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Review

Stabilizers for nitrate ester-based energetic materials and their mechanism of action: a state-of-the-art review

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ABSTRACT

Aliphatic nitrate esters are currently the most widely used energetic ingredients in single-, double-, and triple-base propellants. These nitrate esters are unstable at ambient conditions, and stabilizing agents should be incorporated into the energetic compositions to inhibit and slow down the decomposition reactions that can occur. However, the currently used stabilizers present a number of environmental and human health issues. To overcome these shortcomings, many stabilizers have been appeared in the past few decades and continue to be developed. Furthermore, several analytical techniques have been introduced to monitor the stability of nitrate ester-based energetic materials as well, since the existing ones could not be efficiently applied. Therefore, this review paper discusses and summarizes the current and emergent stabilizers as well as their mechanisms of action. A critical and analytical examination of their advantages and drawbacks is made.

Introduction

Energetic material broadly refers to a component or formulation which reacts rapidly and liberates large amount of force (through the generation of high-velocity products species) or energy (in the form of light and heat) from condensed phase upon ignition or initiation [1, 2]. The term *energetic material* encompasses a wide variety of materials, ranging from conventional explosives to insensitive and/or green materials at different scales (e.g., nanomaterials). These energetic materials (EMs) are commonly used in primers, main charges, propellants and pyrotechnics [3–6]. Basically, EMs are relatively easy to prepare but require specific knowledge and important precautionary and control. Their performances can be predicted and tailored by adjusting the stoichiometry of the chemical reacts [7]. For years, they have been widely utilized in civilian and military fields as construction, demolition, mining, safety equipment, gunpowder, missile and space propulsion applications [3]. EMs have drawn a growing interest by scientific community, military and civil industries since they are very attractive sources of onboard energy to generate gas, heat and power [7–9]. Nevertheless, they have been providing scientists with several challenges over the centuries on numerous levels. These challenges include: synthesis, formulation, characterization, scaling-up, safe handling, packaging, storage, sensitivity reduction,

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performance improvement, compatibility and stability, storage, environmental issues and cost control [1, 3, 10, 11]. Intensive efforts worldwide have been made, and different strategies have been adopted by researchers to improve the current methodologies and to establish novel procedures to overcome mainly vulnerability and stability issues of nitrate ester-based energetic materials.

Material scientists, interested in energetic materials, have widely investigated and developed different energetic compounds including nitramines, difluoro nitramines, azides, furazans, tetrazoles, nitrocubanes and nitrate esters, to cite a few [9, 12]. Some of the most significant discoveries of the nitrate esters class have been occurred in the nineteenth century, but it still impacts the world of EMs today [3, 13–16]. These nitrate esters such as nitrocellulose (NC), nitroglycerine (NG), pentaerythritol tetranitrate (PETN), triethylene glycol dinitrate (EGDN), 1,2-propylene glycol dinitrate (PGDN), 1,2,4-butanetriol trinitrate (BTTN) have been widely utilized in various military and civilian applications for many years [2, 3]. Unfortunately, because of their slow decomposition even under normal conditions of temperature, pressure and moisture, nitrate ester-based energetic materials (Fig. 1) are inherently chemically instable [17–19]. Without any stabilizing agent, this instability can lead to numerous degradation phenomena in both the service life and the ballistic performance giving rise eventually to autocatalytic decomposition, self-heating and cook-off safety hazards [15, 20–26].

The continuous decomposition of nitrate esters is mainly due to the low bonding energy of nitrate ester functional group, $CH_2–O–NO_2$ [15]. Consequently, gaseous products, especially nitrogen oxides, are released and nitrous and nitric acids are produced under severe environments (high temperature or acid chemical environment) [27–29]. Without the incorporation of any stabilizer, these generated products play a catalytic effect on the decomposition processes [30]. The additives, however, cannot prevent the nitrate ester decomposition, but are able to inhibit it and avoid the catalytic effect caused by the decomposition products such as NO, NO_2, HNO_2 and HNO_3 [21]. The stabilizers react more and more with the gases released by the energetic composition until they depleted completely [31, 32]. The decrease in these primary stabilizers is accompanied by the formation of different derivatives considered as secondary stabilizers, since they also play a stabilizing action [33]. The conventional stabilizers employed for nitrate ester-based energetic materials belong to (a) aromatic amines such as diphenylamine (DPA), 2-nitrodiphenylamine (2-NDPA) and p-nitro-*N*-ethylaniline and (b) urea compounds such as *N*,*N*′-diethyl-*N*,*N*′-diphenylurea (C1), *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea (C2) and *N*-methyl *N*′,*N*′-diphenylurea (AK-II) [34–36]. The Swedish Alfred Nobel was the first to introduce DPA as stabilizer of energetic

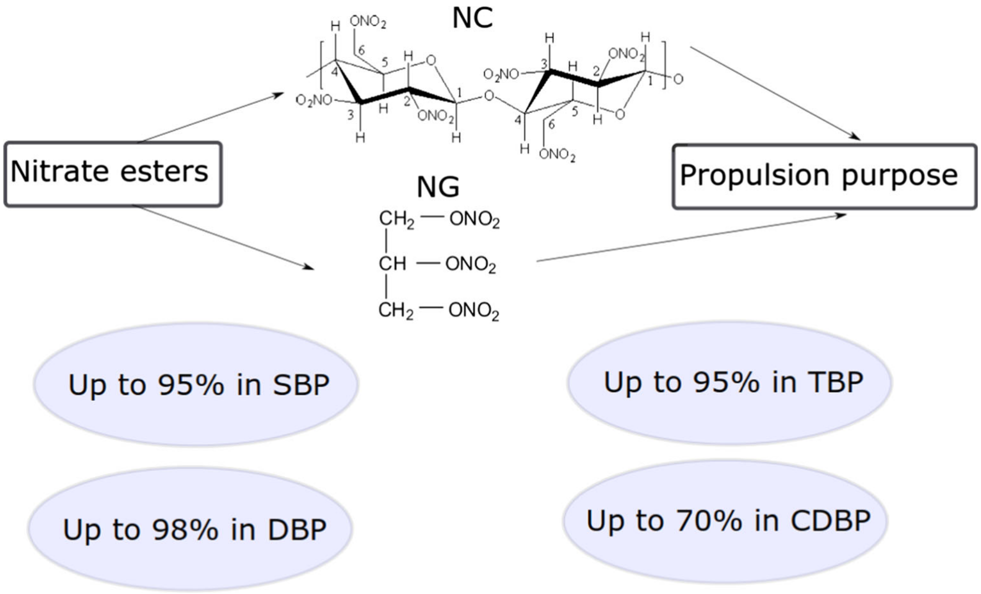


Figure 1 Nitrate ester ratios in different types of propellants: *SBP* single-base propellant, *DBP* double-base propellant, *TBP* triple-base propellant, *CMBP* composite double-base propellant.

composition as reported in a German patent in 1889 [32, 37–39].

By reacting with nitrogen oxides, the conventional stabilizers are converted to a range of nitrosamines and nitroamines. The reactions of these stabilizing agents are complex, and different successive products of the primary stabilizer, named also daughter products, are generated. These latter components may themselves act as stabilizers. Nevertheless, the generated nitroso derivatives are considered toxic and carcinogenic [36, 40]. Therefore, these stabilizers need to be replaced as soon as possible.

Several testing procedures such as Bergmann–Junk test and vacuum stability test, among others, have been used by different countries to monitor the stability of EMs and hence predict the safe service life [21, 25, 30, 41]. Other modern chromatographic, thermal and spectroscopic techniques have been employed to perform qualitative and quantitative analyses of EMs containing conventional stabilizers [42–46]. However, the progress of nitrate ester-based EMs with new stabilizers requires the development of new procedures and techniques to evaluate the chemical stability and the shelf life of EMs, since the existing ones such as STANAG procedures used for conventional stabilizers could not be merely applied.

The present review focuses on the nitrate ester-based energetic material's stabilizers, since no comprehensive review is available yet regarding the different classes of substances used for stabilizing this kind of energetic materials. This article firstly provides an overview on the decomposition of nitrate esters and their stability. The development of different categories of nitrate ester-based energetic material' stabilizers is considered and discussed as well. In addition, we have provided a critical and analytical examination of the advantages and shortcomings of each category and have elucidated the mechanism of action of potential stabilizers.

Decomposition of nitrate esters

Nitrate esters (e.g., nitrocellulose and nitroglycerine) introduced in energetic material formulations are considered as chemically less-stable molecules. Under ambient conditions of temperature, pressure and humidity, their decomposition is slow. However, in severe environmental conditions (high temperature, acid chemical environment), the decomposition of nitrate esters takes an autocatalytic form [47]. The chemical processes, which can occur during the decomposition of nitrate esters, often start with unimolecular (hemolytic) cleavage of the weakest bond accompanied by autocatalytic parallel reactions involving the formed decomposition products [30, 48, 49]. A number of reviews and research papers have already been published which report the state of knowledge of the decomposition of nitrate esters [16, 30, 31, 50–54]. Therefore, only some important details are presented to avoid duplication.

Nitrate esters decomposes intrinsically, means by themselves, in an exothermic manner via thermolysis because of the small bond energy in the nitrate ester group (CO–NO_2), with an activation energy of about 150 kJ mol^{-1} for the cleavage of O–NO_2 bonds [15]; this can cause denitration of nitrate esters and reduce their performance [50]. The homolytic breaking of the weak RO–NO_2 bonds generates two radicals, as reactive species, which react immediately with nearby molecules of nitrate esters [30]. Consequently, a series of exothermic side reactions will trigger, leading to an increase in temperature. This behavior accelerates the homolysis process of nitrate esters, and therefore, an increase in free radicals concentration and secondary reactions is followed. A schematic presentation of the decomposition processes of nitrate ester-based energetic materials and their stabilizing procedure is shown in Fig. 2.

