Overview / Przegląd

Conventional and alternative nitrocellulose stabilisers used in gun propellants

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Abstract: The European Union industry must adapt to the requirements of the REACH regulations, which aim to improve human health and to protect the environment by using less toxic chemicals. The technology for producing nitrocellulose propellants utilises stabilisers that bond volatile products with autocatalytic properties of nitroester degradation. During this process, N-nitroso derivatives are formed, which exhibit toxic/carcinogenic properties. Moreover, some of the impurities found in stabilisers are characterised by toxic properties (e.g. in diphenylamine). In recent years, intensive research has been carried out on alternative nitrocellulose stabilisers with properties similar to or better than conventional stabilisers. The published studies on this subject mainly present research on chromatographic analysis, evaluation of stability using various methods and thermochemical analysis.

Streszczenie: Przemysł w Unii Europejskiej musi dostosować się do wymagań stawianych w rozporządzeniu REACH, które ma na celu polepszenie zdrowia człowieka i ochrony środowiska poprzez stosowanie mniej toksycznych substancji chemicznych. W technologii wytwarzania prochów nitrocelulozowych stosuje się stabilizatory, które wiążą lotne produkty o właściwościach autokatalitycznych rozkładu nitroestrów. W trakcie tego procesu powstają N-nitrozopochodne, które mają właściwości toksyczne/kancerogenne. Również niektóre zanieczyszczenia występujące w stabilizatorach charakteryzują się właściwościami toksycznymi (np. w difenyloaminie). W ostatnich latach prowadzone są intensywne badania nad alternatywnymi stabilizatorami nitrocelulozy, które będą charakteryzowały się właściwościami zbliżonymi lub lepszymi do konwencjonalnych stabilizatorów. W opublikowanych pracach w tej tematyce przedstawiane są głównie badania z analiz chromatograficznych, stabilności różnymi metodami oraz analiz termochemicznych.

Keywords: decomposition of nitrocellulose, “green” stabilisers, eutectic
Słowa kluczowe: rozkład nitrocelulozy, „zielone” stabilizatory, eutektyk

Symbols and abbreviations

- $f$: number of phases
- $f_{Eu}$: eutectic fraction
- $R$: gas constant [J/mol·K]
1. Introduction

Nitrocellulose (NC) is a synthetic polymer, which is widely used in both civil and military industries. The nitrate group (–O–NO₂) found in nitrocellulose is characterised by low binding energy (155 kJ/mol) [1, 2], which causes the bond to break easily. This in effect leads to the release of volatile products – nitrogen oxides, which exhibit autocatalytic properties. NC decomposition is an exothermic transformation and may consequently result in a thermal explosion. Nitrocellulose decomposes under ambient conditions according to three mechanisms: hydrolytic, thermal and photochemical [3]. Thermal aging and photoaging reduce the content of crystal domains in NC. The thermal stability is influenced by, among others, crystallinity and the size of the NC fibres. Lower crystallinity (and thus greater distance between the polymer chains) makes nitrogen oxides migrate from the NC matrix more easily [4]. The activation energy of the micro-fibre decomposition process is 157.4 ±0.4 kJ/mol, while for nano-fibres it is 105.2 ±0.3 kJ/mol [5] storage and usage. In present study, the thermal stability of micron and nano-sized nitrocellulose samples was determined by differential scanning calorimetry (DSC). On the other hand, the increase in NC decomposition heat and the decrease in the temperature
of the decomposition process occur along with the increase of nitrogen content in this polymer [6]. Storage and use. In the present study, the thermal stability of four nitrocellulose samples containing various amount of nitrate groups was determined by differential scanning calorimetry (DSC).

To extend the shelf life of NC-based products, compounds that bind volatile NC decomposition products, *i.e.* stabilisers, are added to its matrix. Effective stabilisers should be characterised by the following parameters [2, 7-9]:

- compatibility with all components contained in a given product,
- very good reactivity with nitrogen oxides,
- acid neutralising properties,
- good nitrogen oxides adsorption properties,
- non-toxicity – both the stabilising compounds themselves and the resulting derivatives and impurities.

2. **Conventional nitrocellulose stabilisers**

Conventional NC stabilisers belong to aromatic amine derivatives or aromatic urea derivatives. The first group includes:

- diphenylamine (DPA),
- 2-nitrodiphenylamine (2-NDPA),
- *p*-nitro-*N*-ethylaniline (pNEA),
- *p*-nitro-*N*-methylamine (pNMA).

