Trends and Prospects in the Use of Energetic Materials: A Comprehensive Analysis of Cyclotrimethylenetrinitramine, Cyclotetramethylene-tetranitramine, and Hexanitrohexaazaisowurtzitane

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ABSTRACT

This article provides a detailed look at how cyclotrimethylenetrinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), and hexanitrohexaazaisowurtzitane (HNIW or CL-20) are currently being used for energy purposes in both civilian and military environments around the world. It highlights the significance of monitoring and prospecting for new technologies to promote innovation in developed and developing countries. This research was carried out by systematically analyzing nonpatent documents and patents from reputable databases such as Scopus, Derwent, and Espacenet. The report recognizes patent documentation as a valuable source of technical information and explores how analyzing patents can provide insights into using and developing high-performance compounds. Moreover, the article discusses the versatile applications of RDX, HMX, and CL-20, which are highly explosive substances that have found uses in multiple sectors. It delves into these materials' chemical composition, structure, and importance in military and industrial contexts. The research methodology involved thoroughly searching and filtering documents from databases, focusing on titles, abstracts, and keywords. The results show the annual growth of publications related to the three explosive compounds and highlight the main research fields associated with each fabric. Overall, this article provides valuable insights into using and developing powerful compounds. It emphasizes the importance of technological monitoring and patent analysis in shaping strategic decisionmaking and fostering innovation. It is a foundation for further research and exploration of energetic materials and their applications.

Keywords: Energetic Materials; Explosives; Military Applications; Patent Analysis; Chemical Composition; Technological Innovation.

INTRODUCTION

Identifying and studying new technologies can bring significant technological innovation to countries and institutions needing higher technical development, a reality for many developing countries. This article overviews trends in using three energetic materials

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(EM) worldwide in civil and military applications. The research used nonpatent and patent documents from Scopus, Derwent, and Espacenet databases. Over the past decade, there has been a significant increase in the number of electronic documents deposited in various scientific areas due to changes in the political, economic, technological, and social landscape, aimed at preserving the environment (Amparo *et al.* 2012). This increase reinforces the need to monitor and systematically prospect the main areas of knowledge. To aid in this pursuit, methodologies and tools based on statistics and information search systems in reliable and up-to-date scientific bases are recommended to filter and optimize the relevance of the materials found, their diversity, quantity, and adherence to the proposed theme (Barros and Porto 2021).

Effective and agile technological monitoring is a recurring challenge for organizations in dynamic and highly competitive markets. Technical differentiation, the ability to predict possible changes in their areas of activity, and understanding the consequences that new developments can bring to organizations are crucial tools for optimizing decision-making and acquiring competitive advantages in the market (Hoffmann 2011). Patent documentation is an effective option for technological monitoring for innovation searches. Patents are considered documents of high informational value as they represent cutting-edge knowledge (De Falani *et al.* 2019). This instrument makes decision-making, identification of relevant technologies, market niches, studies of innovations and competition, new lines of research, development, and other relevant information for the technical-scientific environment much more effective (OECD 2009).

The protection of inventions is often achieved through patents, which companies, institutions, or individuals obtain to facilitate industrial property discovery. However, before a dream can become an innovation, other business efforts are required, such as developing, manufacturing, and marketing it (Trippe 2015). Patents provide the right to prevent other institutions, researchers, or companies from claiming property in the same area of the invention, which can have commercial and legal implications.

In addition to patents, some companies may choose not to provide information in the patent format and instead opt for trade secrets as a protective strategy. This allows them to safeguard their discoveries while keeping information confidential. To conduct searches, Instituto Nacional de Propriedade Industrial (INPI) uses the International Patent Classification (IPC) or Cooperative Patent Classifications (CPC), which are displayed on the patent application cover page. The IPC is the most commonly used classification in over 90 countries (Oldham 2022).

In general terms, published results on patent categorization often suffer from a lack of transparency or are limited to specific industry applications. The IPC, a complex hierarchical categorization system, encompasses sections, classes, subclasses, and groups. The classification includes eight sections, approximately 120 classes, about 630 subclasses, and around 69,000 groups, and categorizes all technological fields into sections designated by uppercase letters from A to H, with designations such as A for "Human necessities," B for "Performing operations, transport," C for "Chemistry, metallurgy," D for "Textiles, paper," E for "Fixed constructions," F for "Mechanical engineering, lighting, heating, weapons, explosives," G for "Physics," and H for "Electricity." Each section is further divided into classes identified by symbols, consisting of the section symbol followed by a two-digit number – for example, A01. In turn, each class is subdivided into multiple subclasses, with symbols including the class symbol followed by an uppercase letter, for instance, A01B (Fall *et al.* 2003).

The IPC is available in two authentic versions, English and French, which are published online (www.wipo.int/classifications) and in printed form by World Intellectual Property Organization (WIPO). Complete IPC texts are also prepared and published in other languages by national industrial property offices, including German, Spanish, Czech, Hungarian, Polish, Russian, Japanese, Korean, and Chinese versions. Currently, updates are primarily focused on the group and subgroup levels within this classification, while the classes and subclasses remain essentially stable (Fall *et al.* 2003).

Analyzing a group of patents involves several steps, including initial scoping searches, exploratory data analysis, defining a primary dataset, dividing the primary set into more minor data, cleaning and comparing it with other data sources, visualizing the information, and preparing reports. By conducting technological prospection, it is possible to guide potential behaviors and trends that contribute to the interests of society. The relevance of technical information obtained from the patent analysis can be observed by evaluating the annual growth of patent documents worldwide. Patents can cover all technological fields and be accessed in national or international offices (Cerveira *et al.* 2022).

