS, viscosity, and rheology, which can preview the stability of a freshly manufactured emulsion within maximum 30 days, since it can undergo physically (centrifugation, compression, and direct contact with water). Thermal tests for (freeze-thaw) can also be performed.

keywords: explosive emulsion, stability, ammonium nitrate, crystallization.

1. Introduction

Explosive emulsions (EE) are widely used in blasting operations, such as structural demolition, mineral extraction, quarries and tunneling (Oluwoye *et al*., 2017; Silva *et al*., 2006). Recent studies show that EEs can also be used to obtain metallic nanoparticles (spherical zinc oxide, iron oxide, doped copper, nanometer sheets of composites of zinc and lithium oxides) because it is a low-cost method to manufacture nanomaterials on a large scale through controlled detonation (Xie *et al*., 2006; Wang *et al*., 2020; Luo *et al*., 2012; Xie *et al*., 2009). They are also used in metalworking, explosion, welding, and bar connection because of their acceleration ability (Yunoshev *et al*., 2018; Yunoshev *et al*., 2013).

The latest developments of ammonium nitrate-based explosives are liquid-liquid suspensions, providing a safer explosive with good water-resistance after ANFO (Ammonium nitrate fuel oil) (Wang, 1994). EE is a polydisperse system of two immiscible liquids, where 5 – 85% of a supersaturated aqueous solution (known as the oxidant phase),

mainly composed of ammonium nitrate and other salts (sodium nitrate, calcium nitrate, sodium perchlorate, ammonium perchlorate, urea nitrate), is dispersed into 2 – 7% of the fuel phase (paraffin, mineral oil, vegetable oil and/or diesel oil), together with 0.5 – 2.5% of surfactants. This reduces the interface between both phases and organizes them in polyhedral structures named micelles. Owing to the position of the liquid phases, it is classified as water-in-oil (W/O) and because of the range of the dispersed particle size, as macroemulsion. It is a significantly stable suspension of liquid particles, presenting good kinetic stability over several weeks. However, it is a thermodynamically unstable system (Wang, 1994; Tadros, 2009; Rosen, 2004; Leal-Calderon *et al*., 2007; Kovalchuk *et al*., 2012; Wilson, 2018; Tian *et al*., 2011).

Stability is one of the key properties of emulsions, since the emulsion goes through several pumping processes until its final application. It depends on temperature, composition, distribution of droplet size, surface area and separation

distance between droplets (Tadros, 2009; Rosen, 2004; Leal-Calderon *et al*., 2007; Harnby *et al*., 1992).

There are some recent reviews about explosive emulsions. Kramarczyk *et al*. (2022) presented main aspects of explosive emulsions (definition, stability, sensitization, additives, detonation performance and applications) in a summarized and didactic way; Zhang & Zhao (2022) presented the mechanisms of stability and instability of emulsions in detail. However, it presents only methodologies to evaluate the emulsion's long-term stability, not presenting tests to predict the instability of a newly manufactured emulsion.

In this article, a brief review is presented regarding the main factors that influence on stability of EEs and their quality. In addition, methodologies used by researchers in the last two decades are described, whether from newly manufactured emulsions or over time. This article aims to serve as a stability guide of EEs for those who would like to learn more about EE stability or work on their development.

2. Main factors affecting EE stability

The main indicator of destabilization of explosive emulsions is the crystallization of ammonium nitrate (Figure 1), which occurs through the nucleation mechanism of ammonium nitrate crystals. It is a kinetically slow process and can take months to occur. The emulsion destabilization mechanisms are not by flocculation, coalescence, or creaming (Wang *et al.*, 2017; Zhang *et al.*, 2017). The next topics describe the main factors that affect the EE's stability.
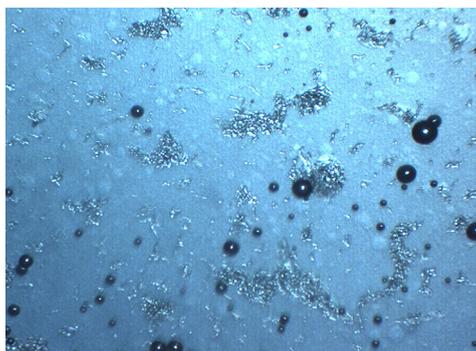

Figure 1 - Signals of destabilization of explosive emulsion through appearance of ammonium nitrate crystals. Note that there are some dark spheres. They are entrapped air bubbles, not crystals.

2.1 Emulsifier

Surfactants (acronym for surface-active agent) are the most widely used emulsifiers, and in addition to dispersing one phase into another, they are also essential to keep the colloidal system stable. Their main function is to decrease the interfacial tension γ, which causes droplet size reduction according to their activity (*a*) or concentration. The reduction in surface tension due to the action of surfactants occurs until the beginning of the formation of micelles (organized structures of surfactants at the interface), which is described by the Gibbs adsorption equation (Eq. 1), stated below, where R is the gas constant, T is the absolute temperature, Γ is the surface excess. The value of γ depends on the nature of the emulsifier and oils (Tadros, 2009; Holmberg *et al.*, 2002).

$$- d\gamma = R\,T\,\Gamma\,lna \tag{1}$$

A semi-empirical method to select a surfactant is the use of HLB, which is the hydrophilic-lipophilic balance, an original concept by Griffin in 1949 (Harnby *et al.*, 1992). In the case of explosive emulsions, the HLB of the surfactant must be between 2 and 6 (Harnby *et al.*, 1992; Masalova *et al.*, 2011) and must be diluted in the continuous phase (oil).

The most used emulsifiers are based on PiBSA (polyisobutylene succinic anhydride), which provides greater stability to EEs, and sorbitan ester, a low molecular weight emulsifier. The usual concentration of surfactants is between 0.1 and 5.0% (Wilson, 2018; Wang, 1994; Tian *et al.*, 2011; Masalova *et al.*, 2011).