As already mentioned, the chemical aging of nitrate ester-based energetic material starts with the homolytic cleavage of the weak O–NO_2 bonds, causing the formation of nitrogen oxide and the corresponding alkoxyl radical as shown in Eq. (1).

$$RCH_2ONO_2 \rightarrow RCH_2O^{\cdot} + {}^{\cdot}NO_2 \quad (1)$$

These reactive species act as catalysts in the decomposition of nearby nitrate ester molecules, where further decomposition reaction channels are opened and various decomposition products are appeared such as NO, N_2O_4, N_2O, CO, CH_4, HCHO, H_2O and C_2H_2O [15, 30, 50, 55–57].

Another foremost decomposition pathway (hydrolysis) concerns the reaction of nitrate esters with water. It takes place in two stages as given in Eqs. (2–7) [55]:

Initiation stage

$$R\text{-}ONO_2 + H_2O \rightarrow ROH + HNO_3 \quad (2)$$

$$R\text{-}OH + HNO_3 \rightarrow R\text{-}CHO + HNO_2 + H_2O \quad (3)$$

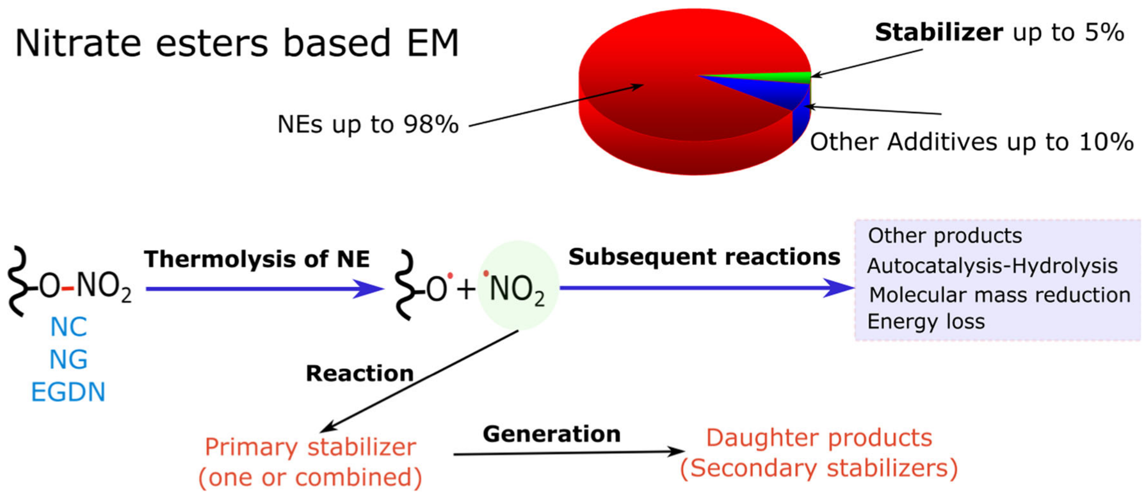


Figure 2 A schematic presentation of the decomposition process of nitrate ester-based energetic materials and their stabilizing procedure.

Stage of propagation

$$HNO_2 + HNO_3 \leftrightarrow N_2O_4 + H_2O \tag{4}$$

$$N_2O_4 \leftrightarrow 2NO_2 \tag{5}$$

$$R\text{-}OH + NO_2^{\cdot} \rightarrow {}^{\cdot}R\text{-}O + HNO_2 \tag{6}$$

$${}^{\cdot}R\text{-}OH + HNO_3 \rightarrow R\text{-}CHO + H_2O + NO_2 \tag{7}$$

Acids, nitrogen oxides and other radicals formed by reactions (1)–(7) play a role of catalysts for both homolytic and hydrolytic decompositions of nitrate esters. This behavior is called autocatalysis decomposition. The primary homolytic decomposition cannot be avoided, whereas the autocatalytic action can be slowed down by the incorporation of some stabilizing agents in order to fix nitrogen oxides, eliminate water or neutralize acids from the system. The commonly employed stabilizers, being electron-rich molecules, are aromatic amines and urea derivatives. They are able to react with free radicals and inhibit the catalytic processes.

The most widely nitrate ester investigated in the literature is the nitrocellulose, since it has received a broad spectrum of applications, with respect to other nitrate esters, such as coating agent, main component of propellant, museum artifacts, biofilter material, solid-phase immobilization support for proteins among others. Its decomposition process was well elucidated. In the Gelernter studies, it was shown that the nitrate group of the second and third position carbon unit glycoside is more unstable than that of the sixth position carbon [58]. Moniruzzaman group has deeply investigated this phenomenon and has confirmed the Gelernter study in calculating the activation energies, corresponding to the decomposition of nitrate esters groups, relating to C2, C3 and C6 positions of the glycoside unit, and they found the values of 141, 102 and 150 kJ mol^{-1}, respectively [16]. The decomposition of nitrate ester group at the sixth carbon generates NO_2, formaldehyde and other residues, involving out the polymeric chain scission of nitrocellulose [17, 59].

Several parameters can affect the decomposition of nitrate esters such as chemical constitution (e.g., ratio of ingredients), morphology (particle size), temperature of storage and exposure to sunlight among others [3, 15, 17, 50]. For example, the decomposition of nitrocellulose (NC) is affected by its particle size. Kinetic data obtained by the ASTM and Ozawa kinetic methods have shown that the ratio of the activation energy between the micronized and nanosized NC is approximately 1.5 [60]. These results show that the nanometer NC size is more sensitive to the heat with respect to the micrometer NC and it needs more precaution and control during storage [60, 61]. Furthermore, residual solvents such as water or ethanol present in the NC could affect sensibly its decomposition process [14].

Stability of nitrate esters

Encyclopedia of chemistry and explosives materials provided a concise definition of the stability, which is the ability of an energetic material to retain its original properties without degradation (or to retain its chemical and physical properties specified by the manufacturer) when exposed to various environmental conditions over a period of time. It is affected by many factors, such as temperature of storage, chemical composition, exposure to sunlight, electrostatic discharge, moisture, thermal cycle, configuration, manufacturing process, shock and vibration [3, 62].

The critical, and most controversial, property of nitrate ester-based energetic materials is its stability. The chemical, physical, mechanical and ballistic properties of nitrate ester-based energetic material are very important for good functioning of any system (e.g., rocket motor). During use and storage, these properties are changing, due to chemical (stabilizer depletion, autocatalysis process, decomposition of nitrocellulose and nitroglycerine), thermal (temperature of thermal decomposition, activation energy,…), physical (humidity, migration and evaporation of plasticizer), mechanical (stress and strain caused by a fast increase in pressure, creep, vibration loads, rotation and acceleration), structural (debonding, cracking) and ballistic (proper functioning if full-scale or sub-scale rocket motors) influences. As a consequence, stability loss and performance decrease can occur [17, 18, 63, 64]. On the other hand, these processes can result in malfunctioning and sometimes lead to several disasters [15, 26, 65, 66]. Recently, the stability of nitrate ester-based energetic materials has garnered tremendous level of attention from research community, what is revealed by the increasing number of scientific publications in the field over the two past decades, as depicted in Fig. 3.

It is well reported that the autocatalytic decomposition process occurred inside an energetic formulation can be avoided if a sufficient amount of stabilizer is available. The amount of this stabilizing agent, which decreases during the stabilization process, can be monitored by several analytical techniques [67, 68]. Numerous tests have been utilized for the determination of the stability of nitrate ester-based energetic material over the last century. The most of the conventional techniques, which are quite simple, were designated for high temperature. This kind of procedures is termed artificial aging which increases the rate of decomposition leading to detectable modifications in a shorter time. The obtained results are commonly used for a prediction of the shelf life at ambient temperature [68]. During the last two decades, modern analytical methods have been developed in this field including thermal, spectroscopic, chromatographic and electrochemical techniques as well as the introduction of the modeling and simulating programs in order to find efficient procedures ensuring adequate surveillance and control of the stability of nitrate ester-based energetic materials [19, 37, 42, 43].

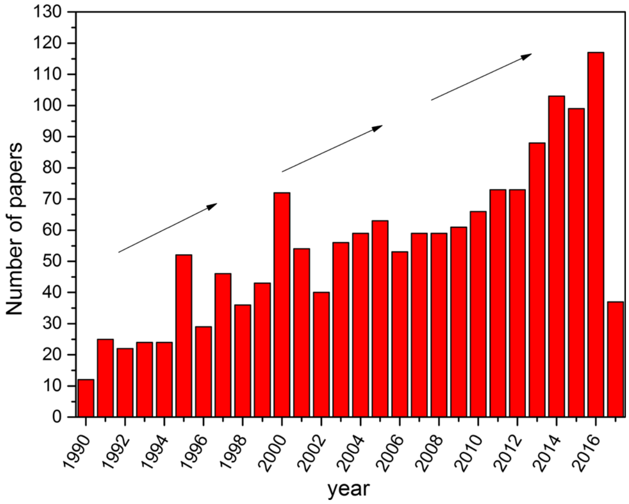


Figure 3 Illustration of the annual number of scientific publications since 1990, using the search terms "stability/propellant." Data analysis completed using Scopus search system on June 08, 2017.

The understanding of the stabilization mechanisms, the translation of the experimental results into terms of stability under various conditions and the evaluation of the shelf life of the energetic material formulation is not an easy way, since the decomposition processes are complex reactions. These reactions include, but not limited to, the interaction between nitrous oxides and the secondary products with the stabilizers, the production of stabilizer derivatives, the formation of small cracks caused by the species diffusions and the decrease in the molecular weight of nitrate esters [53, 54]. Recently, Trache and Khimeche investigated the stability of double-base propellant containing methyl centralite as stabilizer during natural and artificial aging. They revealed that chemical stability based on the stabilizer depletion, the physical stability which depends on the plasticizer content, the ballistic performance based on the heat of combustion and the mechanical properties are closely connected [17]. In another work, Guo et al. [69] have studied the influence of moisture content on the thermal stability of double-base propellant (nitrocellulose and nitroglycerine) and multi-nitro esters propellant (nitrocellulose, nitroglycerine and triethylene glycol dinitrate) by using heat flux calorimeter. The authors have shown that water has remarkable influence on the thermal decomposition of nitrate ester-based energetic materials, where the heat flow curves of the investigated propellant move toward the lower temperature direction with the increase in water content. The behavior is attributed to simultaneous physical and chemical actions.