It is essential to be careful when interpreting documents, as the purpose of documental prospection studies, whether general or focused on patents, is not to predict the future, but to help align and interpret different strategies to achieve a greater goal in the future. The process to be outlined will depend on industry and research knowledge, costs, scope, and interests (Paranhos and Ribeiro 2018).

Energetic materials

Throughout history, countries across the globe have invested in developing war materials for territorial defense and geopolitical reasons. This work highlights three highly EM with civil and military applications among the various types of war materials available on the market.

Synthesizing and selecting the ideal chemical explosive material depends on several factors, such as detonation velocity, pressure, explosive charge density, stability, environmental impacts, and products generated after detonation (Mendonça *et al.* 2018).

The nitroamines groups play a crucial role in the chemical structure of highly energetic explosive molecules such as cyclotrimethylenetrinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), and hexanitrohexaazaisowurtzitane (HNIW or CL-20). These chemicals share a common chemical structure, consisting of carbon, nitrogen, hydrogen, and oxygen arranged in complex ring structures, as shown in Fig. 1. This chemical arrangement allows these substances to release energy extremely efficiently during detonation (Wang 2022).



Source: Adapted from Tang and Zhu (2021).

Figure 1. Chemical structure of HNIW, RDX, and HMX.

The history of HMX and RDX dates back to the mid-20th century. RDX was first developed in the 1899s in Germany and was only used as an explosive in the 1920s (Bachmann and Sheehan 1949; Urbanski 1967). HMX emerged a bit later, around 1941, as a byproduct of RDX synthesis (Baxter 2018). Both were initially used for military purposes due to their exceptional ability to release explosive energy. The longevity of these explosives is remarkable, as both continue to be essential in the composition of military and industrial explosives to this day (Du L-x *et al.* 2022). Their thermal stability, insensitivity to impact, and effectiveness across a wide range of temperatures have contributed to their durability and popularity (Du L-x *et al.* 2022).

CL-20, also known as high nitrogen insensitive explosive (HNIW), is a more recent secondary explosive compared to RDX and HMX. It was developed in the 1990s and represents a more advanced generation of explosives with even higher energy density. Its high nitrogen density makes it attractive for military and industrial applications that require an extremely powerful explosive (Sysolyatin *et al.* 2005).

However, CL-20 also presents some significant limitations. One of the main limitations is its sensitivity. CL-20 is more sensitive to impact and friction than RDX and HMX, making it more challenging to handle safely. Additionally, CL-20 faces challenges associated with mass production due to its complex synthesis and sensitivity (Trott *et al.* 2003). Concerning particle size, precise control of CL-20 particle size is critical to optimize its performance in explosives and propellants. Homogeneous and well-defined particle sizes are necessary to ensure uniform and effective detonation. Therefore, particle size control is a crucial technical aspect when dealing with CL-20, as well as with RDX and HMX (Katin and Maslov 2017).

HMX has four polymorphic forms (α , β , δ , σ), and the most commonly used form is β HMX, due to its stability. Therefore, it is crucial to have well-defined particle sizes to achieve better performance in the artifact (Achuthan and Jose 1990; Urbanski 1967).

In military contexts, nitramines play indispensable roles in high-powered explosives like RDX, HMX, and CL-20. These explosives find applications in ammunition, artillery shells, devices for structural demolition, and various other military equipment. Moreover, these substances contribute significantly to the composition of solid rocket propellants, supplying the essential energy

Δ

for propelling rockets and missiles. Their capacity to generate intense pressure and heat upon detonation adds to their value as secondary explosives. Additionally, their chemical stability ensures secure handling in military settings, thereby enhancing safety protocols and measures (Jiang *et al.* 2023).

In industrial and civil applications, nitroamines such as RDX and HMX are incorporated into polymer-bound explosive formulations. They play a pivotal role in sectors such as mining and oil exploration (Galante *et al.* 2014), as well as in tunnels and demolition, where they are used to enable effective excavation of minerals and rocks, as well as controlled demolition of structures due to their stability and effectiveness. They are also employed in the manufacturing of automotive airbags, where, in the event of a collision, they rapidly generate the necessary gas to inflate the airbag, thereby enhancing the safety of vehicle occupants (Klapötke 2017; Sandstrom 1997; Srivastava *et al.* 2022).

CL-20 is used in gas generators for automotive airbags, improving combustion at lower temperatures, reducing the emission of harmful gases, and thus contributing to vehicular collision safety. Furthermore, CL-20 is incorporated into polymer-bound explosive formulations with industrial applications, such as in mining and demolition (Klapötke 2017).

Nitroamines can be present in plastic-bonded explosives (PBX) and double-base propellants, depending on the specific formulation of the explosive or propellant in question (Zhang *et al.* 2017). PBX, also known as moldable explosives, are explosives that can be shaped into various forms and exhibit malleable properties. They are characterized by their high mechanical strength, good explosive properties, excellent chemical stability, low sensitivity to shock and handling, and low sensitivity to thermal initiation. For instance, RDX and HMX are often used as components in PBX due to their capacity to provide high energy density and stability and are utilized in various explosive and propellant formulations (Liu *et al.* 2016; Zhang 2017).

In antitank missiles, manufacturers utilize double-base propellants, given their smokeless nature. However, these propellants exhibit a low specific impulse. To enhance the energy content of this propellant, manufacturers can incorporate RDX/HMX into the double-base compositions, resulting in what is known as nitramine propellants (Rao *et al.* 2005).