The stability of the formulation with PiBSA-based emulsifiers depends on (Tripathi *et al.*, 2021; Kovalchuk *et al.*, 2012; Zhang *et al.*, 2015): i) its chemical composition because for a stable emulsion, it is necessary to have a good interaction, between the ammonium nitrate and the head group of the PiBSA-based surfactant, and differences in head group functionality can induce crystal nucleation; ii) its manufacturing method, since the higher the molecular weight of the emulsifier, the greater the stability; and iii) their degree of affinity with the water/oil interface. The greater the polarity of the head group, the greater the adsorption force of the molecules (anchoring) on the interface. Thus, the greater the interaction with ammonium nitrate (AN), the greater the stability.

On the other hand, sorbitol monooleate (SMO) is used to reduce the mixing/refining time of the emulsion, since it reduces the droplet size by lowering the kinetic stability during emulsification (Mudeme *et al.*, 2010), and it can provide greater stability to the emulsion, when used together with an emulsifier (Zhang *et al.*, 2015).

Several researchers carried out studies of formulations with different emulsifiers, evaluating their stability. The mains results are presented below, in descending order of stability.

PiBSA-MEA = PiBSA-UREA > PiBSA-MEA/SMO > PiBSA-IMIDE > SMO	Kovalchuk *et al.,* 2012
PiBSA-TEA/SMO > PiBSA-TEA > PiBSA-IMIDEA > SMO	Zhang *et al.,* 2015
PiBSA-TEA > PiBSA-DTEA > PiBSA-L-TEA > PiBSA-STEA	Zhang *et al.,* 2017
PiBSA-MEA > PiBSA-IMIDE ≈ PiBSA-UREA > PiBSA-MEA/SMO > SMO	Tripathi *et al.,* 2021

The emulsion is more kinetically stable under shear when the concentration of emulsifiers is lower because the higher the concentration of the emulsifier, the lower the elasticity of the emulsion, while the interfacial tension remains unchanged (Mudeme *et al.*, 2010). Regarding storage, several studies show stability gain with increasing emulsifier concentration (Zhang *et al.*, 2017; Kovalchuk *et al.*, 2012), since the higher the emulsifier concentration, the greater the compression of the drops, making them smaller (Al-Sabagh *et al.*, 2017; Hayward *et al.*, 2019). However, increasing the emulsifier may not always be an option to increase the stability of the emulsion, since there is an optimal concentration of emulsifier for each formulation (Kovalchuk *et al.*, 2012).

2.2 pH and ionic strength

The stability of the emulsion depends on the separation distance between the drops, resulting from the balance between the electrostatic attraction and repulsion existing between two particles dispersed in a liquid medium (Li *et al.*, 2021). The two main properties that influence the medium are pH and salt concentration.

Changing the pH in the medium will cause direct changes in the distance between the drops, as the behavior of chemical compounds can be dependent on pH (Lin *et al.*, 2021). Because when changing the medium, the hydrodynamic diameter of the dispersed droplets changes, affecting their stability. For chemically sen-sitized explosive emulsions, pH is crucial to provide favorable conditions for reactions (Alilovic *et al.*, 2005; Dlugogorski *et al.*, 2011; O'hara *et al.*, 2001). In addition, it is necessary for the emulsifier to maintain its properties and stability in the final emulsion at a given pH.

Regarding the concentration of salts, the greater the concentration of salts in the medium, the greater the compression of the electric double layer around the particle until a limit, when the salt concentration is very high. With the rupture of the electrical double layer, the particles are vulnerable to agglomeration and desta-bilization. However, when other nitrates, such as sodium and calcium are added, despite the higher concentration of salts, the stability of the formulation increases, as there are structural changes, causing the crystallization point to decrease. Chemically, the distance between nitrate and ammonium ions becomes greater within the droplets (Kovalchuk *et al.*, 2012). Furthermore, the addition of metallic nitrates in the emulsion deteriorates the detonation properties, compared to the emulsion formed only by AN (Xie *et al.*, 2006). The high ionic strength of droplets of emulsions with high concentrations of dispersed phase also contributes to their polyhedral shape (Masalova *et al.*, 2007).

2.3 Particle size and its distribution

The droplet size and its distribution determine the quality of the emulsion needed to have a stable emulsion. The smaller the droplet size of the dispersed phase, the greater the stability (Yakhoub *et al.*, 2010; Zhang *et al.*, 2018). A key parameter complementary to droplet size is the surface area of the particles. It is desirable that the amplitude variation of size be as small as possible, with a lower polydispersity index (PDI) (Harnby *et al.*, 1992; Wang *et al.*, 2016; Li *et al.*, 2021; Zhang *et al.*, 2017).

The crystallization stability of dispersed drops of ammonium nitrate is due to the small size of the dispersed drops. If there is an increase in the size of the drops, there will also be acceleration of crystal-lization and with drop sizes greater than 40 µm in diameter, it will be impossible to avoid crystallization (Masalova *et al.*, 2013). The most stable micelle size range for explosive emulsions is between 0.2 and 5 µm (Wang, 1994).

An emulsion with small micelles in size and with small dispersion in size can be obtained by intense emulsifica-tion (shearing) by a stirrer (Masalova *et al.*, 2013). Also, with the increase in the refining time of an emulsion, there is an exponential droplet size reduc-tion, which has the effect of increasing the viscosity by increasing the area of hydrodynamic interaction between the drops (Sharu *et al.*, 2017).

The micelles have a polyhedral shape, since there is excess energy stored on the surface. This is caused by the elasticity of the system and the high concentration of oxidizing salts, which contribute to high ionic strength (Masalova *et al.*, 2007). So, the drops do not flocculate, aggregate, or cream due to the packing of the drops (Zhang *et al.*, 2017).

By following the size of micelles throughout their aging, a variation in the size of drops was noted, showing that destabilization occurs with the crystal-lization of the supersaturated solution of oxidizing salts (Zhang *et al.*, 2017). However, moments before crystallization, it is not possible to verify significant changes in the size and distribution of the dispersed drops (Wang *et al.*, 2017).