Stabilizers

Stabilizer is an indispensible component introduced in the composition of nitrate ester-based energetic material, since nitrate esters degrade throughout the lifetime of the energetic formulation, from the moment of manufacture. The consequences of nitrate esters decomposition may include alterations in the chemical, physical and ballistic properties [15, 17, 19, 20, 30, 70]. As the energetic composition ages, there is a risk of ignition, which can lead to disastrous consequences during manufacture, storage and use. The physical properties may change as well, due to the changes in the structure of the nitrate esters. Cracking or the grain fractures can even influence the performance characteristics due to modifications in the surface area of the formulation, which may generate unexpected behaviors.

Stabilizer is a chemical substance added to the composition of energetic material to slow down its decomposition and to increase its shelf life, without sacrificing the performance. It was revealed that its role is not to completely prevent the decomposition of the nitrate ester-based energetic material, but to slow down the catalytic decomposition process [23, 71, 72]. The action of the common stabilizers can be explained by their ability to establish chemical bonds with the decomposition products which are evolved during storage. Several chemicals have been tested for use as stabilizers in nitrate ester-based energetic materials [21, 23]. Any potential new stabilizer must fulfill a number of essential requirements, in order to gain widespread acceptance as a potential energetic material's stabilizer [21, 23, 25, 27, 70, 71]. It is desirable that an effective and safe stabilizer and its products present a good compatibility with all energetic formulation components and should not have any detrimental action. The effective stabilizers should not be volatile at ambient conditions. Its quantity needs to be small to avoid impacting the energy output, but it imparts good stability to the energetic composition by disrupting the degradations reactions and reacting with free radicals thus absorbing nitrogen oxides or by neutralizing free acids. Some stabilizers may improve the physical properties (softening or gelatinizing) of the nitrate ester-based energetic formulation and consequently contribute to ease its manufacturing [3, 73]. The homogeneously distribution within the energetic formulation without any phase separation or migration to the surface of the formulation is strongly recommended. Furthermore, one of major current issues is the toxicological effect of stabilizer or its derivatives, which is the most critical drawback of the current industrial stabilizers giving rise to nitroso derivatives. Thus, the next generation of stabilizers must be non-toxic and has non-toxic chemical derivatives to minimize adverse effects during production, storage or use of energetic formulation.

A wide range of chemicals have been introduced in energetic formulations as stabilizers. However, none of these proposed stabilizers completely fill the requirements for a safe and effective stabilizer. The area of stabilizers research is active, seeking a stabilizer that is effective and presents fewer potential negative environmental and health impacts.

Current stabilizers

The most widely used stabilizers (Fig. 4) are from the classes of aromatic amines (e.g., Diphenylamine, 2-nitrodiphenylamine, para-nitro-methylaniline) and urea derivatives (e.g., akardite-II, akardite-III, ethyl centralite, methyl centralite) [15, 36, 47, 74, 75]. Historically, other compounds that have been used as stabilizers include readily oxidized compounds such as higher alcohols, camphor and unsaturated hydrocarbons [70]. Stabilizers can be either used singly or in mixtures to optimize the stability of the energetic material formulation. Some characteristics and applications of some conventional stabilizers are summarized in Table 1, whereas their physical properties are displayed in Table 2.

Aromatic amine-based stabilizers

Diphenylamine (DPA) has been in use since 1905 as a stabilizer of nitrate ester-based energetic material

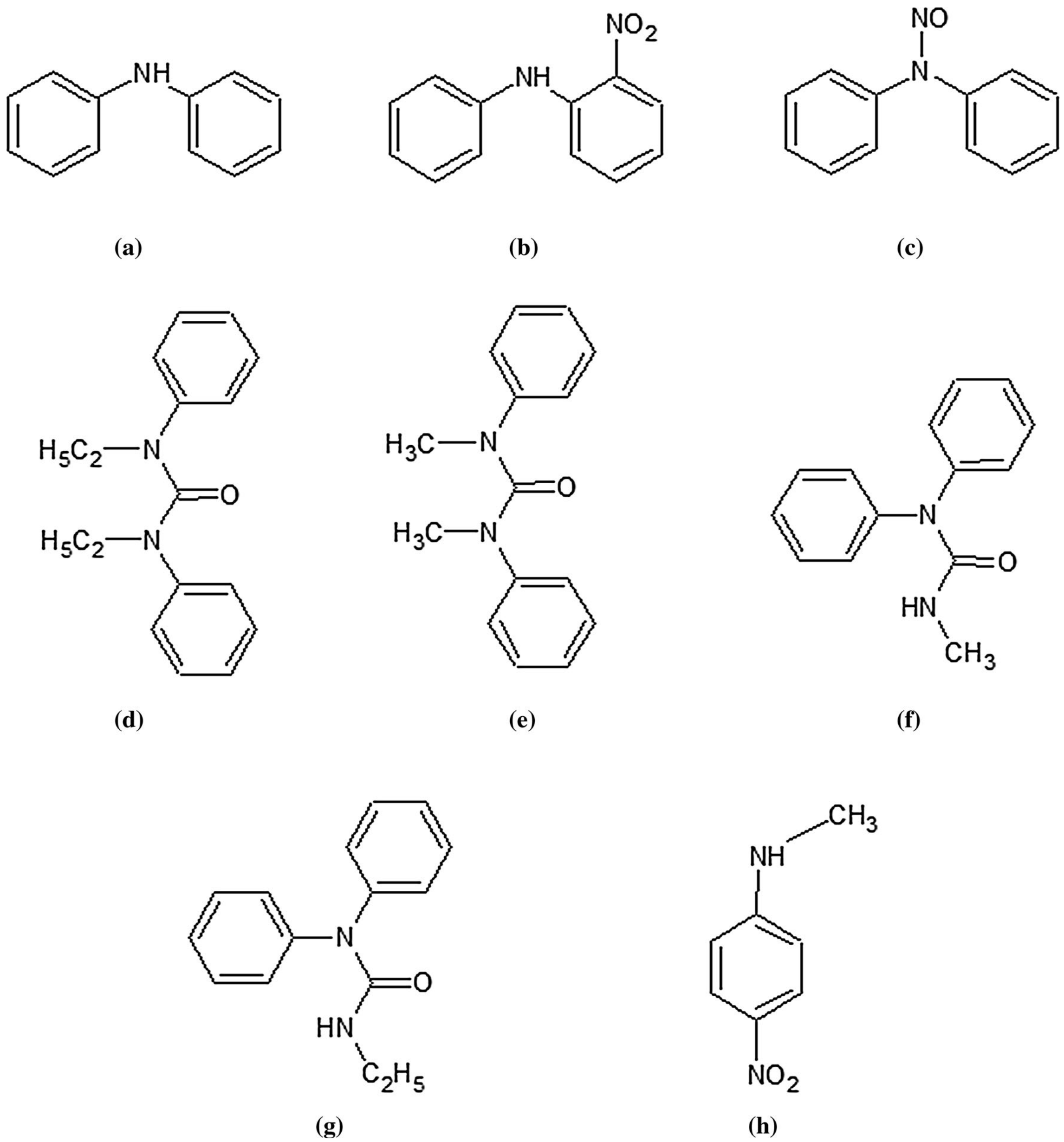


Figure 4 Structure and nomenclature of some conventional stabilizers; **a** DPA; **b** 2-NDPA; **c** N-nitroso-DPA; **d** ethyl centralite (EC); **e** methyl centralite (MC); **f** akardite-II; **g** akardite-III; **h** N-methyl-p-nitroaniline (MNA).

[40, 70]. It appears in the form of a crystalline white substance with a melting point of 54 °C and a boiling temperature of 302 °C [32]. DPA is industrially used as an antioxidant of rubber, insecticide and in the preservation of apples after harvesting. It is also used to manufacture azo dyes, pharmaceuticals and veterinary medicine.

In the field of energetic materials, DPA acts as stabilizer by fixing nitrogen oxides by a series of nitrosation and nitration reactions. The derivatives of diphenylamine act themselves as stabilizers, which significantly enhances the effectiveness of diphenylamine as stabilizer. One of the advantages of DPA is its reactivity. It is a basic stabilizer for single-base propellants (containing only NC as energetic component) and cannot be used in double base or other propellants because of its interaction (incompatibility) with nitroglycerine [72, 76]. DPA is a toxic substance that poses a direct danger for the human health such as eczema formation, hypertension and bladder diseases [40]. This stabilizer has a negative effect on the environment as well, especially in the

Table 1 Characteristic and application of some current stabilizers [3, 4, 131]

Compound	Characteristics	Application
Calcium carbonate ($CaCO_3$)	Odorless white powder	Added as an inorganic stabilizer for NC (used in propellants) to neutralize residual traces of H_2SO_4 in the fibers of NC
Diphenylamine (DPA)	White crystalline solid Melting point 54 °C	Mainly used for single-base propellants, but too basic for double-base and triple-base propellants
Urea	White powder Melting point 132.7 °C	Readily absorbs nitrogen oxides, which result from the decomposition of NC and NG, but too strong base to be used as stabilizer
Ethyl centralite	White crystals Melting point 72 °C	Very weak base due to the presence of phenyl groups and used as a stabilizer, gelatinizer and coolant, also imparts better rollability to rocket propellants formulation
Methylcentralite	White crystals, melts at 121 °C	It is useful as a stabilizer and surface gelatinizer (moderant) for NC powders
2-nitrophenylamine (2-NDPA)	Yellowish orange solid material, melts at 76–78 °C	Superior replacement of DPA, generally used for rocket propellants

Table 2 Physical properties of some current stabilizers: molar volume, $V^{298.15}$; melting temperature, T_m; and enthalpy of fusion, ΔH_m

Compound	$V^{298.15}$ ($cm^3\ mol^{-1}$)	T_m (K)	ΔH_m ($kJ\ mol^{-1}$)
Diphenylamine	145.90[a] 142.45[c]	326.7[b] 325.2[d] 326.3[e]	19.68[b] 17.53[a] 17.86[e]
2-Nitrodiphenylamine	167.36[f]	348.0[b] 346.2[d] 348.0[g]	26.14[b]
Ethyl centralite	241.36[m] 230.40[c]	345.1[b] 346.2[d]	33.54[b]
2,2′-Dinitrodiphenylamine	180.48[c]	445.5[b] 445.7[h]	18.36[b]
N-ethyl-4-nitro-N-nitrosoaniline	140.99[c]	391.8[b] 392.2[i]	31.15[b]
N-(2-acetoxyethyl)-p-nitroaniline	169.40[m]	387.1[j] 388.2[k]	20.8[j]
Methyl centralite	200.20[c]	393.2[j] 393.2[l]	33.5[j]

[a] Ref. [132], [b] Ref. [29], [c] Ref. [133],[d] Ref. [127], [e] Ref. [134], [f] Ref. [131], [g] Ref. [135], [h] Ref. [136], [i] Ref. [89], [j] Ref. [124], [k] Ref. [85], [l] Ref. [127], [m] Ref. [137]

marine environment [40]. Its decomposition products during the stabilization of energetic materials are carcinogenic, especially those containing nitrosamine groups [36, 40, 70, 77]. In contrast to the DPA, its derivative, 2-nitrodiphenylamine (2-NDPA) is widely utilized in the field of double- and triple-base propellants. The reaction of 2-NDPA with nitrogen oxides is complex with many nitration and nitrosation products being formed. These latter derivatives play a stabilizing effect as well [78–81].