Therefore, the presence of nitroamines in PBX and double-base propellants depends on the specific formulation of the explosive or propellant material and the desired properties for their application. These compounds are valued for their energy efficiency and stability, making them viable choices in various applications (Patil *et al.* 2022).

The EM community aims to develop higher performance and reduced sensitivity explosives. Explosives classified as primary are less stable than secondary explosives, require less energy to initiate, and have a lower capacity to generate damage. To achieve this goal, reducing the particle size of EM is a viable approach that can strongly influence reactivity and sensitivity (Little *et al.* 2022). In today's society, the need for highly EM remains a relevant topic, and the search for more oxidizing materials capable of generating high energy or serving as a fuel source has become increasingly important. In summary, secondary explosives play a crucial role in various industries and applications, and the compounds RDX, HMX, and CL-20 play a fundamental role in enhancing their explosive properties. This combination of secondary explosives plays a vital role in the engineering of safe and effective explosive devices for various purposes (Wang *et al.* 2023).

Based on the studies by Oyler *et al.* (2016), we will discuss below some of the secondary energy materials of great relevance today, namely RDX, HMX, and HNIW (Oyler *et al.* 2016).

Activities developed, methods, and procedures

A selection of three commonly used high-energy materials from 2011 to 2021 was made to assess the global geopolitical situation and evaluate the impact of recent pandemics on scientific publications. RDX, HMX, and HNIW were chosen due to their historical significance, widespread use, physical-chemical properties, and environmental and human health effects. Despite the challenges associated with using these materials in solid fuels, their composition is still based on mixtures of ammonium perchlorate (AP), aluminum, and compounds based on resins that result in aluminum oxides and hydrochloric acid. RDX and HMX contain a high concentration of hydrogen atoms, so combustion of these nitramines produces low molecular weight gases. Therefore, they create relatively high specific impulses. Furthermore, the combustion products are not only smokeless, but also noncorrosive (Rufino *et al.* 2013). The article by Rufino *et al.* (2013) provides a comprehensive exploration of technological advancements related to hydroxylterminated polybutadiene (HTPB)-based propellants used in solid and hybrid rocket engines in the previous decade. The analysis is based on a wide compilation of scientific and technological data sourced from articles, conference papers, reviews, and patents obtained from the United States Patent and Trademark Office (USPTO) database. This article offers valuable insights into the progress achieved in propellant technology and its applications during the specified period.

Rufino *et al.*, in 2013, also emphasizes that propellants composed of HTPB as a binder continue to be one of the most used and researched propulsion technologies. Approximately half of the publications in this field are attributed to private research institutes and government agencies. China leads in research investments, followed by the United States, with Brazil also having a notable presence. The research focuses on enhancing the properties of compositions using AP as an oxidizer and explores the use of catalysts and nanometals. A shift towards "green" propellants is also observed, with the transition from HTPB/ammonium nitrate (AN) compositions to EM as oxidizers.

The main contribution of this article lies in the way the author approached document prospecting. This is reflected in the ability to monitor technological trends, make informed decisions, and provide valuable insights into the development of HTPB-based propellants. The comprehensive analysis of scientific articles, conference papers, reviews, and patents allows for a deeper understanding of the technological landscape and ongoing innovations (Rufino *et al.* 2013).

Next, research bases for documentary prospecting were identified and divided into two stages: nonpatent literature (NPL) and patent literature. The Scopus and Derwent databases were used for NPL documentation, while Espacenet and Derwent patent databases were utilized for patent documentation. Search filters were established for each database, considering their specificities and previous technological prospecting studies by Rufino *et al.* (2013). The main synonyms for each EM and a stipulated date interval were also considered.

A restriction filter was applied to article titles, abstracts, and keywords to refine the search and focus on the most relevant documents. Filters for work areas, types of documentation, and countries were selected, taking into account the top five results obtained. Additionally, an institutions filter was also used, with an analysis of the top 10 results found. This strategy aimed to obtain a larger sample set for quantitative analysis of documents published by each institution and to facilitate more in-depth studies. After applying the parameters, the search string, responsible for the combination of all text, numbers, and symbols entered earlier, was created. Searches for each EM were conducted in Scopus and Derwent. Similarly, searches for patent documentation followed most of the same steps, with some specific adjustments for patent searches. The use of the same search tools on each site ensured that the results used the same search string (Antunes *et al.* 2018).

All the documentation found was made available for consultation. The documentation search filter, used to arrange synonyms, was restricted to titles and abstracts. The restriction filter for a specific date range was fixed in the period from 2011 to 2021. The other filters used for searches in Espacenet and in Derwent's patent base took into account the availability of these same filters on both floors. Thus, the following filters were selected for specific searches in the database: institution and main IPC groups. For the filter of institutions, research was stipulated with the 10 main constituents of this topic to carry out a more in-depth study on the institutions associated with these EM. For the filter of the main IPC groups available in the patent search bases, the IPCs were selected: C06, C07, and G01.

WIPO (2022) categorizes section C as Chemistry and Metallurgy, with subclass C06 covering explosives and matches, including explosive or thermal compositions, detonating or fusing devices, means to produce smoke or mist, and games. Subclass C07, under organic chemistry, focuses on the preparation, purification, separation, stabilization, or use of additives. Section G pertains to Physics, with subclass G01 encompassing measuring instruments, indicating or recording devices with a similar structure, and signaling or control devices related to measurement (INPI 2017).