2.4 Temperature

The temperature of preparation and storage is a very important parameter in the stability of the product. In manufacturing, the temperature between the phases must be close, as a sudden cooling could prevent an adequate emulsification of some types of emulsions (Wang, 1994). In storage, the chemical species can suffer degradation and/or thermal oxidation, presenting a change in color as a visual indication (Gumus *et al.*, 2016).

2.5 Concentration of the dispersed phase (oxidant)

Explosive emulsions have a high concentration of the dispersed phase above 74%, denominated highly concentrated emulsions. It is not possible to obtain a stable emulsion with more than 95% of oxidizing solution, since it is close to the phase inversion point, where the external phase inverts to an internal one and so on (Hayward *et al.*, 2019). The formation of a high concentration system is possible due to the compression of the emulsion, with the transition from spherical to polyhedral droplets in the dispersed phase. Therefore, there is the formation of a viscoplastic liq-uid presenting a gel-like behavior (Mudeme *et al.*, 2010; Zhao *et al.*, 2021; Sharu *et al.*, 2017). For this reason, explosive emulsions do not have mechanisms of destabilization by flocculation, aggregation, or creaming (Wang *et al.*, 2017).

Determining dispersed phase concentration is usually cost and stability dependent. The concentration of the dispersed (aqueous) phase must be determined by the oxygen balance, a thermochemical parameter, so that the formulation can release its energy completely, from the redox reaction between the reagents (Mahadevan, 2013; Wang, 1994).

2.6 Viscosity

Emulsion stability was associated with viscosity according to Stokes' Law for Reynolds laminar flow (Eq. 2 and Eq. 3) in which the higher the viscosity and smaller particle size, the lower the rate of flotation of the emulsion droplets, where (Biessikir-ski *et al.*, 2019; Ma *et al.*, 2017):

$\vec{F}$ – friction; r – Stokes radium of the particle; η – liquid's viscosity; $\vec{v}$ – particle's velocity; V_s – sedimentation velocity of particles; g – gravitational acceleration; ρ_p – particle's density; ρ_f – fluid's density.

$$\vec{F} = - 6 \, \pi \, r \, \eta \, \vec{v} \qquad (2)$$

$$V_s = \frac{2}{9} \, \frac{r^2 \, g \, (\rho_p - \rho_f)}{\eta} \qquad (3)$$

The key properties that impact on viscosity are droplet size, dynamic viscosity of the continuous phase, volumetric fraction of the dispersed phase and the thickness of the interfacial film (Das *et al.*, 1992; Harnby *et al.*, 1992).

Explosive emulsions are classified as non-Newtonian fluids of the Hershel Bulkley type, whose mathematical model is represented by the power law (Eq. 4), where σ is the shear stress, σ_y is the initial yield stress, γ is the shear rate, K and n are constants that characterize the flow (Zhang *et al.*, 2015; Wang *et al.*, 2013). For EEs, $\sigma_y > 0$.

$$\sigma = \sigma_y + K \, \gamma^n \qquad (4)$$

2.7 Type of oil

The type of oil plays an important role in determining the ability to form and stabilize emulsions. The most suitable oils for explosive emulsions are mineral oil and lubricating oil, since they have a consistency that is better than diesel oil. The surfactant must have a similar HLB value, knowing that the higher its viscosity, the greater the balance value (Wang, 1994).

The oil polarity should be as low as possible, since increasing polarity increases the rate of delivering emulsifier monomers to the interface during emulsification, reducing emulsion refinement kinetics and increasing droplet size. Also, the higher the polarity of the oil, the lower the performance. An example of polar oil is biodiesel (Zhang *et al.*, 2017; Mudeme *et al.*, 2010).

Regarding oil viscosity, there is no direct relationship with stability. In the study by Zhang *et al.* (2017), it was verified that the viscosity of the oil that obtained the best stability was 5.65 mm³/s (results between 2.46 and 9.84 mm²/s), because the higher the viscosity of the oil, the greater the hydrodynamic stress, which helps to reduce the size of droplets, but if the viscosity is too high, more time is required for the emulsifier molecules to adhere to the interface.

2.8 Shear forces during and after emulsification

For the preparation of an emulsion, it is necessary to supply energy to expand the interface between the phases and reduce the size of droplets using shear forces, since the formation of an emulsion is not a spontaneous process. For a smaller droplet size, it is necessary to use a high concentration of surfactants and/or high energy, related to the pressure difference inside and outside the droplet. For the drops to be broken into smaller ones, they need to be strongly deformed into ellipsoids, which occurs with an increase in Laplace pressure (Tadros, 2009).

The cutting actions acting in the formation of the emulsion depend on the type of equipment used, which can be high pressure, micro fluidization, membrane or microchannels (Leal-Calderon *et al.*, 2007).

2.9 Composition

Initially, the type of ammonium nitrate used is of great importance. The AN used in emulsions should not be porous or fertilizer grade (FGAN) mixed with urea (UAN), as the AN has an amorphous structure, not forming stable emulsions (Biessikirski *et al.*, 2019). Furthermore, fertilizer grade ammonium nitrate should not be used directly in explosive emulsions, since it contains oily anti-caking agents that destabilize the emulsion. To make its use feasible, the FGAN can be previously treated to remove the anticaking, or additives can be used in the oxidizing solution, to keep the organic material stable in the formulation (Consolin, 2019).

Regarding the concentration of ammonium nitrate in the oxidizing solution, the higher the concentration of ammonium nitrate, the greater its performance. However, with a concentration of ammonium nitrate from 85% on, it is no longer possible to obtain a stable emulsion. So, a commonly used concentration in industries is 83% (Hayward *et al.*, 2019).

The use of complementary nitrate salts in the aqueous phase, such as sodium or calcium nitrate, alters the properties of the oxidizing solution. With their addition at a concentration above 0.1% by mass, there will be a charge separation within the droplets, reducing the chemical kinetics and the point of crystallization, consequently increasing the stability of the emulsion (Kovalchuk *et al.*, 2012; Hayward *et al.*, 2019).