N-methyl-nitroaniline (MNA) had previously been proved to be a quite effective stabilizer of nitrate ester-based energetic materials [25, 82–84]. It has a good capability to retain the nitrogen oxides, but it is consumed too fast and consequently a rapid use of the stabilizer. Furthermore, it was shown that MNA was easily crystallized because of the less compatibility with nitrocellulose and nitroglycerine, what limited its large application in solid propellant formulations [25].

MNA and 2-NDPA are often used together in cast double-base propellant compositions. The latter is a good overall stabilizer which confers a reasonable crack-free life and long-term stability on the propellant [80, 81]. Some derivatives of MNA are considered to be adequate for stabilizing some energetic formulations. P-nitro-*N*-(2-methoxyethyl) aniline (MENA) and p-nitro-*N*-(2acetyloxyethyl) aniline

(ANA) were recommend to be used as stabilizers to replace MNA in cross-linked modified double-base propellants and nitrate ester plasticized polyether propellants [85, 86].

Urea-based stabilizers

In addition to DPA, other commonly used stabilizers include centralites (ethyl and methyl) and akardites [47]. Numerous studies dealing with identification of the centralites and akardites derivatives as well as their preparation have been conducted. Their stabilizing action in the energetic material formulations has also been demonstrated [50, 70, 74, 87–89]. The centralite derivatives include 2-nitroethyl centralite, 4-nitroethyl centralite, 2,4-dinitroethyl centralite, 4,4-dinitroethyl-centralite, *N*-nitroso-ethylaniline and *N*-nitroso-4-nitroethylaniline among others [74, 87]. *N*-nitroso-alkylanilines produced from centralite have been shown to be more toxic than *N*-nitroso-DPA produced from DPA or 2-NDPA [88, 90]. The chemical derivatives of akardite-II (AK-II) are mainly similar to those of DPA [15]. Other nitro-derivatives products of akardite-II are thermolabiles and denitrosate easily though N–NO–AK–II [88]. Therefore, the same health and safety risks that are present with diphenylamine are also suspected for centralites and akardites.

Ethyl centralite has a melting temperature of 72 °C, and it can ensure double function. It plays the both stabilizing and plasticizing effects. It is fully compatible with nitroglycerin, which allows its broad use in multi-base propellants. Usually, centralites are not appropriate to be used in propellant grains with large web thickness. This is mainly due to the poor solubility and diffusivity of the gaseous products generated during the stabilization reaction [91].

Emergent stabilizers

Marqueyrol group is considered as the pioneer in the introduction of substances, as energetic material' stabilizers, other than aromatic amines or urea derivatives [92]. In their work, the authors investigated the stabilizing effect of several chemicals such as carbazol, *N*,*N*-biphenyl benzamide, naphthalene and mono-nitronaphthalene. Since Marqueyrol studies, extensive research works have been conducted in this field in order to obtain effective stabilizers. Several chemical substances have been developed to fulfill the required characteristics of efficient stabilizers such as triphenylamine [93], ketones [94, 95], phenols [96], natural products [27, 28], malonanilides [23, 24, 33], polymers [97], ionic liquids [98], zeolites [20] and *N*-methyl-p-nitroaniline derivatives [25]. Figure 5 displays some examples of these emergent stabilizers. Detailed descriptions of several of them, their advantages and limits are given below.

Triphenylamine

Triphenylamine (TPA) was firstly introduced as a stabilizer in 1937 and was demonstrated to have similar efficiency than DPA at a relatively high level of 2%. A few years later, an American research group produced TPA and revealed that it depleted at a faster rate than akardite-II or ethyl centralite, but at a slower rate than DPA [70]. TPA reacts mainly with nitrogen oxides by a series of nitration reactions that occur predominantly in the para-position of the aromatic rings, with solely minor fractions detected in the ortho-position. The TPA is expected to have a potential to replace conventional stabilizers (DPA, centralite) that form toxic nitroso derivatives. The kinetics of degradation reaction of TPA is quite simple to follow, since it is occurred in consecutive steps without parallel reactions. The activation energy for the consumption of triphenylamine has been reported by Wilker et al. as being in the range of 129–133 kJ mol^{-1} [93]. However, its depletion is so fast, especially for double-base propellants. This makes the evaluation of the stability difficult using the current procedures such as the standard method of AOP 48 [99]. Furthermore, the TPA nitro derivatives such as 4-NO_2-TPA and 4,4′-dinitro-TPA are found to be less effective as secondary stabilizers [93].

Ketones

5-phenyl-cyclohexane-4-carboxanilide-1,3-dione has been tested as stabilizer for double-base propellants by Soliman and El-Damaty [95]. They showed that it is able to be used as stabilizer, since they have compared the synthesized ketone to ethyl centralite, and interesting results have been obtained. The nitro derivatives of the ketone formed during the stabilization of the propellants are non-toxic for human being and do not pollute the environment. It is insoluble in water and allows the reduction of the influence of moisture. Consequently, an ease

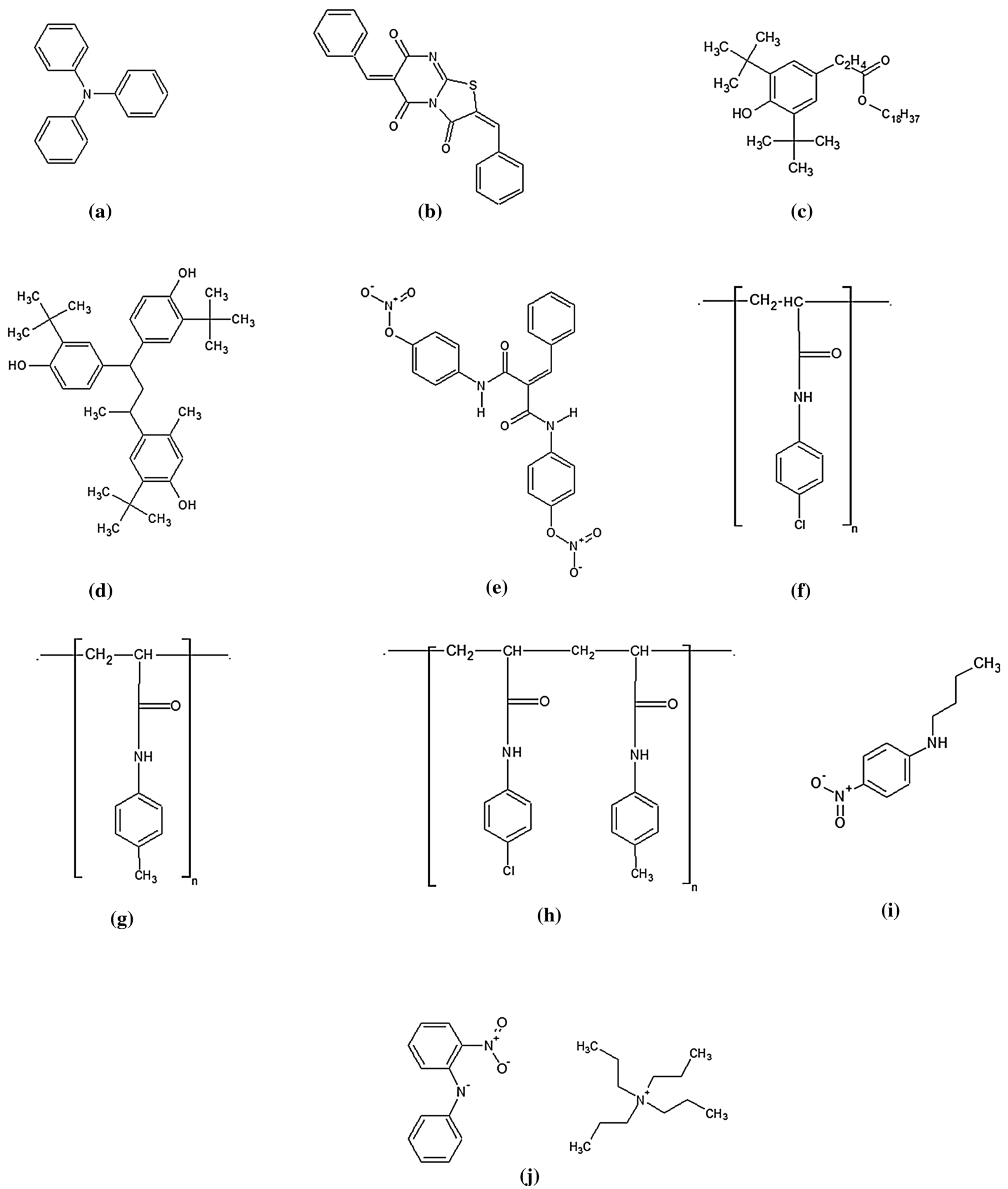


Figure 5 Structure and nomenclature of some emergent stabilizers; **a** TPA; **b** 2, 6-diarylmethylene-thiazolo [3, 2-a] pyrimidine-3, 5, 7-trione; **c** 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionic acid octadecyl ester; **d** 1,1,3-tri-(2-methyl-4-hydroxy-5-tert-butyl-phenyl)-butane; **e** *o*,*o*′-dinitromalonanilide; **f** poly N-(4-chlorophenyl) acrylamide (CPA); **g** poly N-(4-methylphenyl) acrylamide (MPA); **h** copolymer of CPA and MPA; **i** N-n-butyl-p-nitroanilide (n-BNA); **j** tetrabutylammonium 2-NDPA.

homogeneity can be obtained during the manufacture of an energetic composition. However, the reagents employed to prepare this stabilizer such as ethyl cinnamate and acetoacetanilide are difficult to synthesize. The use of high-performance liquid chromatography to study the stability of propellant samples and the identification of nitro derivatives seems to be very difficult, which limits its utilization in real energetic compositions [95]. In another work, Soliman's group has investigated another ketone compound which may show superior properties as stabilizer, 2,6-diarylméthylène-thiazolo [3,2-a] pyrimidine-3,5,7-trione, in comparison with the conventional ones [94]. The authors indicated that this ketone presented an interesting stabilizing effect with respect to the conventional stabilizers. They confirmed this fact by chromatography and Bergmann–Junk test, where they demonstrated the nitration of the benzene rings in the molecule. Furthermore, the ortho- and para-nitro derivatives exhibited a remarkable stabilizing effect.