The search parameters were set to search for selected EM, including filters, synonyms, and date ranges. Then, patent documents were searched in Espacenet and patent Derwent databases. The search results were filtered according to the set parameters, providing several patent documents for analysis and consultation.

RESULTS AND DISCUSSION

Annual evolution of public documents (NPLs)

Using the Scopus and Derwent databases and applying the specified filters, a search was conducted for the total annual publications on RDX, HMX, and CL-20 explosives from 2011 to 2021. Figures 2–4 display the results.



Figure 2. Annual evolution of NPL's documents in the databases Scopus and Derwent for the explosive RDX in the period from 2011 to 2021.



Figure 3. Annual evolution of NPL's documents in the bases Scopus and Derwent for the HMX explosive in the period from 2011 to 2021.



Figure 4. Annual evolution of NPL's documents in the bases Scopus and Derwent for the explosive CL-20 in the period from 2011 to 2021.



Based on the data presented in Figs. 2–4, it is clear that the Scopus database generally contains more documents by year than the Derwent database. This is likely because Scopus needs a specialist reviewer to guide on indexing published documents, unlike Derwent. As a result, Derwent can more precisely define the research areas related to the published work, leading to fewer but more refined results. On the other hand, Scopus tends to produce a more significant and generic number of documents related to EM.

Another important observation is that some studies and institutions have published scientific documentation multiple times under similar titles in the Derwent database. This may reflect a strategy by some institutions to increase their publication range, as well as the fact that some research has been continued by subsequent researchers in the analyzed period.

It is also worth noting that while the Derwent database summarizes documentation published directly in English, the Scopus database includes specific journals not published in English. In addition, the author's self-written abstract can sometimes make it difficult to compensate for research themes and index the proposed content.

Furthermore, the number of publications related to the energetic agent CL-20 was lower than that of RDX and HMX. This could be because CL-20 is a relatively new material compared to the others, with the first recorded synthesis dating back to 1987 by the United States Naval Air Warfare Center (Sysolyatin *et al.* 2005).

Distribution of NPL's documents retrieved by work areas

The following evaluation carried out in this research aimed, based on searches in NPL documents in the Scopus and Derwent databases, to identify the five main areas of work related to the documentation found. Therefore, the results presented ahead were found for searches with the RDX, HMX, and CL-20 materials for the period from 2011 to 2021.

For the research referring to the five main areas of work highlighted for the RDX material, information was found in the Scopus research base, and lead was found according to Table 1 and Fig. 5.

Material	Research base	Chem.	Mater. Sci.	Eng.	Phys. and Astron.	Chem. Eng.	Others	Physicochem.	Multidiscip. Chem.	Appl. Chem.	Multidiscip. Mater. Sci.
עחס	Scopus	698	458	417	281	423	387	-	-	-	-
нUЛ	Derwent	-	-	-	-	345	753	311	271	270	266

Source: Elaborated by the authors

Table 1. Main areas of work for RDX in Scopus and Derwent in the period from 2011 to 2021.



Source: Elaborated by the authors.

Figure 5. Overview of the five main areas of work related to the RDX material in the base (a) Scopus and (b) Derwent in the period from 2011 to 2021.

Regarding researching HMX explosive substance, Table 2 and Fig. 6 offer valuable insights into the five key focus areas.

Table 2. Main areas of work for HMX in Scopus and Derwent in the period from 2011 to 2021.

Material	Research base	Chem.	Mater. Sci.	Eng.	Phys. and Astron.	Chem. Eng.	Others	Physicochem.	Multidiscip. Chem.	Appl. Chem.	Multidiscip. Mater. Sci.
	Scopus	683	423	370	345	377	314	-	-	-	-
	Derwent	-	-	-	-	287	715	296	254	215	266

Source: Elaborated by the authors.





In the latest analysis of work areas, the CL-20 EM was examined in the five most relevant regions found in the Scopus and Derwent databases. Table 3 and Fig. 7 provide details of the findings.



Material	Research base	Chem.	Mater. Sci.	Eng.	Phys. and Astron.	Chem. Eng.	Others	Physicochem.	Multidiscip. Chem.	Appl. Chem.	Multidiscip. Mater. Sci.
	Scopus	187	129	96	69	78	44	-	-	-	-
UL-20	Derwent	-	-	-	-	87	186	69	73	72	67

Source: Elaborated by the authors.



Source: Elaborated by the authors.

Figure 7. Overview of the five main areas of work related to CL-20 material in the base (a) Scopus and base (b) Derwent in the period from 2011 to 2021.

After conducting a comprehensive data analysis in the period from 2011 to 2021, we have identified the primary research areas for high-energetic compounds like RDX, HMX, and CL-20. Notably, the chemical work domain had the highest number of publications for all three materials in Scopus and Derwent databases. Specifically, this area accounted for 32% of the publications on RDX, while it represented 32 and 36% for HMX and CL-20, respectively. Additionally, the "others" category was vital in providing context for the work areas and highlighting their significance in the field.

Distribution of retrieved NPL documents by type of publication

Regarding the analysis of various kinds of evidence documents, the following results pertain to RDX, HMX, and CL-20 explosives in the period from 2001 to 2021. Table 4 displays the inferred results, while Fig. 8 provides a general overview in percentages.

Table 4. Main types of documents for RDX, HMX, and CL-20 EM in the Scopus database in the period from 2011 to 2021.

Material	Research base	Articles	Conference papers	Review access	Book chapters
RDX		1,158	82	16	7
HMX	Scopus	1,090	94	18	8
CL-20	-	265	5	6	1

Source: Elaborated by the authors.