Whereas the second group includes:

- acardite I: *N,N*-diphenylurea (AkaI),
- acardite II: *N*-methyl-*N'*-*N*-diphenylurea (AkaII),
- centralite I: *N,N'*-diethyl-*N,N'*-diphenylurea (CI),
- centralite II: *N,N'*-dimethyl-*N,N'*-diphenylurea (CII).

The DPA content used in nitrocellulose powders is approx. 1% [7]. One of the advantages of applying DPA to propellants is its reactivity towards volatile NC decomposition products [10]. It is only used for single-base propellants (NC constitutes 90 wt.%), because DPA is incompatible with nitroglycerine (NG), which is used in double- and triple-base propellants. Diphenylamine binds nitrogen oxides arising from the decomposition of NC and forms derivatives such as [11, 12]:

- *N*-nitrosodiphenylamine (N-NODPA),
- 2- and 4-NDPA,
- 2- and 4-nitro-*N*-nitrosodiphenylamine (2- and 4-N-N-NODPA),
- 2,4'- and 4,4'-dinitrodiphenylamine (2,4'- and 4,4'-DNDPA).

Total DPA consumption occurs after aging the propellant for 4-6 days at 100 °C [13]. The effect of aging at 100 °C on the decomposition process measured by differential scanning calorimetry (DSC) is not significant. The determined process parameters (maximum temperature, onset temperature and heat of decomposition) are similar within the error limit. The decomposition rate constant of the aged propellant determined by a thermogravimetric method (TG) (9 days, 100 °C) is 38% higher compared to the non-aged propellant. Katoh *et al.* [14] studied the induction period of various stabilisers, which they defined as the intersection of the tangent increase in heat flow with the baseline of the DSC curve (onset). DPA and its nitro derivatives (2-NDPA, N-NODPA) cause an increase in the NC induction period and a decrease in the amount of heat released over time. Lussier *et al.* [11] studied the chemistry of the DPA reaction and its nitro derivatives with nitrogen dioxide under normal conditions during storage. They determined the possibility of two reaction mechanisms, *i.e.* N-nitrosation and C-nitration. The N-nitrosation reaction is favoured because additional energy is needed for C-nitration to obtain a resonance transition structure. The reactivity of diphenylamine nitro derivatives towards DPA decreases in the following order: N-NODPA, 2-NDPA and 4-NDPA. Table 1 summarises the content of the stabiliser and its derivatives in the single-base propellant, which was aged naturally for 32 years under normal conditions. The content of N-NODPA and 4-N-N-NODPA is similar, while there are less of the mono- and dinitropic derivatives in comparison to N-NODPA.
Table 1. The content of diphenylamine and its nitro derivatives in naturally aged single-base propellant [11]

| Compound       | Content [wt.%] |
|----------------|----------------|
| DPA            | none           |
| N-NODPA        | 0.18           |
| 2-NDPA         | 0.08           |
| 4-NDPA         | 0.07           |
| 2-N-N-NODPA    | none           |
| 4-N-N-NODPA    | 0.17           |
| 4,4′-DNDPA     | 0.01           |
| 2,4′-DNDPA     | 0.04           |

The biggest disadvantage of DPA is its toxicity and negative impact on the environment. DPA is in the third place on the list of compounds polluting the environment in the European Union. For this reason, in recent years, studies have been conducted to find ecological as well as environmentally and human friendly NC stabilisers [15] in the perfumery, and as antioxidants in the rubber and elastomer industry. DPA is also widely used to prevent post-harvest deterioration of apple and pear crops. DPA is a parent compound of many derivatives, which are used for the production of dyes, pharmaceuticals, photography chemicals and further small-scale applications. Diphenylamines are still produced worldwide by the chemical industries. First reports showed that DPA was found in soil and groundwater. Some ecotoxicological studies demonstrated the potential hazard of various diphenylamines to the aquatic environment and to bacteria and animals. Studies on the biodegradability of DPA and its derivatives are very sparse. Therefore, further investigation is required to determine the complete dimension of the potential environmental hazard and to introduce possible (bio).

