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**CHEMICAL TECHNOLOGY:
SCIENCE, ECONOMY AND PRODUCTION**

ЗБІРНИК НАУКОВИХ ПРАЦЬ

VI Міжнародної науково-практичної конференції

**ХІМІЧНА ТЕХНОЛОГІЯ:
НАУКА, ЕКОНОМІКА ТА ВИРОБНИЦТВО**



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У збірнику висвітлюються актуальні питання спеціальної хімічної технології і виробництва боєприпасів, утилізації відходів виробництв різних галузей, енергозбереження, моделювання технологічних процесів, соціально-економічні аспекти виробництва та природокористування в умовах війни.

Збірник корисний робітникам хімічної промисловості, науковим співробітникам, аспірантам і студентам спеціальностей хіміко-технологічного та соціально-економічного профілів, фахівцям інформаційних технологій виробництва.

Наукові праці учасників конференції подаються в авторській редакції.

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EXPLOSIVE FORMULATIONS CONTAINING CONCENTRATED HYDROGEN PEROXIDE – POTENTIAL SOLUTIONS TO KEY DRAWBACKS OF CURRENTLY USED EXPLOSIVES?

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Explosives are extensively used for civilian purposes, with blasting operations playing a crucial role in mining (underground and open pit) [1,2], civil engineering (demolitions, tunnel construction) [3,4] and materials processing (e.g. explosive welding) [5]. Virtually all explosives that are currently used for the above purposes contain ammonium nitrate, nitric acid esters or nitrocompounds.

Despite their widespread use in blasting operations, such explosives are burdened by significant drawbacks (**D1 – D7**), the most significant of which are:

- D1:** Manufacture from non-renewable resources via highly energy-intensive processes;
- D2:** Significant threat to human health and to the environment in the case of nitric acid esters and nitrocompounds [6,7];
- D3:** Emission of large amounts of toxic and highly corrosive gases (carbon monoxide, nitrogen oxides) upon detonation [8];
- D4:** Gradual decomposition, particularly of liquid nitric acid esters, as well as gradual leakage of liquid nitroesters from the explosives, necessitating the use of stabilising and anti-leakage agents [9];
- D5:** Susceptibility to misfires (primarily in the case of explosives based on ammonium nitrate), currently being one of the primary threats associated with blasting operations [10,11];
- D6:** Susceptibility to theft and subsequent criminal misuse [12], due to maintaining the ability to detonate even following improper storage or a misfire during blasting;
- D7:** Significant risk of fire / explosion during production [13], transport and disposal [14], due to susceptibility to undergo detonation caused by various stimuli (e.g. impact, friction) [15].

The above issues have long been recognised in the field of explosives and safety considerations are likely the key reason for the development of emulsion explosives [16], which contain no nitric acid esters or nitrocompounds, while achieving only slightly lower energetic parameters than explosives utilising such compounds.

In regards to safety considerations, bulk emulsion explosives should be mentioned, as they can be transported in the form of non-explosive components (classified by the United Nations as oxidising agents – class 5.1 rather than as explosives – class 1) and produced directly at the site of the intended blasting operations [15]. The possibility of entirely eliminating the risk associated with the transport of explosives is chief among the reasons for the continuously increasing market share of this type of explosives [17].

Although bulk emulsion explosives partially resolve some of the above issues, they are not a satisfactory solution, as their energetic performance is relatively weaker than that of both traditional explosives and of cartridged emulsion explosives (Tab. 1). Moreover, cases of theft and criminal misuse of emulsion explosives have been reported in literature [12] and the abovementioned issues of nitrogen oxide emissions, reliance on energy-intensive processes and non-renewable resources remain unresolved.

Consequently, the resolution of the entire set of these issues necessitates a different material solution.

Table 1. Relative ability of selected explosives to perform mechanical work (via ballistic mortar method).

Explosive	Relative ability to perform mechanical work	Ref.
RDX	100 % (reference explosive)	[18]
Dynamite	84 %	[19]
ANFO	51 %	[19]
TNT (flaked)	67.7 %	[18]
Emulinit 8L ^a	62.6 %	[18]
BK-1 ^b	68.8 %	[18]
BK-2 ^b	69.6 %	[18]
OSM ^c	65.1 – 84.7 %	[20]

^a – commercial bulk emulsion explosive

^b – experimental bulk emulsion explosive formulations

^c – experimental formulations of explosives based on hydrogen peroxide

One potential avenue of research is based on the use of concentrated (>50 wt. % of hydrogen peroxide) hydrogen peroxide (cHP) solutions, as they contain no nitrogen compounds, while being capable of undergoing detonation, with a velocity of detonation (VoD) of 6.6 km/s being reported [21]. The added value of cHP is that it is produced with only minimal environmental impact (hydrogen and air are raw materials, anthraquinone is recycled in a closed loop) via the anthraquinone process, with ongoing work on developing a production method with no environmental impact [22]. Explosives in the form of cHP solutions are, therefore, free of the drawbacks of traditional explosives related to human health and environmental impact (**D1 – D3** above). By itself, however, cHP has a large critical diameter (40.6 mm at 50°C and decreasing with increasing temperature), making them impractical for any blasting operations.