(c) CL-20 in the Scopus database in the period from 2011 to 2021.

Our evaluation of the Scopus database unequivocally shows that articles make up the majority of scientific publications on explosives RDX, HMX, and CL-20, accounting for a staggering 90% of the total publications during the evaluated period. As for the Derwent base in the period from 2001 to 2021, it is crystal clear that RDX, HMX, and CL-20 are the most commonly studied explosives, as evidenced by Table 5 and Fig. 9.

Material	Research base	Articles	Conference papers	Review articles	Early access	Meeting summary
RDX		880	47	7	10	6
HMX	Derwent	815	34	10	6	6
CL-20	_	228	5	2	-	-
		Source	e: Elaborated by the a	uthors.		

Table 5. Main document types for RDX, HMX, and CL-20 EM in the Derwent base in the period from 2011 to 2021.

(c) 2% 1% Articles Articles Articles Conference papers Conference papers Conference papers Review access Review access Review access 93% Early access Early access Meeting summary Meeting summary

Source: Elaborated by the authors.

Figure 9. Overview of the primary document types for the EM (a) RDX, (b) HMX, and (c) CL-20 in the Derwent base in the period from 2011 to 2021.

Based on the data from the Scopus and Derwent databases, it is evident that articles are the predominant format for publishing information on RDX, HMX, and CL-20 energetic substances. This demonstrates the prevalence of articles as the primary means of presenting information on these materials.

Distribution of redeemed NPL documents by country of origin

The next step was to analyze the rescued documents in the Scopus and Derwent databases to quantify the five major countries associated with the NPL documents of powerful compounds, such as RDX, HMX, and CL-20. The results obtained from the searches conducted for the EM studied in the Scopus database are organized in Table 6. Additionally, Fig. 10 displays the classifications for each EM by country and their representation compared to other world powers.

Table 6. Main countries for EM RDX, HMX, and CL-20 evidenced in the Scopus database in the period from 2011 to 2021.

Material	Research base	China	United States of America	Czech Republic	Russia	United Kingdom	Poland	Hong Kong	Egypt	Others
RDX		1,152	140	15	-	7	-	5	-	28
HMX	Scopus	1,029	203	5	6	6	-	-	-	15
CL-20		252	-	26	-	-	3	2	17	5

Source: Elaborated by the authors.





The research indicates that China dominates in depositing general documentation, accounting for over 80% of the deposits for the three high-performance materials. It is worth noting that the Derwent base was also thoroughly examined for these materials, as demonstrated in Table 7 and Fig. 11.

Table 🛛	7. Quantification of documents found in Derwent for the energetic compounds
	RDX, HMX, and CL-20 in the period in the period from 2001 to 2021.

Material	Research base	China	United States of America	Czech Republic	Russia	Poland	India	Egypt	Others
RDX		662	189	54	-	-	73	26	33
HMX	Derwent	681	164	4	4	-	48	-	18
CL-20		202	-	22	16	З	-	14	З





The information shows China has significantly contributed to publishing NPL's documents on evaluated high-energetic substances. China's publications account for over 80% of the searches in the Scopus base and over 50% in the Derwent base. This highlights China's remarkable scientific contributions in recent years and that Scopus displayed more documents than Derwent.

Distribution of NPL's documents redeemed in the leading institutions

The institutions of origin were considered in the latest assessment of NPL's records from 2011 to 2021. Figure 12 displays the number of documented evidence and related institutions for explosive such as RDX, HMX, and CL-20 in the Scopus database.

Chinese institutions are leading the way in researching and publishing technological innovation for some of the most pivotal EM today. Our evaluation of significant institutions related to the found documents shows that China dominates the powerful compounds field. Four of the five most relevant institutes are in China, followed by the United States. The results also reveal Brazil's relatively lower position than other world powers. This could be attributed to the country's lower investment in research over the last decade and the impact of the global coronavirus disease 2019 (COVID-19) pandemic on large research institutions worldwide.



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Figure 12. Overview of the primary source institutions for NPL's documents in the Scopus database related to (a) RDX, (b) HMX, and (c) CL-20 in the period from 2011 to 2021.

Figure 13 displays the RDX, HMX, and CL-20 quantities and the institutions associated with each high-EM for NPL's research at the Derwent base in the period from 2011 to 2021.





Figure 13. Overview of the primary source institutions for NPL's documents in the Derwent database related to (a) RDX, (b) HMX, and (c) CL-20 in the period from 2011 to 2021.

Cumulative annual evolution of patent documentation

Figures 14–16 show the annual growth of patent documents for RDX, HMX, and CL-20 energetic components in the period from 2001 to 2021, based on searches performed in the Espacenet and Derwent databases.















The graphs presented indicate an upward trend in publications over the past decade. It is evident from Figs. 14–16 that the Espacenet database consistently has more documents by year than the Derwent database. This discrepancy can be attributed

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to Derwent's use of an expert proofreader for better document indexing, while Espacenet fails to eliminate possible document duplications. Derwent's indexing approach leads to a more precise definition of research areas, resulting in relatively fewer but more refined results than Espacenet.

Distribution of patent documents based on the IPC

For our analysis, we searched for the IPCs of patent documents in the Espacenet and Derwent databases. Specifically, we evaluated the IPCs C06, C07, and G01 to determine the number of papers published in the period from 2001 to 2021 for RDX, HMX, and CL-20 materials. This information is presented in Table 8, and the corresponding percentages for each EM are displayed in Fig. 17.