3. Stability evaluation methods

In this section, a bibliographic search of stability analysis of explosive emulsions will be presented, which were divided into 3 groups: (i) tests to evaluate the stability, that is, measurements performed under different conditions to compare the results; (ii) tests with newly manufactured emulsions to predict their long-term stability, with a maximum duration of 30 days; (iii) Evaluation of long-term stability (shelf life), when stored in a predetermined condition.

3.1 Means of evaluation
3.1.1 Particle size and its distribution

In literature, simple methodologies were found for evaluating the size of dispersed droplets and their distribution, based on image analysis obtained from a microscope and treatment with ImageJ software (National Institute of Health, USA). In both studies presented in the Table 1, measurements were made at least 24 h after production.

Table 1 - Methodology of analysis of droplet size with microscope.

Equipment	Methodology	Reference
Olympus IX 81 combined with FV-500	A drop of emulsion was poured over a glass slide. Then, a cover slip was posed, and a drop of immersion oil was poured.	Sharu *et al.*, 2017
Optical Microscope Bioptika	The emulsion was diluted in mineral oil and one drop of this mixture was poured over a glass slide. Over it, a cover slide was positioned, and one drop of immersion oil was poured. The image was captured with a 100x-zoom lens.	Funaki, 2020

Before the analysis through a software, it is necessary to set calibration scale with a calibration slide that is to know the correspondent distance (μm) in a pixel.

The main methodology to automatically evaluate the droplet size is through DLS (Dynamic Light Scattering). The stated methodologies are presented in Table 2. To avoid the light scattering, the emulsion was diluted in oil.

Table 2 - Equipment to analyze the droplets' size.

Equipment	Methodology	Reference
LA-500 (Horiba)	Dilution of hot emulsion in paraffinic oil until it acquires fluidic consistency, so it can flow. Then, a drop of the mixture is poured in hexane under agitation and circulation in a quartz cell, until it reaches an adequate transmittance	Das *et al.*, 1992
Mastersizer-2000 (Malvern Instruments)	Dispersion of emulsion in oil to obtain a diluted solution to avoid the agglomeration of the droplets	Kovalchuk *et al.*, 2012

The results are shown directly by the equipment at the end of the evaluation.

Another methodology tested to measure the size of the drops is using nuclear magnetic resonance, as shown in the study by Hayward *et al.* (2019).

3.1.2 Microscopic evaluation

Changes in stability can be assessed through droplet size and dispersion, analysis of microscopic structures and morphology. In the case of explosive emulsions, whose internal aqueous phase is supersaturated, the appearance of crystals is an indication of the rupture of the droplets, which can be observed microscopically (Funaki, 2020). The use of microscopes to evaluate different properties are presented in Table 3.

Table 3 - Methodologies for microscopical evaluation.

Microscope	Evaluation	Sample preparation	Methodology	Reference
Nikon DS-Fi1 optical microscopy	Microstructure	-	-	Zhang *et al.*, 2017
Leica optical microscope	Crystal formation	-	Use of 500x-zoom lens with unpolarized and crossed polarized together	Al-Sabagh *et al.*, 2017
Cryo-FEG-SEM	Microstructure	The emulsion was frozen with liquid nitrogen at -190 °C. Then, it was fragmented and sublimated at -90°C for 5 minutes. Finally, the samples were covered with platinum at 10 mA for 30 s.	Resulting image was obtained with acceleration voltage of 5 kV	Sharu *et al.*, 2017
Metallographic microscope	Crystal formation	-	Use of 10x-zoom lens	Funaki, 2020

3.1.3 Viscosity

Viscosity is the resistance to flow of a fluid that provides information on the structure of emulsions and serves as a guide to assess stability over time (Becher, 1972; Mahadevan, 2013).

In the research carried out in 2020, the Brookfield rotational viscometer was used to measure the dynamic viscosity before and after each stability test at the same temperature (20 °C) with 50 rpm of rotation and with the use of rotor number 7, which presents the best geometry for the viscosity range of explosive emulsions. Results showed that the most stable formulations had the lowest viscosity variation.

3.1.4 Rheology

The rheological study of explosive emulsions began to be widely studied in the last two decades, with several publications

relating rheology with stability (Zhang *et al.*, 2018; Zhao *et al.*, 2021; Zhang *et al.*, 2015) and with performance (Zhang *et al.*, 2018), since traditional test methods are not sensitive to structural changes in emulsions over time (Zhang *et al.*, 2017).

The study by Zhao, *et al.* (2021) shows that there is a direct correlation between rheology and the stability of explosive emulsions. First, the concept of Bingham number (Bn) was presented, and used to estimate the stability mechanism during shear, where τ_y is the shear stress, σ is the interfacial tension and R is the radius of the dispersed droplet (Eq. 5).

$$Bn = \frac{\tau_y}{(\sigma \, / \, R)} \qquad (5)$$

Afterwards, the increase in the storage modulus (G') was correlated with a reduction in the stability of the matrix by observing that the aging of the emulsion is associated with the crystallization of ammonium nitrate, which directly affects its microstructure and its rheological properties, giving the emulsion solid-like properties. Initially there were needle-shaped crys- tals clumped together to form larger crystals (Zhao *et al.*, 2021; Zhang *et al.*, 2015; Zhang *et al.*, 2017). It was also observed that with aging, there is a reduction in the Newtonian flow region (Masalova *et al.*, 2007). When there is an intense crystallization with its de-characterization, there is so much destruction in the microstructure that it loses its viscoelastic properties in its rheology (Zhang *et al.*, 2017).

In the studies by Masalova *et al.* (2007), the elastic modulus is proportional to the concentration of the dispersed phase and to the inverse of the square of the droplet size, both are parameters that influence the stability of EEs.

Below (Table 4), parameters of rheological tests performed by researchers are presented.

Table 4 - Rheological measurements parameters.