Another commonly used stabiliser is CI. This compound also displays nitrocellulose plasticising properties. Hence, a higher content of CI (1.0 to 7.5%) is used in propellants [7]. During NC decomposition, the formed volatile NC decomposition products react with CI to form 2-nitroCI and 4-nitroCI. Simultaneously, the breakdown of CI molecules can occur, which leads to the formation of N-ethylaniline derivatives [7]. Increasing the CI content from 2 to 5.2 wt.% increases the induction period by 12 h and reduces the amount of heat released from 11 to 8.6 mW [14]. CI exhibits similar stabilising properties. Trache et al. [16, 17] studied the effects of natural aging (air humidity did not exceed 60%, temperature in the range of –5 to 45 °C) on the thermal properties of double-base propellants containing 2.5 wt.% CII after 15 and 25 years of storage. With longer aging, a reduction in the content of CI and NG in the propellants and a reduction in the heat of propellant combustion were observed. The activation energy of the propellant decomposition process decreases from 146.1 to 141.2 kJ/mol (DSC measurements, kinetic parameters determined by the Ozawa method).

AkaII is another urea derivative used as a nitrocellulose stabiliser. It is an effective stabiliser in double-base propellants [10]. The induction period of AkaII is greater than DPA as well as its nitro derivatives and CI [14]. In propellants with the addition of AkaII, no large heat effects were observed for 7 weeks in microcalorimetric measurements at 85 °C (similarly to propellants containing CI) [18]. In these conditions, AkaII consumption is less than CI during the measurement.

3. Alternative nitrocellulose stabilisers

There are numerous publications concerning the use of new, eco-friendly NC stabilisers. Research on alternative NC stabilisers is conducted due to the carcinogenic properties of conventional stabilisers and N-nitrosamines, which are formed during NC decomposition. In freshly produced propellants containing stabilisers such as AkaII, CI or 2-NDPA, the percentage of N-nitrosamines is 0.01-0.1%, while in propellants with DPA, it is as much as 0.1-0.5% [1, 2]. Alternative NC stabilisers are proposed [9], e.g.:

– triphenylamine (TPA) [1],
– phenol derivatives (which contain at least one aromatic ring in their structure) [14, 19-21],
– ionone derivatives (trimethylcyclohexenylbut-3-en-2-one) [22],
– tocopherol derivatives [23],
– trialkoxy benzene derivatives [24],
– epoxidised oils (Lankroflex E2307 – epoxidised soybean oil, Lankroflex L – epoxidised linseed oil, Lankroflex ED6 – epoxidised octyl stearate) [2],
– malonoanilide derivatives [25-27],
– polymers, e.g. copolymers and homopolymers of \( N-(4\text{-methylphenyl})\text{acrylamide} \) and \( N-(4\text{-chlorophenyl})\text{acrylamide} \) [28],
– inorganic compounds, e.g. hydrated aluminosilicate (clinoptilol) [29] the surface area of stabilizer increases and the ability to absorb pronounce amount of hazardous nitrogen oxides increases. In this work clinoptilolite in nano-scale (30nm).

Most of the listed alternative stabilisers have a better or comparable nitrocellulose stabilising effect compared to conventional stabilisers. The authors of research on new NC stabilisers mainly present the results of chromatographic studies (analysis of the amount of stabiliser before and after aging in NC or propellants), stability tests (Abel’s test, Bergmann-Junk test), analysis of thermal properties (including determination of process activation energy and stability assessment in accordance with the STANAG 4582 standard). Little information is available on other properties, e.g. solubility of stabilisers in various solvents or analysis of mechanical and energy-ballistic properties of NC and/or propellants with alternative stabilisers.

Triphenylamine (TPA) is a tertiary amine and therefore does not form carcinogenic \( N\)-nitrosamines. During NC decomposition, the following nitro derivatives are formed: 4-nitrotriphenylamine (4-NTPA) and 4,4’-dinitrotriphenylamine (4,4’-DNTPA). Wilker et al. [1] examined the thermal stability of single, double and triple-base powders based on TPA. Based on the analysis of the vacuum stability and a microcalorimetric test (89 and 120 °C), it was found that all types of the studied TPA propellants are stable and compatible. During aging, TPA is consumed faster than CI, AkaII and 2-NDPA, and only DPA is consumed faster than TPA. For example, in DPA powders at 80 °C, after 7 days, there is 0.51% stabiliser loss, while for TPA it is 0.32% [7]. It has been observed that the stability of TPA nitro derivatives rapidly decreases in the following order [1]: TPA > 4-NTPA > 4,4’-DNTPA. The stabilising properties of TPA are analogous to DPA [30, 31]. In the case of high costs associated with the production of alternative stabilisers compared to the conventional ones, mixtures of stabilisers may be used. The simplest system of this type is a two-component mixture with eutectic composition. A eutectic (Eu) system is characterised by the lowest melting point and highest solubility. The dependence of the composition of the saturated solution in relation to the crystals of the “i”-th component on temperature is described by the liquidus equation of component “i” [32, 33]:

\[
\ln(x_{i}/\gamma_i) = -\frac{\Delta H_{mp,i}}{R} \left( \frac{1}{T_{eq}} - \frac{1}{T_{mp,i}} \right) + \frac{\Delta C_{p,mp,i}}{R} \left[ \frac{T_{mp,i}}{T_{eq}} - \frac{T_{mp,i}}{T_{eq}} \ln \left( \frac{T_{eq}}{T_{mp,i}} \right) \right]
\]  

where: \( x \) – molar fraction of component “i”, \( \gamma_i \) – the coefficient of activity of component “i”, \( \Delta H_{mp,i} \) – enthalpy of melting of component “i”, \( R \) – gas constant, \( T_{eq} \) – equilibrium temperature [K], \( T_{mp,i} \) – melting point of component “i” [K], \( \Delta C_{p,mp,i} \) – the difference in heat capacity of substance “i” in solid and liquid state for the assumption of temperature independence.

DSC tests can be carried out to determine the phase diagram of a two-component system with eutectic composition [34, 35]. Measurements should be made at the lowest possible rate of temperature increase to ensure conditions closest to the thermodynamic equilibrium (most often measurements carried out at 1 or 2 °C/min) [32, 35]. Examples of DSC curves obtained in a two-component TPA+CI system are presented in Figure 1.
The first peak corresponds to the melting process of the eutectic and the second peak corresponds to the “i”-th component (the component being in excess relative to the eutectic). The melting of the eutectic always occurs at the same temperature, while the melting point of the “i”-th component increases with the increase of its content. The discussed dependencies result from the Gibbs’ phase rule (for isobaric conditions) [37].

\[ s = z - f + 1 \]  

where \( s \) – number of degrees of freedom, \( z \) – number of independent components, \( f \) – number of phases.

At the point of eutectic composition, three phases coexist (two solid phases and liquid solution); therefore, the number of degrees of freedom is 0 \((z = 2, f = 3, s = 2 - 3 + 1)\). Zero degrees of freedom result in the temperature stability of the eutectic. Other points located on the liquidus line are characterised by a degree of freedom of \( s = 1 \), i.e. depending on the temperature \((z = 2, f = 2, s = 2 - 2 + 1)\).

Melting points and enthalpies of melting of the eutectic and the “i”-th component can be determined from the DSC curves. The eutectic composition is determined using various approaches. The first method is to determine the eutectic composition at the intersection of the liquidi of the “i”-th components (phase diagram for the liquid-solid system). The second approach involves extrapolating the enthalpy of melting of the “i”-th component from the molar fraction of the “i”-th component to a value of zero [38]. The third method is to calculate the eutectic fraction \( (f_{Eu}) \) for individual compositions of two-component systems [32, 39-41] according to the following equation:

\[ f_{Eu} = \frac{\Delta H_{mp,En}}{\Delta H_{mp,En} + \Delta H_{mp,i}} \]  

Subsequently, for \( f_{Eu} = 1 \), the eutectic composition in a two-component system is obtained. The literature describes the compositions of eutectics in systems containing aniline derivatives, conventional stabilisers or their nitro derivatives. The melting point of the eutectic \((T_{mp,En})\) and the composition of the eutectic \((x_{Eu,i})\) in such systems are presented in Table 2.
Table 2. Melting points of the components ($T_{mp,1}$) and eutectic ($T_{mpEu}$) and molar fraction of the eutectic composition ($x_{Eu,1}$) in two-component systems containing aniline derivatives, conventional stabilisers or their nitro derivatives