Table 8. Distribution by leading groups of IPC of patent documents for each EMstudied in the Espacenet base in the period from 2001 to 2021.

Figure 17. Documents by IPC classification for (a) RDX, (b) HMX, and (c) CL-20 on Espacenet base in the period from 2011 to 2021.

The data analysis of Fig. 17 indicates that IPC C06 overwhelmingly dominates the classification, constituting more than 70% of the analyzed explosive materials.

In analyzing the patent documents in the Derwent database, we considered the IPCs C06, C07, and G01, just like in Espacenet. Our evaluation focused on the number of papers published for these classifications in the period from 2001 to 2021, specifically for RDX, HMX, and CL-20 materials. Table 9 provides a breakdown of the results, while Fig. 18 shows the percentage of each EM researched.

Table 9. Distribution by leading groups of the IPC of patent documents for eachEM studied in the Derwent base in the period from 2001 to 2021.

Material	Research base	C06	C07	G01
RDX		407	35	24
HMX	Derwent	430	42	40
CL-20	-	334	54	20

Source: Elaborated by the authors.



Source: Elaborated by the authors.

Figure 18. Documents by IPC classification for (a) RDX, (b) HMX, and (c) CL-20 in Derwent base in the period from 2011 to 2021.

The Espacenet patent research database findings indicate that IPC C06 is the most widely used classification for patent document requests. This is particularly true for energetic substances, with over 80% of the analysis falling under this category. A study of publications and relevance in the period from 2011 to 2021 further confirms the superior performance of IPC C06 for EM such as RDX, HMX, and CL-20.

Distribution of patent documents because of the institutions

From 2011 to 2021, the institutions associated with the patent documents for EM RDX, HMX, and CL-20 were evaluated using the previously established methodology. The findings for each institution were analyzed and are presented in Fig. 19, which depicts the graphical representations of institutions by country for EM



Source: Elaborated by the authors.

Figure 19. Institutions found for patent documents (a) RDX, (b) HMX, and (c) CL-20 in Espacenet base in the period from 2011 to 2021.

In the Derwent database, you can find an analysis of patent documents on RDX, HMX, and CL-20 explosive substances. The data cover the period from 2011 to 2021 and are presented in Fig. 20. The graphical representations are arranged by country and institution for each type of active material.

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Trends and Prospects in the Use of Energetic Materials: A Comprehensive Analysis of Cyclotrimethylenetrinitramine, Cyclotetramethylene-tetranitramine, and Hexanitrohexaazaisowurtzitane



Source: Elaborated by the authors

Figure 20. Institutions found for patent documents (a) RDX, (b) HMX, and (c) CL-20 in Derwent base in the period from 2011 to 2021.

In the Espacenet and Derwent databases, an evaluation of institutions related to patent documents was conducted. Results showed that the two most relevant institutions in China ranked within the three most important for all EM surveyed. Chinese institutions also dominated the 10 most relevant for most published patent documents related to these EM. Notably, Chinese institutions produced the most significant number of published patent documents for the three EM evaluated. These findings suggest that Chinese institutions are leading research and publications on technological innovation for some of the most critical EM today, in general documentation and patent documents. However, there were indications that other countries, such as South Korea, England, and the United States, were also interested in publishing scientific content in patent protection.

It is essential to note Brazil's position in EM research compared to other leading global economies. According to Scopus research, Brazil ranks 23rd in RDX EM with 11 published documents. Instituto Militar de Engenharia (IME) stands out with six published papers, along with contributions from Universidade Federal do Pará (UFPA), Universidade Federal do Rio de Janeiro (UFRJ), and Universidade Federal de Pernambuco (UFPB). In the Derwent base, Brazil ranks 16th with four documents, including four from IME. For HMX, Brazil ranks 32nd in the Scopus base with two published papers, with the Universidade Federal de São João del-Rei (UFSJ) and UFPA being the main contributors. In the Derwent ground, Brazil ranks 22nd with three documents, two of which are related to UFPA and one from Universidade Estadual Paulista (UNESP). Unfortunately, no publications were found for CL-20 explosive in both Scopus and Derwent bases from 2011 to 2021.

The current position of Brazil is concerning when compared to major world powers like China, the United States, France, and Japan. This is evident from various surveys and reports. Moreover, Brazil's scientific standing is also worrying, as it has published only 11 documents on RDX material in the Scopus base, while China has published 1,357 documents. It is worth noting that Brazil is among the 10 most relevant countries with the highest gross domestic product (GDP) (FUNAG 2021), making it a potential participant in scenarios of arms power. However, the low number of publications can be attributed to the systematic uncertainties and lack of resources in the public research sectors, which face budget cuts and a shortage of new researchers every year.

CONCLUSION

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Technological advancement is crucial for organizations, companies, and nations to maintain their competitive edge and achieve economic growth and social welfare. Leaders, educators, and managers must utilize technological prospecting to make strategic plans and resource allocation decisions for research and technology areas.

A recent study revealed that the Scopus and Espacenet databases had more documents on the three high-explosive materials studied than the Derwent database. Chinese institutions dominated the documentation with approximately 80% of articles and publications. IPC C06 was the primary classification for explosives in patent documents from Chinese institutions, representing over 80% of published patents.

Brazil's science, technology, and innovation activities are complex and require multidisciplinary efforts to assess social needs and the applicability of new technology to the consumer market. Future studies on EM and other aerospace sectors, such as thermal protection, engine envelopes, liquid propellants, and solid propellants, could highlight Brazil's representativeness in the scientific community. It is also feasible to research highly energetic components less harmful to the environment and operators during loading, considering the carcinogenic and toxic components in some propellants, explosives, thermal protections, and adhesion materials.