Phenols and its derivatives

Various sterically hindered phenols have been evaluated as stabilizing agents [96, 100]. These phenols were added to nitrate ester-based energetic material formulations. While it was deduced that these phenols stabilize the energetic compositions, they were not efficient with respect to the conventional stabilizers. It was, however, found that the mechanism of stabilization is different between DPA and these phenols, where diverse radicals are fixed [100, 101]. It is advanced that the stabilization mechanism is accompanied by the production of peroxide radicals that could negatively affect the stability of nitrate ester-based energetic material. The labile hydrogen on the hydroxyl functional group of radicals leads to unwanted degree of acidity that can further catalyze the degradation reaction. Another limit of these sterically hindered phenols is the large size of the substituents that renders the aromatic ring less susceptible to substitute because of the steric hindrance. More recently, Krumlinde et al. [71] have suggested another type of electron-rich phenols with less steric hindrance that could act as both stabilizer and gelatinizing agent. The authors synthesized several phenol-based stabilizer candidates (Fig. 6) and evaluated their ability to stabilize nitrocellulose as a nitrate ester. The different synthesized chemicals are electron-rich owing to the methoxy-substituents on the aromatic rings and are therefore susceptible to electrophilic substitution. This investigation has shown that the burning behavior of the bis(2,6dimethoxyphenyl) triethyleneglycol (Stab-5)-stabilized rocket propellant indicated a plateau behavior at around 15–25 MPa and the overall burning rate is comparable to that of rocket propellants stabilized with centralite I and akardite-II. The heat flow calorimetric measurements have revealed that Stab-5 is an effective stabilizer according to STANAG 4582. In addition, the derivatives of Stab-5, formed in the reaction between Stab-5 and the decomposition products of nitrocellulose, have been identified using high liquid chromatography coupled to mass spectrometry, and the obtained results indicated the formation of four different less hazardous compounds [71].

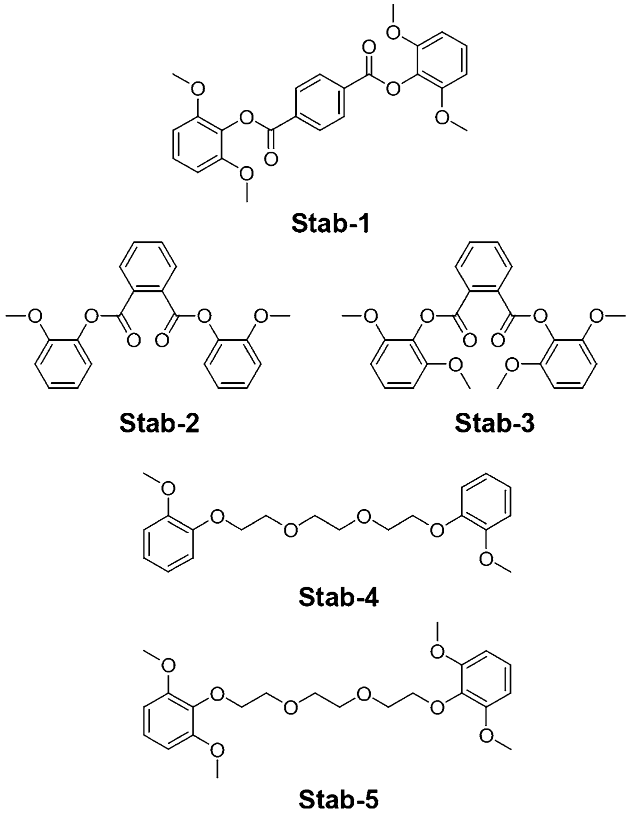


Figure 6 Structure of some phenols with less steric hindrance as stabilizers. Reprinted from Ref. [71] with permission. Copyright© John Wiley and Sons.

Other organic compounds

Some urethane compounds containing m-phenylene substituents and para-nitroaniline compounds were found to be useful as stabilizers for composite modified double-base propellants (CMDBP). Examples of these urethanes are 1,3-bis (n-methoxyphenylurethane) benzene, 1,3-bis(n-m-tolylurethane), 1,3-bis(n-m-chlorophenylurethane)benzene, 1,3-bis (n-mphenylurethane) benzene, 1,3-bis(n-ethylurethane) benzene and bis (m-methoxyphenyl) urethane. n and m are integers from 1 to 3. These urethanes do not react with isocyanate and therefore are particularly useful as stabilizers for CMDBP cross-linked with isocyanate [85, 102]. Hydrazine and alkyl hydrazine were also proposed as stabilizers [103]. It has been demonstrated that these chemicals and their derivatives are suitable as stabilizers for nitrocellulose propellants. These classes of chemicals are suspected to be carcinogen and are, therefore, unsuitable as non-toxic stabilizers. Some imines have been investigated as stabilizers for double-base propellants as well. While imines presented some activity as stabilizers, they were not as efficient as classical ones [70].

Natural products

Natural product derivatives such as deoxidized soya bean oil, deoxidized linseed oils and a deoxidized mixture of fatty acids have been studied as stabilizers [27, 28]. These natural product derivatives, frequently employed by the cosmetics industry, are reported to be of low toxicity. Some researchers described the evaluation of epoxidized soybean oil, namely Lankroflex E2307, as stabilizer for double- and triple-base propellants using chemical stability tests and microcalorimetry. Very promising results have been reported. Fryš et al. have tested other epoxidized oils in double-base propellants. These stabilizers, unlike conventional ones, meet the current requirements for toxicity affecting man and the environment. However, epoxidized soya bean oil showed low stabilizing effect when the weight loss of heated propellant was considered, but achieved suitably when analyzed by microcalorimetric techniques. The stabilizer effectiveness was still less than that of classical stabilizers [27, 28, 104].

Malonanilide derivatives

The malonanilide derivatives have a variety of applications, which include dyes and pigments [105, 106], pharmaceuticals [107], polymer stabilizers [108, 109], anti-inflammatory action [110] and thermal recording materials [111]. The possibility of using malonanilide derivatives as stabilizers for double-base propellants has been evaluated by an Egyptian group [23, 24, 33]. Different analytical techniques have been used, such as Abel heat test, international storage test at 100 °C, Dutch heat test at 105 °C and Bergmann–Junk at 120 °C to evaluate the stability of malonanilide-based propellants. The reported results demonstrated that the malonanilide derivatives have a potential stabilizing effect with respect to the classical ones. The use of non-isothermal thermogravimetric analysis (TGA) revealed that the employment of malonanilides improved the thermal stability of propellants as shown in Table 3. The malonyl *o*,*o*′-dinitromalonanilide dimer is considered as the best stabilizer between the different investigated malonanilide derivatives.

Polymers

A number of polymers have been investigated as stabilizers for nitrocellulose [97, 112, 113]. These polymers include acrylamido polymers and copolymers. They are not commercially available, which limits their potential use in large-scale manufacture. Other polymers that have been tested include bisphenol A-based epoxy resin, bromine containing epoxy resin, chlorinated polyvinylchloride and chlorinated rubber [97]. Similar research group has developed and used homopolymers and copolymer as stabilizers for nitrocellulose in comparison with the classical stabilizer, ethyl centralite. They found a great improvement in the thermal stability of nitrocellulose using polyN-(4-nitrophenyl) acrylamide which has an NO_2 group in the p-position. In continuation to this research work, poly *N*-(4-chlorophenyl) acrylamide (CPA), poly *N*-(4-methylphenyl) acrylamide (MPA) and their copolymer have been studied (CPA and MPA) [112]. Thermal analysis and Bergmann–Junk techniques have shown that the copolymer (CPA and MPA) and homopolymers (CPA, MPA) with high activation energy [112, 113] are much more efficient stabilizers than ethyl centralite (Table 4). These relatively high activation energy values were due to the more orientation or packing of nitrocellulose chains as a result of dissolving during mixing process, which increases the heat content of the mix. Consequently, the nitrocellulose mix stabilized by the copolymer needs the highest amount of activation energy for decomposition, which in turn demonstrates the highest

Table 3 Decomposition temperatures of DBPs samples containing different malonanilide stabilizers using TGA [23]

Stabilizers	Temperatures of starting decomposition (°C)	DTG peak temperature (°C)	Rate of maximum weight loss (mg min^{-1})
N,*N*′-diethyldiphenylurea	153.3	203.4	0.29
Malonanilide	153.3	201.6	0.39
N,*N*-diethylmalonanilide	153.0	205.0	0.36
o-dinitromalonanilide	151.5	223.0	0.53
m-dinitromalonanilide	155.8	210.0	0.39
p-dinitromalonanilide	156.0	221.0	0.49

Table 4 Activation energy of the thermal decomposition of nitrocellulose samples containing different stabilizers [112, 113]

Stabilizer	E_a (kJ mol^{-1})
Poly N-(4-chlorophenyl) acrylamide (CPA)	241.4
Poly N-(4-methylphenyl) acrylamide (MPA)	228.7
Copolymer (CPA and MPA)	311.4
Centralite	204.3
Diphenylamine	186
Poly 2-acryloyl-*N*,*N*-bis(4-nitrophenyl) propandiamide	257
Poly 2-acryloyl-*N*,*N*-bis(4-methylphenyl) propandiamide	372

efficiency of the copolymer as propellant stabilizer. Furthermore, the activation energy for poly (CPA) is higher than that of poly (MPA) owing to the difference in the electronic effects of Cl atom and CH_3 group. The high efficiency of the copolymer, however, is due to the fact that each repeat unit contains two phenyl rings which offer a wider possibility for the reaction with nitrocellulose decomposition products.