Rheometer	Sample preparation	Methodology	Reference
MCR 101 (Anton Paar) with PP50 flat	Gap of 1 mm 25°C	**Amplitude sweep test:** strais from 0.1% to 200% at frequency of 1Hz.	Alilovic *et al.*, 2005
MCR300 (Paar Physica)	Bob-in-cup and cylinder-in-cylin- der measuring units with a sandblasted bob surface	**Stress:** stress from 1 to 300 Pa with duration of 200 s. **Steady shear rate measurement:** flow curves from 1.10^{-4} to 1.10^{3} s^{-1}. **Dynamic measurements:** amplitude sweep regime with different frequencies and/or a frequency sweep regime at small amplitudes of deformations (stresses)	Masalova *et al.*, 2013
Gemini HR Nano200	25°C in stationary mode, coneplate and a PP20 flat	**Amplitude sweep test:** strains from 0,05% to 50% at a frequency of 1 Hz. Temperature of 25°C. **Steady shear rate measurement:** 10 – 0.00015 s^{-1} **Stress:** from 50 to 500 Pa at 25°C and 1 Hz **Temperature variation:** Under 100 Pa external force and 1 Hz, a sample is manteined at temperature from 25 to 80°C during 1200 s, then kept at 80°C for 100 s and finally at temperatures from 80 to 25°C for 1200 s.	Wang *et al.*, 2013
Rotational stress rheometer MCR 502 (Paar Physica)	Sandblasted plate- plate geometry with 50 mm diameter and 1 mm gap	**Amplitude sweep test:** strains from 0.01% to 200% at a frequency of 1 Hz. Temperature of 30°C. **Steady shear measurement:** flow curves from 10^{-4} to 10^{2} s^{-1}. Temperature of 85°C.	Al-Sabagh *et al.*, 2017
Physica MCR 501 (Paar Physica)	25 °C, parallel plates (diameter of 25 mm) spaced 1 mm	**Amplitude sweep test:** strains from 0.1% to 200% at a frequency of 1 Hz. **Frequency sweep test:** range of frequencies of 0.01 to 300 rad/s at 0.1% strain. **Steady shear rate measurement:** flow curves from 0.001 to 30 s^{-1}.	Haru *et al.*, 2017

Brief description of each measurement. **Amplitude sweep test:** used to evaluate the elastic and viscous modulus-strain and phase angle-strain through evaluation of the storage (G') and loss modulus (G''). **Steady shear measurement:** viscosity is an output of this evaluation. **Stress:** Evaluate the flow behavior if there is a yield stress. **Frequency sweep test:** evaluate the frequency dependence of the storage modulus (G') during deformation in the LVE range. **Temperature variation:** evaluate changes in rheological properties due to temperature variation.

3.2 Stability prediction methods
3.2.1 Physical stability

The physical stability of the emulsion can be evaluated by performing tests with centrifugal force or compression.

A centrifuge accelerates destabilization by separating the oil phase from the matrix (Funaki, 2020). For this evaluation, the separated fuel content was not measured, since the amount was practically the same in all the samples.

The parameters used for evaluation are presented in Table 5. The greater the size variation, the lesser the stability.

Table 5 - Methodologies to evaluate physical stability.

Rotation	Cycles	Evaluation	Reference
3.600 rpm	2 x 15 min	Mean droplet size before and after the procedure	Funaki, 2020

This analysis allows to test the samples with different settings of rotation and time.

As the products undergo several processing operations, such as mixing and shearing, it is important that the emulsion has good stability when transported, without losing its properties (Noshad *et al.*, 2015). Explosive emulsions must have good compression stability to be transported and pumped to the final application over long distances without crystallizing (Sharu *et al.*, 2017).

For the test, fill about 4 mL of emulsion into a 5 mL syringe without the plunger. Then, place the plunger and squeeze it, so that at the end there is only 1 mL of emulsion inside without the presence of air bubbles. The syringe is positioned in a system, where the pressure compression is adjustable, and a glass slide is positioned at the outlet. The expelled emulsion is spread with another slide and the image is captured through the microscope. The stability assessment is comparative, using image analysis, where crystals are converted into black pixels and counted (Funaki, 2020).

3.2.2 Thermal stability

In this test, the samples must be placed in separate and standardized containers. The samples can be heated or cooled to a certain time to simulate a critical temperature condition to which it can be submitted (Funaki, 2020).

The most common thermal test is the freeze-thaw, which aims to evaluate the stability of the emulsion when freezing and thawing. Freezing affects the stability of the emulsion, since when freezing emulsions, water crystallization can occur, as well as interfacial phase transitions that can destabilize emulsions after thawing (Noshad *et al.*, 2015). Freeze-thaw stability depends on the product composition (emulsifiers), homogenization condition and freeze-thaw conditions (Zhu *et al.*, 2017). When the emulsion is frozen, the water and/or oil phase crystallizes and as a result, the stability and properties of the resulting emulsion are affected. In the thawing process the emulsions partially break down, eventually resulting in oil phase separation. The destabilization process in the thawing process can be attributed to crystallization of the water or oil phase and changing conditions of the droplets (dramatic changes in pH, ionic strength, increase in osmotic pressure, viscosity).

Examples of thermal tests are presented in Table 6. All freezing was done in a freezer, followed by thawing in a bain-marie or oven.

Table 6 - Parameters for freeze-thaw test.

Freezing temperature/ time	Temperature of thawing/ time	Method of freezing	Method of thawing	Cycles	Evaluation	Reference
-18°C/22h	40°C/2h	Freezer	Water	0 – 3	Droplet size and physical stability	Xu *et al.*, 2016
-10°C/16h	50°C/8h	Test chamber with high and low temperature		40	Emulsion mass	Wang *et al.*, 2017
-20°C/12h	65°C/12h	Dynamic climatic chamber (Binder)		14	Viscosity, droplet size and microstructure	Funaki, 2020

This analysis allows to test the samples with different settings of temperature and time.

To have a more controlled heating-freezing process (and vice versa), Funaki (2020) and Wang *et al*. (2017) used climatic chambers.