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Conceptualization: Oliveira TAB, Silva G, Mattos ECM; **Methodology:** Oliveira TAB, Silva G; **Formal analysis:** Oliveira TAB, Silva G; **Investigation:** Oliveira TAB, Silva G, Mattos ECM; **Resources:** Oliveira TAB, Silva G, Mattos ECM; **Data Curation:** Oliveira TAB, Silva G; **Writing - Original Draft:** Oliveira TAB, Mattos ECM; **Writing - Review & Editing:** Oliveira TAB, Silva G, Mattos ECM; **Visualization:** Oliveira TAB, Silva G; **Supervision:** Mattos ECM; **Final approval:** Mattos ECM.

CONFLICT OF INTEREST

Nothing to declare.

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The data will be available upon request.

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REFERENCES

[FUNAG] Fundação Alexandre de Gusmão (2021) As 15 maiores economias do mundo. Ministério das Relações Exteriores Brasil. [accessed Mar 04 2023]. https://www.gov.br/funag/pt-br/ipri/publicacoes/estatisticas/as-15-maiores-economias-do-mundo

[INPI] Instituto Nacional da Propriedade Industrial (2017) Introdução à Classificação Cooperativa de Patentes (CPC). Anexo III. INPI. Coordenação Geral de Estudos, Projetos e Difusão de Informação Tecnológica. [accessed Jun 30 2022]. https://www.ufpb.br/inova/contents/documentos/tutorial-cpc-inpi.pdf

[OECD] Organization for Economic Cooperation and Development (2009) OECD patent statistics manual. Paris: OECD Publishing. https://doi.org/10.1787/9789264056442-en

[WIPO] World Intellectual Property Organization (2022) Publicação IPC. IPCPUB v8.5. Last modified: 2022. 12. 14; CPC 2022 08. FI 2022.04.01. WIPO. [accessed Mar 12 2023]. https://ipc.inpi.gov.br/classifications/ipc/ipcpub/?notion=scheme&version=20230101&symbol=B&menulang=pt&lang=pt&viewmode=f&fipcpc=no&showdeleted=yes&indexes=no&head-ings=yes¬es=yes&direction=o2n&initial=A&cwid=none&tree=no&searchmode=smart

Achuthan CP, Jose CL (1990) Studies on octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) polymorphism. Propell Explos Pyrot 15(6):271-275. https://doi.org/10.1002/prep.19900150609

Amparo KKS, Ribeiro MCO, Guarieiro LLN (2012) Case study using mapping technology foresight as the main tool of scientific research. Perspect Ciênc Inf 17(4):195-209. https://doi.org/10.1590/S1413-99362012000400012

Antunes MAS, Parreiras VMA, Quintela CM, Ribeiro NM (2018) Métodos de prospecção tecnológica, inteligência competitiva e foresight: principais conceitos e técnicas. In: Ribeiro NM. Prospecção tecnológica. Salvador: Instituto Federal de Educação, Ciência e Tecnologia da Bahia. https://www.profnit.org.br/wp-content/uploads/2018/08/PROFNIT-Serie-Prospeccao-Tecnologica-Volume-1-1.pdf

Bachmann WE, Sheehan JC (1949) A new method of preparing the high explosive RDX. J Am Chem Soc 71(5):1842-1845. https://doi.org/10.1021/ja01173a092

Barros MC, Porto Jr FGR (2021) Prospecção tecnológica: o que é e para que serve? A prospecção tecnológica como ferramenta de planejamento estratégico na gestão pública. Palmas: Editora da Universidade Federal do Tocantins. https://umbu.uft.edu. br/handle/11612/2685

Baxter CF (2018) The secret history of RDX: the super-explosive that helped win World War II. Lexington: University Press of Kentucky.

Cerveira GS, Magalhães JLd, Antunes AMS (2022) Status and trends of membrane technology for wastewater treatment: a patent analysis. Sustainability 14(21):13794. https://doi.org/10.3390/su142113794

De Falani SYA, Torkomian ALV, Filho MG, Tinoco DJB (2019) The use of technological prospecting in product development: a systematic literature review. Paper presented 2019 VIII CONBREPRO: Brazilian Congress of Production Engineering: the Engineering and the Industry 4.0. Ponta Grossa, Brazil.

Du L-x, Jin S-h, Shu Q-h, Li L-j, Chen K, Chen M-l, Wang J-f (2022) The investigation of NTO/HMX-based plastic-bonded explosives and its safety performance. Defen Technol 18(1):72-80. https://doi.org/10.1016/j.dt.2021.04.002

Fall CJ, Torcsvari A, Benzineb K, Karetka G (2003) Automated categorization in the International Patent Classification. ACM SIGIR Forum 37(1):10-25. https://doi.org/10.1145/945546.945547

Galante EBF, da Costa DMB, Haddad AN, dos Santos IJAL (2014) Risk assessment for hexamine nitration into RDX. J Aerosp

Technol Manag 6(4):373-388. https://doi.org/10.5028/jatm.v6i4.380

Hoffmann W (2011) Monitoramento da informação e inteligência competitiva: realidade organizacional. InCID: Rev Cien Info e Doc 2(2):125-144. https://doi.org/10.11606/issn.2178-2075.v2i2p125-144

Jiang L, Li H, Lv R, Wang J, Song S, Sun N, Gozin M, Wang K, Zhang Q (2023) Energetic hydrogen-bonded open-framework as promising green combustion catalyst for nitramine-based solid propellants. Combust Flame 257(Part 2):113048. https://doi.org/10.1016/j.combustflame.2023.113048

Katin KP, Maslov MM (2017) Toward CL-20 crystalline covalent solids: on the dependence of energy and electronic properties on the effective size of CL-20 chains. J Phys Chem Solids 108: 82-87. https://doi.org/10.1016/j.jpcs.2017.04.020

Klapötke TM (2017) Chemistry of high-energy materials. 4. Berlin: Walter de Gruyter GmbH.