The efficiency of the poly 2-acryloyl-*N*,*N*-bis(4-nitrophenyl) propandiamide and poly2-acryloyl-*N*,*N*-bis(4-methylphenyl) propandiamide stabilizers and their synergistic effect were investigated using thermogravimetric analysis, Bergmann–Junk test and differential scanning calorimetry [113]. It was reported that both polymers and their 50:50% blend ratio are more efficient stabilizers of nitrocellulose than diphenylamine. The high molecular weight of polymer stabilizers with respect to the conventional ones can extend the life of these stabilizers, which will certainly improve the propellants life span, and the gelatinizing effect provided by the polymer can increase the activation energy of propellants and thus increase the safety of use and storage [112, 113]. The main potential advantage of a polymeric stabilizer over existing ones is that it would prevent migration problems, since in an aged energetic formulation the conventional stabilizer derivatives can migrate and diffuse [114, 115].

Zeolites

Recently, a number of inorganic non-toxic compounds (zeolites) have been introduced as stabilizers for double-base propellants [20, 21]. Zeolites are a large group of natural and synthetic hydrated aluminum silicates. They are characterized by complex three-dimensional structures with large, cage-like cavities that can accommodate water molecules, organic molecules, and even positively charged atoms or atomic clusters such as cations. Ions and molecules in the cages can be eliminated or exchanged without destroying the aluminosilicate framework. Zeolites find a wide range of applications such as catalysts, ion-exchange agents, and molecular filters in many industrial processes [116].

Clinoptilolite is not the well-recognized, but one of the more useful natural zeolites. It is a hydrated sodium potassium calcium aluminum silicate ((Na, K, $Ca)_2$-3 Al_3(Al, $Si)_2$ $Si_{13}O_{36}$; $12H_2O$). Clinoptilolite has received much attention, and it is used in many applications such as a chemical sieve, a gas absorber, a feed additive, a food additive, an odor control agent and as a water filter for municipal and residential drinking water and aquariums. Clinoptilolite is well appropriate for these uses owing to its chemical neutrality, large amount of pore space and high resistance to extreme temperatures [116, 117]. Different tests were utilized by Zayed et al. to check the stability of double-base propellants (DBP) containing clinoptilolite as stabilizer [20, 21]. The obtained results revealed that the percentage of 4% w/w of nano-clinoptilolite can be considered as good stabilizer for DBP, since it showed a pronounced stabilizing effect. The employment of such inorganic stabilizers for double-base propellants stabilization can solve the issue of reaction of organic stabilizers with nitrous oxides gases evolved to form volatile harmful and carcinogenic products like nitrosamines.

Ionic liquids

Ionic liquids (ILs) have been previously tested in liquid propellant uses in the late seventies, but due to development constraints they have been discarded for stabilizing application [98]. They have been suggested as space monopropellants to substitute hydrazine, and numerous research papers appeared in this field. A general review focusing on the catalytic decomposition of propellants, including ionic liquids is reported [118]. Other reviews concerning new energetic ionic liquids have been appeared as well [119–121].

ILs have reported for their potential use in developing the next generation of stabilizers. This is because ILs have a design flexibility that allows the chemist to choose two counter ions for the formulation of ionic liquid and the use of molecules that provide task-specific performance with high affinity to nitrous oxides, since a large number of organic molecules can be ionized by alkylation or protonation. However, the most of ionic liquids, based on anionic form of 2-nitrodiphenylamine or diphenylamine, are sensitive to water and thus contribute to accentuate the hygroscopic character of energetic material formulation, which currently limits their application [98].

Eutectic composition of stabilizers

Although the behavior of conventional stabilizers has been the subject of numerous investigations [122], relatively little is known about the nature of the reactions occurred in a propellant containing a mixture of two stabilizers. The thermodynamic properties and structural details of these mixtures are very scarce [123]. Studies have shown that energetic material contained in its composition binary mixtures of organic stabilizers, with molar fractions similar to that of the eutectic compositions, may be used without any risk if they present high eutectic temperature. [29, 124, 125]. In contrast, the employment of mixtures of organic stabilizers which have lower values of eutectic temperature, a risk of melting, migration and evaporation can occur, causing a loss of stability, cracks in the block and change of the surface combustion, and leading to catastrophic circumstances (Fig. 7).

N-methyl-P-nitroaniline derivatives

Several *N*-methyl-p-nitroaniline derivatives such as *N*-ethyl-p-nitroaniline (ENA), *N*-n-propyl-p-nitroaniline (n-PNA), *N*-i-propyl-p-nitroaniline (i-PNA), *N*-n-butyl-p-nitroaniline (n-BNA) and *N*-t-butyl-p-nitroaniline (t-BNA) have been designed and synthesized by increasing the carbon chain length on nitrogen atom by Tang [25]. The obtained results showed that the solubility of these stabilizers in nitroglycerine could be improved owing to the long paraffin substitution groups such as n-propyl and n-butyl on the nitrogen atom of p-nitroaniline, therefore leading to the high-temperature stabilization effect of these stabilizers. It was demonstrated that the stability of CMDBP with n-BNA was the best and therefore can be considered as the most promising candidate as a stabilizer of CMDBP.

Mechanism of stabilization

Action of diphenylamine and centralite

The stabilization mechanism of nitrate ester with DPA is very complex. This mechanism follows either the ionic, free radical or charge transfer complex pathway, or all of them, depending upon the acidity and moisture of the composition and structure of the energetic composition [55]. The stabilization of nitrate esters with DPA develops in a range of reactions which results in the formation of nitroso-diphenylamine and may even form tri-, tetra- or hexa-nitrodiphenylamine, knowing that the appearance of the dinitro derivatives indicates a harmful and rapid

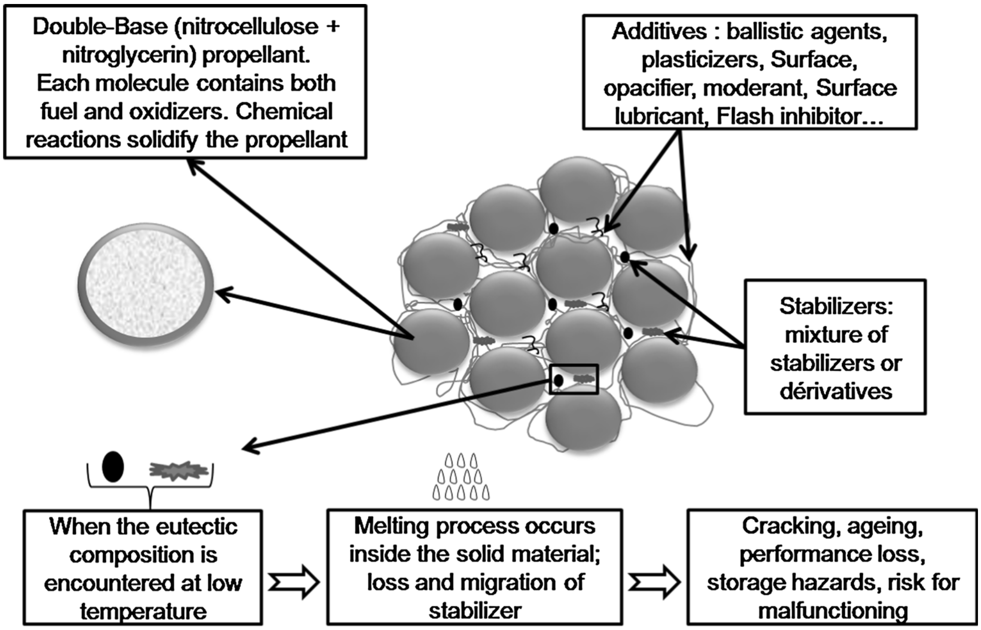


Figure 7 Schematic of the stabilizers melting phenomenon inside the energetic material. Reprinted from Ref. [125] with permission. Copyright© Elsevier Limited.