Another approach to cHP-based explosives involved mixtures of cHP with liquid organic fuels [23]. Multiple organic fuels (e.g. acetic acid, acetone, aniline, ethanol, ethyl acetate, glycerol) were reported as viable components for producing explosive mixtures with cHP [24]. More recently, mixtures of cHP with components of the working solutions used to produce cHP on an industrial scale via the anthraquinone process were found to be explosive and sensitive to initiation by impact in a broad range of chemical concentration ratios [25]. Relatively little information is available on the energetic performance of such liquid explosive mixtures, likely due both to the high

reactivity of cHP and to the generally marginal application of liquid explosives in blasting operations.

Existing works on cHP-based explosives largely include gelling agents in their formulations, granting the materials minor mechanical strength, resistance to spillage and limiting the contact of cHP with potential contaminants [26]. This modification of HP-based explosives has attracted greater research interest and was labelled as “green” explosives [27], primarily due to the fact that their formulations do not involve any nitrogen compounds and, hence, cannot lead to nitrogen oxide emissions upon detonation [28]. Consequently, even gel-like cHP-based explosives avoid drawbacks **D1** – **D3** by design.

In terms of energetic parameters, cHP-based explosives have exhibited moderately high performance, varying with the specific choice of fuel, gelling agent and auxiliary compounds, as well as with explosive charge dimensions and casing (Tab. 2). In general, however, performance comparable with that of nitroester-based explosives (e.g. dynamites) and exceeding that of ammonium nitrate-based explosives was observed, while good initiation reliability was reported, possibly indicating that these materials are not as prone to misfires as explosives based on ammonium nitrate (**D5**). It should also be noted that such materials can be produced on-site from non-explosive components, much as in the case of bulk emulsion explosives, mitigating another drawback (**D7**) of traditional explosives.

Table 2. Energetic performance of cHP-based explosives reported in literature

Fuels	Auxiliary	V _{DET} [km/s]	Ref.
Glycerol	Ammonium nitrate (oxidising agent), glass microspheres (sensitising agent)	5.4 – 5.7	[27]
Glycerol, aluminium powder	Ammonium nitrate (oxidising agent), glass microspheres (sensitising agent)	3.6 - 5.5	[29]
Glycerol	Glass microspheres / gas bubbles / expanded polystyrene hollow spheres (sensitising agents)	3.0 – 5.5	[28]
Glycerol	Glass microspheres	2.6 – 5.1	[30]
Glycerol, aluminium powder	Ammonium nitrate (oxidising agent), glass microspheres (sensitising agent)	4.4 – 5.2	[20]

It should be noted, that works on the subject of cHP-based explosives tend to focus on the impact of various factors (e.g. water content, charge diameter, use of different sensitising agents) on the achieved velocity of detonation (VoD). Consequently, virtually no fundamental information on the physicochemical properties of these

materials or their correlation with their energetic parameters is available. This deficit of information is significant enough that our preliminary and shallow investigation of the aging of these materials revealed an entire new facet of their properties, i.e. that the decomposition of cHP within them does not need to take place through a violent chemical reaction and that it can be controlled [20].

Although documenting the different rates of cHP decomposition within these explosives is highly relevant, these rates are tied to utilising different types and amounts of aluminium powders. Consequently, modifying the rate of hydrogen peroxide decomposition requires modifying of the energetic parameters of the explosives, which is highly undesirable in terms of any blasting operations. Hence, even though our initial work shows that the drawback of being susceptible to theft (**D6**) can be resolved, a different approach, one that does not influence the energetic parameters of the material, while allowing it to be reliably deactivated after a specified time, is required.

In regards to the issue of gradual decomposition, literature reports that high purity, 90 wt. % solutions of hydrogen peroxide can be stored at 30°C, losing “1% per year” due to decomposition, which is sufficient to allow long term storage of cHP [24]. Mixing cHP with other components of the explosive formulation, however, greatly accelerates this decomposition, which is rapid enough to significantly and adversely affect the energetic parameters of cHP-based explosives (e.g. loss of approx. 11% of initial VoD over 180 minutes), as seen in our initial work [20]. It should also be noted that predicting the rate of this decomposition is severely hindered by the limited available kinetic data, as literature primarily reports data for the decomposition kinetics of dilute (<50 wt. %) hydrogen peroxide solutions.

Summarising, while cHP-based explosives are an excellent emerging alternative to traditional explosives, due to their non-toxicity, environmental friendliness, high energetic parameters and relative safety, the issue of their gradual decomposition (**D4**) needs to be resolved and a methodology for their timed deactivation that does not influence their energetic parameters over time needs to be developed (**D6**) before this interesting new class of explosive materials can become the subject of applied research (e.g. development of automated production and borehole-loading machines, optimisation of energetic parameters for specific applications) and be commercialised.

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