Little BK, Smith DK, Crouse CA, Slizewski DT, inventors; Government of the United States, as represented by the Secretary of the Air Force, applicants. 2022 Aug 18. Synthesis of high explosive nanoparticles by turbulent mixing. United States patent US 20220259118.

Liu K, Zhang G, Luan J, Chen Z, Su P, Shu Y (2016) Crystal structure, spectrum character and explosive property of a new cocrystal CL-20/DNT. J Mol Struct 1110:91-96. https://doi.org/10.1016/j.molstruc.2016.01.027.

Mendonça FB, Gonçalves RFB, Urgessa GS, Iha K, Domingues M, Rocco JAFF (2018) Emprego de química computacional na verificação e validação da pressão de detonação de explosivo plástico-PBX. Quim Nova 41(3):310-314. https://doi. org/10.21577/0100-4042.20170169

Oldham P (2022) The WIPO manual on open source analytics. 2nd ed. Geneva: World Intellectual Property Organization. https://wipo-analytics.github.io/manual

Oyler KD, Metha N, Savithra GHL, Winter CH (2016) Lead-free primary explosives and beyond. Paper presented 2016 42nd International Pyrotechnics Society Seminar. Grand Junction, United States.

Paranhos RCS, Ribeiro NM (2018) Importância da prospecção tecnológica em base de patentes e seus objetivos da busca. Cad Prospecç 11(5):1274-1292. https://doi.org/10.9771/cp.v12i5.28190

Patil VB, Bělina P, Trzcinski WA, Zeman S (2022) Preparation and properties of co-mixed crystals of 1,3-di- and 1,3,5-triamino-2,4,6-trinitrobenzenes with attractive cyclic nitramines. J Ind Eng Chem 115:135-146. https://doi.org/10.1016/j. jiec.2022.07.043

Rao S, Krishna Y, Nageswara Rao B (2005) Fracture toughness of nitramine and composite solid propellants. Mater Sci Eng A 403(1-2):125-133. https://doi.org/10.1016/j.msea.2005.04.054

Rufino SC, Silva G, Iha K (2013) An overview of the technological progress in propellants using hydroxyl-terminated polybutadiene as binder during 2002-2012. J Aerosp Technol Manag 5(3):267-278. https://doi.org/10.5028/jatm.v5i3.242

Sandstrom J, Hafstrand A, Sjoberg P, inventors; Bofors Explosives AB, Karlskoga, Sweden, assignee. 1997 Dec 9. Airbag device and propellant for airbags. United States patent US5695216A. https://patents.google.com/patent/US5695216A/en

Srivastava V, Boczkaj G, Lassi U (2022) An overview of treatment approaches for octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX) explosive in soil, groundwater, and wastewater. Int J Environ Res Public Health 19(23):15948. https://doi.org/10.3390/ijerph192315948

Sysolyatin SV, Lobanova AA, Chernikova YT, Sakovich GV (2005) Methods of synthesis and properties of hexanitrohexaazaisowurtzitane. Russ Chem Rev 74(8):757-764. https://doi.org/10.1070/RC2005v074n08ABEH001179

J. Aerosp. Technol. Manag., São José dos Campos, v16, e1326, 2024

19

Tang L, Zhu W (2021) Computational design of high energy RDX-based derivatives: property prediction, intermolecular interactions, and decomposition mechanisms. Molecules 26(23):7199. https://doi.org/10.3390/molecules26237199

Trippe A (2015) Guidelines for preparing patent landscape reports. Geneve: World Intellectual Property Office. https://www.wipo.int/edocs/pubdocs/en/wipo_pub_946.pdf

Trott S, Nishino SF, Hawari J, Spain JC (2003) Biodegradation of the nitramine explosive CL-20. Appl Environ Microbiol 69(3):1871-1874. https://doi.org/10.1128/AEM.69.3.1871-1874.2003

Urbanski T (1967) Chemistry and technology of explosives. 3. Warszawa: PWN Polish Scientific Publishers.

Wang H, Cheng Y, Zhu S, Li Z, Shen Z (2023) Effects of content and particle size of TiH₂ powders on the energy output rules of RDX composite explosives. Defen Technol. https://doi.org/10.1016/j.dt.2023.05.002

Wang S, Yang L, Han J, Yan Z (2022) MOF as the rigid shell to improve the mechanical sensitivity of nitramine explosives. Mater Lett 306:130940. https://doi.org/10.1016/j.matlet.2021.130940

Yang J, Wang G, Gong X, Zhang J, Wang YA (2018) High-energy nitramine explosives: a design strategy from linear to cyclic to caged molecules. ACS Omega 3:9739-9745. https://doi.org/10.1021/acsomega.8b00614

Zhang F, Zhu D-p, Liu Q, Liu Z-t, Du P (2017) Study on the effect of RDX content on the properties of nitramine propellant. Defen Technol 13(4):246-248. https://doi.org/10.1016/j.dt.2017.05.020