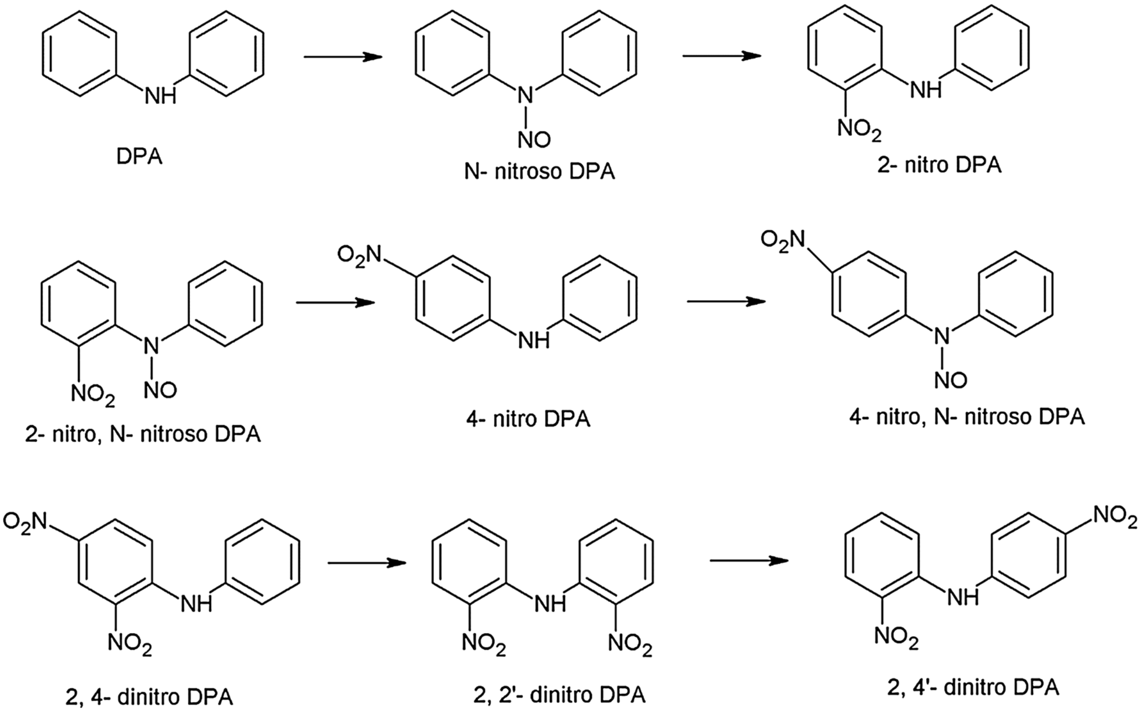


Figure 8 Decomposition pathways of diphenylamine.

degradation [126]. Two reaction channels are involved with the DPA, nitration and nitrosation (Fig. 8). In the case of the nitrosation, nitroso derivatives (N–NO) are formed. Similarly, the reaction of nitration gives rise to C-nitro derivatives. The nitro substitution takes place on the 2, 4 or 6 position of the phenyl group (ortho or para). This observation is quite clear from the fact that it results from an electrophilic substitution on the phenyl group, influenced by the ortho/para-orientation tendency of the amine group in DPA [67, 75, 127]. It is worthy to note that each NO_2 group added introduces an acidity which initially neutralizes the reported basicity, but then makes the product capable of

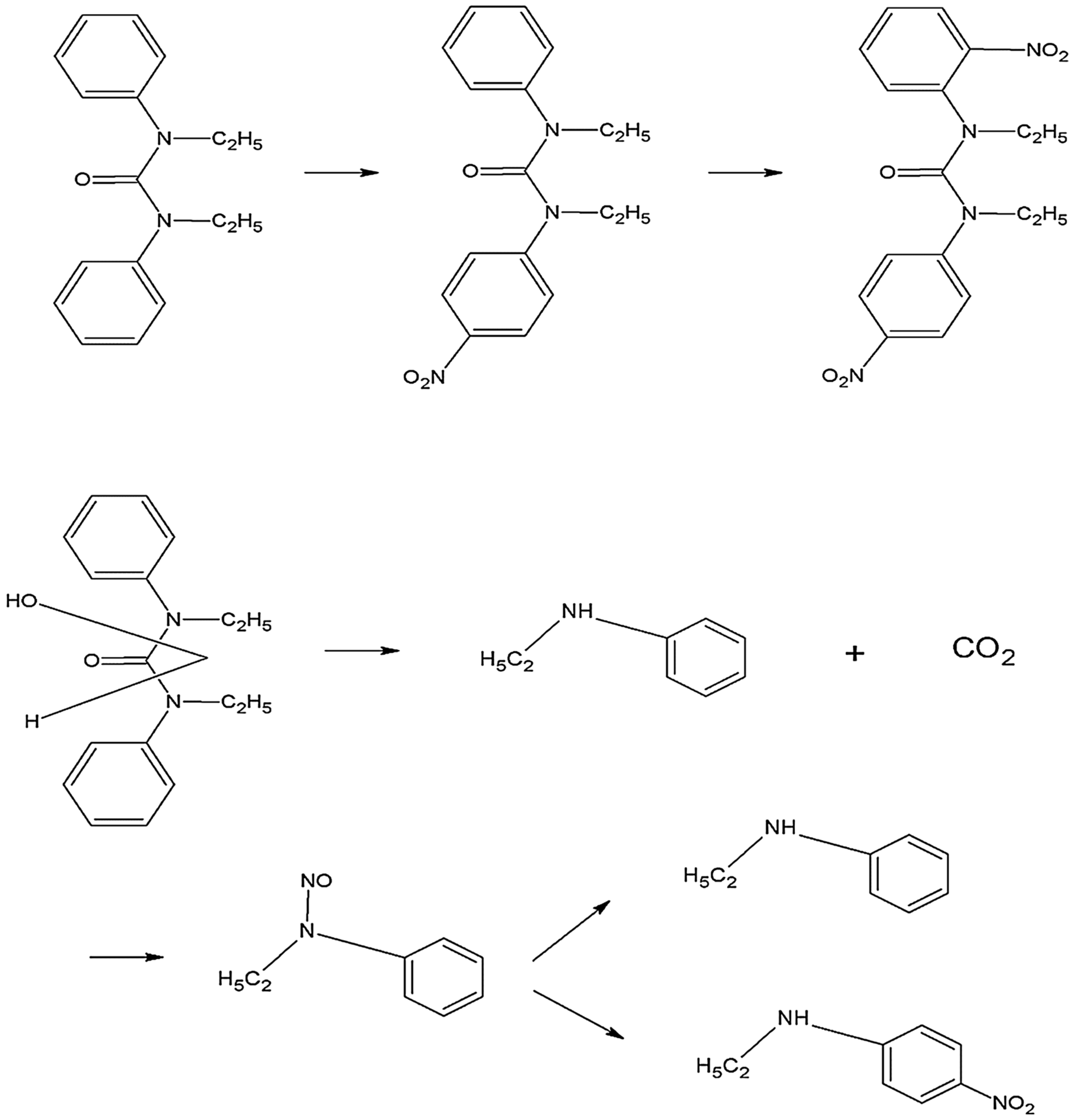


Figure 9 Decomposition pathways of ethyl centralite.

hydrolyzing the nitrate ester at an advanced stage of degradation [91]. In addition, some rearrangement reactions can occur to transform nitroso derivatives to nitro derivatives [55].

The centralite depletion sequence is even more complicated and begins with one of the aromatic rings, but, at the same time, the molecule is hydrolyzed by water, in an acid medium, with the emission of carbon dioxide and formation of ethylaniline. Centralite reacts with nitrogen oxides by nitrosation and nitration reactions such as diphenylamine [128]. The release of CO_2 due to the reaction of the centralite may be the origin of cracking found in propellants with large web thickness [91]. Unlike diphenylamine, ethyl centralite gives rise to the cleavage of the urea bond as illustrated in Fig. 9, according to a process involving a nitrosoammonium ion as intermediate. Once the urea bond is split, there is a formation of monoaromatic derivatives.

The comprehensive work is that of Volk [129], who studied several propellants stabilized by diphenylamine and ethyl centralite, which have undergone accelerated aging between 65 and 90 °C and which have been analyzed by thin-layer chromatography in regular intervals. Volk has demonstrated the appearance of 30 derivatives of diphenylamine and

25 derivatives of ethyl centralite. This study confirms the formation of the N-nitroso and nitro derivatives with a preference for ortho- and para-substitutions.

Action of triphenylamine and zeolites

TPA differs from other stabilizers by its reaction pathway. It does not have a nitrosation step, which usually is the first reaction to occur with DPA, 2-NDPA or anilines. In all reaction steps, the nitration reaction occurs in the para-position, with only minor fraction found in the ortho-position. A very clear reaction scheme (Fig. 10a) was firstly established by Schroeder et al. [130]. The conversion of TPA ends by the formation of 4,4′,4′′-trinitrophenylamine. This component is basically insoluble in any solvent and so is not easily quantified. The 4-nitro-triphenylamine, however, is the first derivative of TPA which is less efficient than the primary stabilizer [70, 93]. Stabilizing effect of TPA and its derivatives has been studied by Wilker et al. [93] using microcalorimetry and weight loss test. As illustrated in Fig. 10b, the content of different components decreases rapidly in the following order: TPA > 4-NO_2-TPA > 4,4′-di-NO_2-TPA.

The mechanism of stabilization of clinoptilolit ((Na_2, K_2, Ca) $_3$ $Al_6Si_{30}O_{72}$; $24H_2O$) takes place in three stages [20]. A schematic presentation of the stabilizing mechanism of this zeolite is depicted in Fig. 11. The first step concerned the physico- or chemisorption of the evolved nitrous oxides (NO_x) via interactions with cationic surface to form