| Component 1 | Component 2 | $T_{mp,1}$ [$°C$] | $T_{mp,2}$ [$°C$] | $x_{Eu,1}$ | $T_{mpEu}$ [$°C$] | Ref. |
|-------------|-------------|-----------------|-----------------|-----------|-----------------|-----|
| DPA         | N-N-NODPA   | 53.5            | 66.9            | 0.4815    | 23.3            | [41]|
|             | NE-4-NA     | 95.1            | 74.8            | 0.7042    | 42.9            | [40]|
|             | 2-NDPA      | 74.8            | 85.9            | 0.6987    | 40.7            | [39]|
|             | MENA        | 85.9            | 85.9            | 0.6871    | 59.0            | [42]|
| 2-NDPA      | MENA        | 74.8            | 85.9            | 0.6095    | 59.0            | [42]|
| 2,4-DNDPA   | 4,4'-DNCI   | 158.2           | 147.3           | 0.4941    | 119.8           | [41]|
| 2,2'-DNDPA  | NE-4-N-N-NOA* | 172.3         | 118.6           | 0.2595    | 104.3           | [39]|
| CI          | 2-NPDPA     | 71.8            | 74.8            | 0.4908    | 52.3            | [41]|
|             | CII         | 120.0           | 127.7           | 0.7509    | 61.0            | [43]|
|             | TPA         | 95.1            | 113.8           | 0.6002    | 64.1            | [36]|
|             | NE-4-NA     | 113.8           | 118.6           | 0.7516    | 66.0            | [32]|
|             | ANA         | 95.1            | 118.6           | 0.8021    | 55.2            | [42]|
|             | NE-4-N-N-NOA* | 118.6        | 85.9            | 0.5695    | 64.0            | [39]|
|             | MENA        | 85.9            | 85.9            | 0.5695    | 55.2            | [42]|
| CII         | NE-4-NA     | 120.0           | 95.1            | 0.4579    | 72.8            | [40]|
|             | ANA         | 113.9           | 114.0           | 0.5002    | 90.4            | [32]|
|             | 2,4-DN-N-EA | 114.0           | 127.7           | 0.4015    | 91.9            | [41]|
| AkaII       | TPA         | 170.3           | 127.7           | 0.21      | 117.7           | [36]|
| ANA         | NE-4-NA     | 113.8           | 95.1            | 0.4481    | 77.2            | [40]|
|             | 2-NDPA      | 74.8            | 85.9            | 0.2114    | 66.0            | [32]|
|             | MENA        | 85.9            | 85.9            | 0.3312    | 72.1            | [42]|
| NE-4-NA     | MENA        | 95.1            | 85.9            | 0.4725    | 62.0            | [44]|
|             | ENA         | 108.0           | 108.0           | 0.6041    | 80.8            | [44]|

The introduction of a mixture of stabilisers with a eutectic composition also has advantages during the technological process of producing propellant pulp. The lower melting temperature of such a mixture (lower than its components) results in greater solubility of the components; hence, an easier introduction of the stabiliser mixture into the nitrocellulose matrix takes place. On the other hand, the melting temperature of the eutectic cannot be too low, as the stabiliser mixture may melt in the range of temperatures utilised for propellants. Stabilisers in the liquid phase may undergo migration or evaporation, thus changing the chemical composition of the propellant or the surface of the propellant grain [9]. In terms of designing technological processes for the production of nitrocellulose propellants using new stabilisers or mixtures of stabilisers with a eutectic composition, it is necessary to remember to determine their solubility in the process media. Good solubility of stabilisers in process solvents leads to their distribution in the nitrocellulose matrix, which translates into obtaining a product with uniform properties.

Research work on alternative stabilisers in Poland is mainly concerned with the analysis of the basic properties and stability of propellants with triphenylamine or eutectics containing various stabilisers. This type of research is conducted by teams at the Warsaw University of Technology, Łukasiewicz Research Network – Institute of Industrial Organic Chemistry and Military University of Technology. There are no available publications on the synthesis or application of new compounds as potential nitroester stabilisers, which may be a potential direction for the development and application works in Poland in the field of alternative, non-toxic stabilisers for nitrocellulose propellants.
4. Conclusions

Stabilisers play an important role when it comes to propellants containing nitroesters (nitrocellulose, nitroglycerine), extending the storage period and use of these types of product. The conventional stabilisers, some of their nitro derivatives and/or the impurities present in them are highly toxic. This results in the development of research on new effective nitrocellulose stabilisers that may be applicable to single, double or multi-base propellants. Before introducing new stabilisers into the technological processes for the production of nitrocellulose propellants, a number of tests should be carried out to determine the physico-chemical, thermal, mechanical and energy-ballistic properties. Alternative stabilisers should be characterised by highly effective performance. Moreover, compounds and their nitro derivatives should be environmentally friendly, have very good or good solubility in process media, while the cost of their production should be relatively low. A number of proposals on new, alternative stabilisers for nitrocellulose propellants can be found in the literature; however, most of the available information relates to basic research (stability, thermochemical properties).

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