The study by Volkov *et al.* (2018) determined the critical temperature, at which aqueous droplets of emulsion break when subjected to high temperatures. This determination is possible through a recording of a fine cloud of aerosol with a high-resolution camera (Photoron AS 1.1 CMOS), since the disruption of the droplet occurs due to the boiling water, and it is sprayed to where the temperature exceeds the boiling temperature of the water (Volkov *et al.*, 2018).

The study by Kovalchuk *et al.* (2012) aimed to determine the freezing point of the emulsion as a function of the concentration of electrolyte (oxidizing salts) and the type of emulsifier when submitting their samples in DSC Q 2000 (Perkin Elmer) from 30°C to -70 °C at a rate of 2K/min. Thus, it was determined that the lower the freezing/crystallization temperature, the greater the stability of the emulsion (Kovalchuk *et al.*, 2012).

3.2.3 Solvent resistance

It is known that since EEs are water-in-oil type emulsions, explosive emulsions have good resistance to water. To evaluate this property, water is placed in contact with the emulsion in a beaker and the pH and conductivity of the supernatant

water are analyzed over days. The higher the conductivity and the lower the pH, the greater the diffusion of the ammonium nitrate and other oxidizing salts present in the aqueous phase, that is, less resistance to water (Funaki, 2020). Complementarily, Ni *et al.* (2012) evaluated the performance of the emulsion in contact with water after 144 h. As a result, there was a loss of 1.5% of AN, without significant reduction in the performance of emulsions.

Unlike water, direct contact of EEs with nonpolar solvents should be avoided, as the oil phase, located externally to the emulsion, interacts, destabilizing the droplets and causing crystallization. Hexane and petroleum ether, for example, are highly used to open emulsions to evaluate the chemical composition of EE in forensic analysis (Tian *et al.*, 2011; Wang *et al.*, 2017) and toluene, to evaluate the water content in the formulation (Xu *et al.*, 2013).

3.3 Long-term stability evaluation (shelf life)

The storage stability or shelf-life test aims to evaluate the appearance of the emulsion after storage at a certain time interval. Samples should be stored under normal handling/storage conditions.

For the evaluation of storage stability, the Emulsion Stability Index (ESI) can be obtained from the average droplet size (Eq. 6). The ESI is determined by the equation below,

where D_0 is the droplet size of the new sample and D_7 after 7 days of storage (Ko *et al.*, 2021). The upper index can be adapted for longer evaluation times.

$$ESI = \frac{D_7}{D_0} \qquad (6)$$

Zhang *et al.* (2015) and Al-Sabagh *et al.* (2017) placed emulsions with different storage times in a container with 100 ml of deionized water for 10 hours, to measure the concentration of crystallized NA in the matrix by titration. The higher the concentration of NA in the water, the lower the stability of the emulsion.

4. Conclusion

In this article, stability evaluation tests carried out in the last 20 years were compiled, from simple and low-cost tests to those that require the use of complex instruments, which can be performed for a better practical understanding of the crystallization mechanisms of ammonium nitrate in explosive emulsions.

A test that has been of great interest in the study of explosive emulsions is rheology because while it evaluates stability, it also has the potential to correlate with droplet size and performance. For low-cost evaluation, microscopy and image analysis has been used as an alternative of deep stability comprehension.

References

ALILOVIC, I.; RECKZIN, E. *Canada Patent* No. US 6,855,219 B2, 2005.

AL-SABAGH, A. M.; HUSSEIN, M. A.; MISHRIF, M. R.; EL-TABEY, A. E.; ELAWADY, A. A. Preparation and investigation of emulsion explosive matrix based on gas oil for mining process. *Journal of Molecular Liquids,* 2017. DOI: https://doi.org/10.1016/j.molliq.2017.04.085

BECHER, P. *Emulsiones*: teoria y practica. 2 ed. Madrid: Editorial Blume, 1972.

BIESSIKIRSKI, A.; KUTERASINSKI, L.; DWORZAK, M. Comparison of structure, morphology, and topography of fertilizer-based explosives applied in the mining industry. *Microchemical Journal,* 144, p. 39-44, 2019. DOI: https://doi.org/10.1016/j.microc.2018.08.044

CONSOLIN, J. C. *Estudo da influência dos aditivos do nitrato de amônio grau fertilizante na estabilidade de emulsões explosivas.* 2019. Dissertação (Mestrado em Engenharia Química) - Universidade Federal do Paraná, Curitiba, Brasil, 2019.

DAS, A. K.; MUKESH, D.; WAYAMBUNATHAN, V.; KOTKAR, D. D.; GHOSH, P. K. Concentrated emulsions. 3. Studies on the influence of continuous-phase viscosity, volume fraction, droplet size, and temperature on emulsion viscosity. *Langmuir,* 8, p. 2427-2436, 1992.

DLUGOGORSKI, B. Z.; KENNEDY, E. M.; RAYSON, M. S.; DA SILVA, G. *USA Patent* No. US 2011/0132505 A1, 2011.

FUNAKI, A. R. *Estudo teórico-experimental de formulações de emulsões explosivas.* 2020. Dissertação (Mestrado em Engenharia Química) - Universidade Federal do Paraná, Curitiba, Brasil, 2020.

GUMUS, C. E.; DAVIDOV-PARDO, G.; MCCLEMENTS, D. J. Lutein-enriched emulsion-based delivery systems: impact of Maillard conjugation on physicochemical stability and gastrointestinal fate. *Food Hydrocolloids,* 60, pp. 38-49, 2016. DOI: http://dx.doi.org/10.1016/j.foodhyd.2016.03.021

HARNBY, N.; NIENOW, A. W.; EDWARDS, M. F. *Mixing in the process industries.* 2 ed. Butterworth-Heinemann, 1992.

HAYWARD, N. E.; LING, N. N.; JOHNS, M. L. Explosive emulsion characterization using nuclear magnetic resonance. *Propellants, Explosives, Pyrotechnics,* 44, p. 531-540, 2019. DOI: https://dx.doi.org/10.1002/prep.201800314

HOLMBERG, K.; JÖNSSON, B.; KRONBERG, B.; LINDMAN, B. *Surfactants and polymers in aqueous solution.* 2 ed. Est Sussex: John Wiley & Sons, 2002.