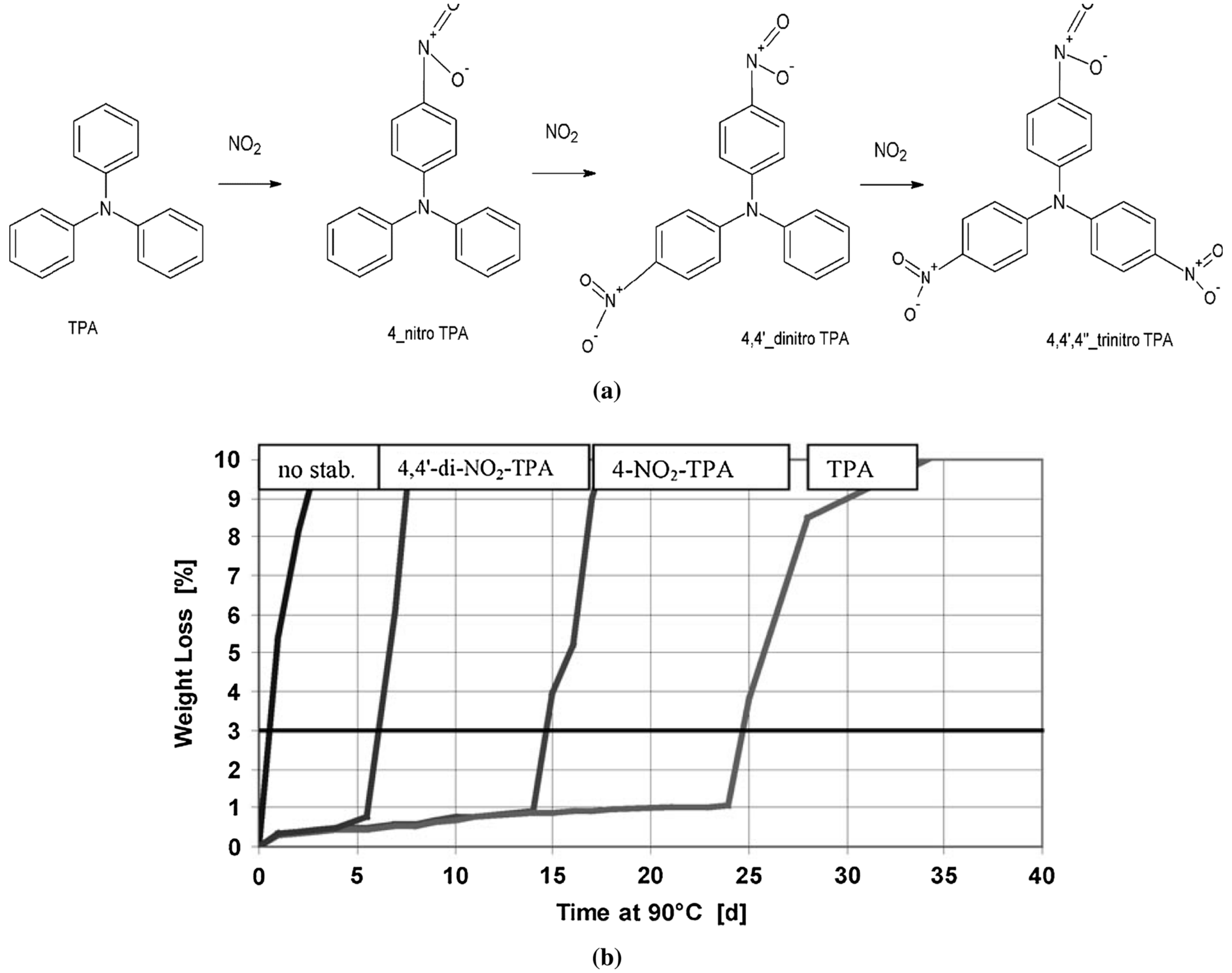


Figure 10 **a** Decomposition pathways triphenylamine; **b** weight loss results at 90 °C of propellants stabilized with TPA and its derivatives compared to non-stabilized propellant. Reprinted from Ref. [93] with permission. Copyright© John Wiley and Sons.

Figure 11 Sketching drawing of (NO_x) forming a bi-layer (tail to tail) on the surface of clinoptilolite, NO_x partitioning into the bulk and specific base binding of gas radicals. This scheme is drawn based on Fig. 12 in Ref. [20].

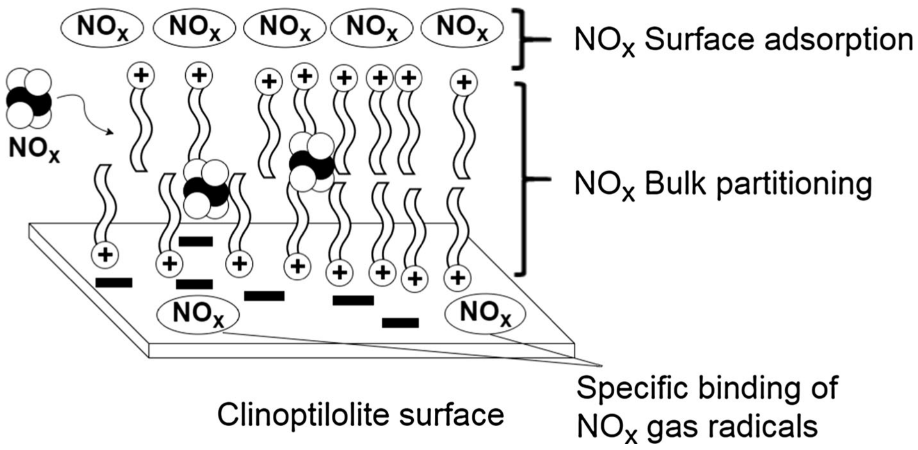
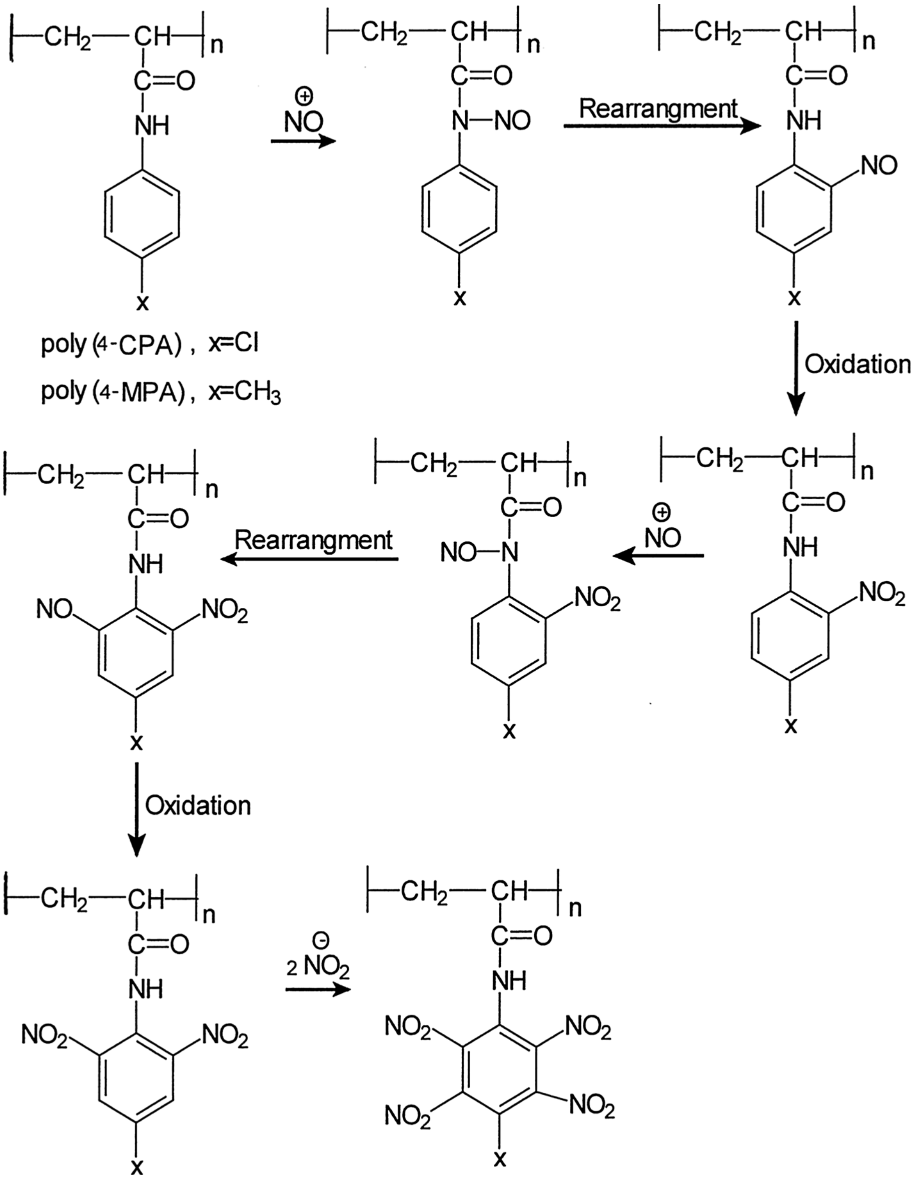


Figure 12 The probable mechanism for the reaction of homopolymers (CPA and MPA) with decomposition products of nitrocellulose. Reprinted from Ref. [112] with permission. Copyright© Elsevier Limited.



stable bi-layer on the external surface of the cliptilolite. The second one encompassed the distribution of the released NO_x gases into the internal cavities of zeolite together. The last step may involve specific binding of the adsorbed NO_x radicals with cationic form of cliptilolite at its internal base structure. It was shown that the grain size of inorganic stabilizer played a crucial role in the stabilizing process.

Action of polymers and copolymers

Figure 12 illustrates the mechanism suggested by Shehata and Hassan [112] for the reaction of poly *N*-(4-Chlorophenyl) acrylamide (CPA) and poly *N*-(4-Methylphenyl) acrylamide (MPA) as stabilizers with the evolved degradation products of nitrocellulose. The NO^+ attacks the nitrogen atom of the amide group forming N-nitroso compound which undergoes rearrangement to the ortho-position and then oxidizes to a nitro derivative. Another NO+ attack to form another nitroso group that also undergoes rearrangement to the other ortho-position and oxidation to a nitro derivative would occur. The remaining two positions on each phenyl ring are believed to be merely attacked by NO_2, leading to the formation of tetra-nitro derivatives. Similar mechanism could be suggested in the case of the reaction of the copolymer with nitrocellulose decomposition products, taking into account that every repeating unit of the copolymer structure comprises two phenyl rings.

Conclusion

The deep knowledge of the decomposition behavior and chemical stability of nitrate ester-based energetic materials (EMs) is one of the main prerequisites in order to ensure the required degree of safety over the entire life cycle. The development of efficient stabilizing agents and reliable test methods for these EMs has received much attention from a number of research groups worldwide. Even though so much progress has been made, there are still many challenges and much work left to be done in order to substitute the conventional stabilizers of nitrate ester-based energetic materials such as diphenylamine and centralite. These current substances generate mainly toxic derivatives. The next generation of stabilizers requires, however, several characteristics to be widely accepted such as efficiency, environmentally friendly derivatives, and availability at reasonable cost. Consistent analytical procedures for the assessment of the EM stability should be developed as well. Hence, the first part of this review article focused on the current and emergent stabilizers of nitrate esters, their advantages and shortcomings, and later has focused on their mechanisms of action and the stability evaluation of EMs. In addition, decomposition mechanisms and stabilization of nitrate ester-based energetic materials have also been discussed for beginners in the field. We believe that the studies presented in this article will increase the interest of researchers on nitrate ester-based energetic material's stabilizers as well as the basic understanding of their mechanisms of action.

Acknowledgements

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