KO, E. B.; KIM, J. Y. Application of starch nanoparticles as a stabilizer for pickering emulsions: effect of environmental factors and approach for enhancing its storage stability. *Food Hydrocolloids,* 120, 2021. DOI: https://doi.org/10.1016/j.foodhyd.2021.106984

KOVALCHUK, K.; MASALOVA, I. Factors influencing the crystallization of highly concentrated water-in-oil emulsions: a DSC study. *South African Journal of Science,* 108, 2012.

KRAMARCZYK, B.; SUDA, K.; KOWALIK, P.; SWIATEK, K.; JASZCZ, K.; JAROSZ, T. Emulsion explosives: a tutorial review and highlight of recent progress. *Materials,* 15, 2022. DOI: https://doi.org/10.3390/ma15144952

LEAL-CALDERON, F.; SCHMITT, V.; BIBETTE, J. *Emulsion science: basic principles.* 2 ed. Springer, 2007.

LI, H.; LI, F.; WU, X.; WU, W. Effect of rice bran rancidity on the emulsion stability of rice bran protein and structural characteristics of interface protein. *Food Hydrocolloids,* 121, 2021. DOI: https://doi.org/10.1016/j.foodhyd.2021.107006

LIN, D.; KELLY, A. L.; MIAO, S. Formation and creaming stability of alginate micro-gel particle-induced gel-like emulsions stabilized by soy protein isolate. *Food Hydrocolloids,* 121, 2021. DOI: https://doi.org/10.1016/j.foodhyd.2021.107040

LUO, N.; LIU, K. X.; LI, X. J.; WU, Z. W.; WU, S. Y.; YE, L. M.; SHEN, Y. Synthesis of graphite-coated copper nanoparticles by the detonation of a copper-doped emulsion explosive. *Mendeleev Communications,* 22, p. 248-249, 2012. DOI: https://doi.org/10.1016/j.mencom.2012.09.006

MA, P.; ZENG, Q.; TAI, K.; HE, X.; YAO, Y.; HONG, X.; YUAN, F. Preparation of curcumin-loaded emulsion using high pressure homogenization: impact of oil phase and concentration on physicochemical stability. *LWT - Food Science and Technology,* 84, p. 34-46, 2017. DOI: http://dx.doi.org/10.1016/j.lwt.2017.04.074

MAHADEVAN, E. G. *Ammonium nitrate explosives for civil applications*: slurries, emulsions and ammonium nitrate fuel oils. Wiley-VHC.

MASALOVA, I.; MALKIN, A. Y. Rheology of highly concentrated emulsions - concentration and droplet size dependencies. *Applied Rheology*, 17, 2007. DOI: https://doi.org/10.1515/arh-2007-0011

MASALOVA, I.; MALKIN, A. Y. The engineering rheology of liquid explosives as highly concentrated emulsions. *Chemical Engineering Research and Design,* p. 204-210, 2013. DOI: http://dx.doi.org/10.1016/j.cherd.2012.07.012

MASALOVA, I.; KOVALCHUK, K.; MALKIN, A. Y. IR Studies of interfacial interaction of the succinic surfactants with different head groups in highly concentrated W/O emulsions. *Journal of Dispersion Science and Technology,* 2011. DOI: https://doi.org/10.1080/01932691.2010.516412

MUDEME, S.; MASALOVA, I.; HALDENWANG, R. Kinetics of emulsification and rheological properties of highly concentrated explosive emulsions. *Chemical Engineering and Processing*: Process Intensification, p. 468-475, 2010. DOI: https://doi.org/10.1016/j.cep.2010.03.012

NI, O.; ZHANG, K.; YU, Z.; TANG, S. Powdery emulsion explosive: a new excellent industrial explosive. *Journal of Energetic Materials.* 2012. DOI: https://doi.org/10.1080/07370652.2010.550599

NOSHAD, M.; MOHEBBI, M.; SHAHIDI, F.; KOOCHEKI, A. Freeze-thaw stability of emulsions with soy protein isolate trhough interfacial engineering. *International Journal of Refrigeration.* 2015. DOI: http://dx.doi.org/10.1016/j.ijrefrig.2015.05.007

O'HARA, H.; STOW, D.; YATES, D. E. *Australia Patent* No. US 7,972,454 B2, 2001.

OLUWOYE, I.; DLUGOGORSKI, B. Z.; GORE, J.; OSKIERSKI, H. C.; ALTARAWNEH, M. Atmospheric emission of NOx from mining explosives: a critical review. *Atmospheric Environment,* 167, p. 81-96, 2017. DOI: https://doi.org/10.1016/j.atmosenv.2017.08.006

ROSEN, M. J. *Surfactants and interfacial phenomena.* 3 ed. New Jersey: John Wiley & Sons, Inc, 2004.

SHARU, B. K.; SIMON, G. P.; CHENG, W.; ZANK, J.; BHATTACHARYYA, A. R. Development of microstructure and evolution of rheological characteristics of a highly concentrated emulsion during emulsification. *Colloids and Surfaces A,* p. 342-350, 2017. DOI: http://dx.doi.org/10.1016/j.colsurfa.2017.04.070

SILVA, G.; DLUGOGORSKI, B. Z.; KENNEDY, E. M. An experimental and theoretical study of the nitrosation of ammonia and thiourea. *Chemical Engineering Science,* 61, p. 3186-3197, 2006. DOI: https://dx.doi.org/10.1016/j.ces.2005.11.059

TADROS, T. F. *Emulsion science and technology.* Weinheim: Wiley-VHC, 2009.

TIAN, F.-F.; YU, J.; HU, J.-H.; ZHANG, Y.; XIE, M.-X.; LIU, Y., . . . HAN, J. Determination of emulsion explosives with Span-80 as emulsifier by gas chromatography-mass spectrometry. *Journal of Chromatography A,* p. 3521-3528, 2011. DOI: https://dx.doi.org/10.1016/j.chroma.2011.03.065

TRIPATHI, S.; TAN, S. N.; BHATTACHARYA, A.; TABOR, R. F. Measuring and modelling the adsorption kinetics of polydisperse PiBSA-based emulsifiers using dynamic interfacial tension measurements. *Colloids and Surfaces A*: Physicochemical and Engineering Aspects. 2021. DOI: https://doi.org/10.1016/j.colsurfa.2021.126728

VOLKOV, R. S.; STRIZHAK, P. A. Using planar laser induced fluorescence to explore the mechanism of the explosive disintegration of water emulsion droplets exposed to intense heating. *International Journal of Thermal Sciences,* 127, 2018. DOI: https://doi.org/10.1016/j.ijthermalsci.2018.01.027

WANG, C.; LIU, Z.; XU, G.; YIN, B.; YAO, P. BSA-dextran emulsion for protection and oral delivery of curcumin. *Food Hydrocolloids,* 61, p. 11-19. DOI: http://dx.doi.org/10.1016/j.foodhyd.2016.04.037

WANG, L.; FANG, J. Rheological properties and water-in-oil structural stability ofemulsion matrixes. *Central European Journal of Energetic Materials,* 10, p. 87-102, 2013.

WANG, X. *Emulsion explosives.* Beijing: Metallurgical Industry Press, 1994.

WANG, X.; GUO, L.; LI, X.; LI, X.; KONG, L.; YAN, H. Controlled detonation synthesis of nano Fe-based oxides/SiO$_2$

core-shell composite particles. *Chemical Physics Letters,* 740, 2020. DOI: https://doi.org/10.1016/j.cplett.2019.137016.

WANG, Y.; WANG, X.-G. Crystallization of interphase droplets in emulsion explosive matrices. *Journal of dispersion science and technology,* 38, p. 1483-1488, 2017. DOI: http://dx.doi.org/10.1080/01932691.2016.1255954.

WILSON, K. N. *Surfactant & emulsion technology in industry*: a formulation chemist's perspective. Cape Town, 2018.

XIE, X.; LI, X.; YAN, H. Detonation synthesis of zinc oxide nanometer powders. *Materials Letters,* 60, p. 3149-3152, 2006. DOI: https://doi.org/10.1016/j.matlet.2006.02.061.

XIE, X.; ZHU, J.; ZHOU, H. Deflagration products from emulsion explosive unconventional nano-powders from ion reaction. *Journal of Physics*: Conference Series, 188, 2009. DOI: https://doi.org/10.1088/1742-6596/188/1/012003.

XU, D.; ZHANG, J.; CAO, Y.; WANG, J.; XIAO, J. Influence of microcrystalline cellulose on the microrheological property and freeze-thaw stability of soybean protein hydrolysate stabilized curcumin emulsion. *LWT - Food Science and Technology,* 66, p. 590-597, 2016. DOI: http://dx.doi.org/10.1016/j.lwt.2015.11.002.

XU, Z.-X.; LIU, D.-B.; HU, Y.-T. Investigation of ammonium nitrate based emulsion ignition characteristic. *Journal of Loss Prevention in the Process Industries*, p. 994-1001, 2013. DOI: http://dx.doi.org/10.1016/j.jlp.2013.10.005

YAKHOUB, H. A.; MASALOVA, I.; HALDENWANG, R. Highly concentrated emulsions: role of droplet size. *Chemical Engineering Communications,* 198:2, p. 147-171, 2010. DOI: http://dx.doi.org/10.1080/00986445.2010.499841.

YUNOSHEV, A. S.; PLASTININ, A. V.; RAFEICHIK, S. I.; VORONIN, M. S. Acceleration ability of emulsion explosives. *Combustion, Explosion, and Shock Waves*, v. 54, n. 4. DOI: https://dx.doi.org/10.1134/S0010508218040135

YUNOSHEV, A. S.; RAFEICHIK, S. I.; PLASTININ, A. V.; SIL'VESTROV, V. V. New applications of emulsion explosives. *Combustion, Explosion, and Shock Waves*, v. 49, n. 2, p. 225-230. DOI: https://dx.doi.org/10.1134/S0010508213020147

ZHANG, K.; NI, O. Rheological properties and stability of emulsion explosive matrix. *Journal of Dispersion Science and Technology,* p. 1532-2351, 2015. DOI: https://doi.org/10.1080/01932691.2014.942315

ZHANG, K.-M.; ZHAO, H.-R. Perspectives in the stability of emulsion explosive. *Advances in Colloid and Interface Science,* 307, 2022. DOI: https://doi.org/10.1016/j.cis.2022.102745

ZHANG, K.-M.; NI, O.-Q.; HUANG, J.-D.; DAI, Y.-M.; ZHAO, H.-R. A facile and efficient method do investigate the effect of the nature of surfactant and continuous phase on the performance of emulsion explosive. *Journal of Molecular Liquids,* p. 203-210, 2018. DOI: https://doi.org/10.1016/j.molliq.2017.10.149.

ZHANG, K.-M.; ZHAO, H.-R.; NI, O.-Q.; REN, X.-M. Storage modulus' variation in aging and its application in assessing the stability of emulsion explosive matrix. *Journal of Dispersion Science and Technology,* p. 1532-2351, 2017. DOI: https://doi.org/10.1080/01932691.2016.1225507

ZHAO, H.-R.; WU, J.; XU, M.-X.; ZHANG, K.-M. Advances in the rheology of emulsion explosive. *Journal of Molecular Liquids,* 336, 2021. DOI: https://doi.org/10.1016/j.molliq.2021.116854

ZHU, X.-F.; ZHANG, N.; LIN, W.-F.; TANG, C.-H. Freeze-thaw stability of pickering emulsions stabilized by soy and whey protein particles. *Food Hydrocolloids,* 69, 2017. DOI: http://dx.doi.org/10.1016/j.foodhyd.2017.02.001