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Closed vessel burning behavior and ballistic properties of artificially-degraded spherical double-base propellants stabilized with diphenylamine

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Abstract

The purpose of solid propellants is to generate gas, which expands to accelerate (and spin, in the case of rifled barrels) a gun projectile so that it achieves the desired launch velocity at the muzzle. Some of the important properties of a propellant are the burning rate and vivacity, both of which strongly influence gun performance and projectile range. However, nitrate ester propellants undergo physical and chemical degradation during storage and this can change the burning rate and/or vivacity, either reducing the propulsive efficiency or increasing the safety risk to the operator during transportation and handling. Here we report the effect of aging on the burning rate and vivacity of spherical double-base propellants containing diphenylamine (DPA) as the main stabilizer. We tested three sets of propellants that were artificially aged at 80 ºC for 5.3, 10.6 and 21.6 days, equivalent to 5, 10 or 20 years of aging at 25ºC according to STANAG 4582. It was found that DPA was progressively lost from the propellants during aging, with the greatest loss observed in propellants aged for the longest time. The DPA was able to fulfil its stabilisation role of propellant when NG was up to 14%, however, failed to stabilize when the nitroglycerin content was nearer to 20%. Aging caused changes in the burning rate and vivacity compared to the unaged propellant batch. The burning rate of propellant containing ~20% nitroglycerin exceeds the burning rates of samples containing 12-14% nitroglycerin. The limited role of DPA as a stabilizer for double-base propellants is discussed. The DPA stabilized double base propellant may undergo significant changes during storage, making them unsuitable for their designated use.

Keywords: stabilizer, burning rate, aging, vivacity, decomposition.

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1. Introduction

Homogeneous solid double-base propellants (composed mainly of nitrocellulose and nitroglycerin) are often used to fire projectiles or missiles. However, propellants based on nitrate esters are intrinsically unstable due to the low activation energy (155 kJ mol^{-1}) of the O–NO_2 (nitrate ester) group. Accordingly, these groups undergo slow decomposition even under ambient conditions, causing the mechanical [1–3], chemical [1, 4, 5] and ballistic properties [6] of the propellants to deteriorate over time. Two decomposition mechanisms are involved in this aging process: thermolytic decomposition, which is triggered by heat, and hydrolytic decomposition, which is triggered by acid. Thermolytic decomposition often starts with the homolytic cleavage of the weak O–NO_2 bonds due to their low activation energy[7–10], releasing nitrogen oxides (NO_x) and the corresponding alkoxy radical (R–O). In contrast, hydrolytic decomposition is caused by the acid hydrolysis of nitrate esters[7, 8, 10] and is exacerbated by moisture and residual acids, or acids formed by reactions between nitrogen oxide radicals and moisture. If the decomposition of nitrate esters is allowed to continue, the performance, shelf life and ballistic properties of propellants are seriously impaired. Furthermore, the accumulation of acids causes polymer chain scission and cross-linking[3], leading to the embrittlement and cracking of grains, thus increasing the surface area. The increase of the surface area can result in pressure rise during burning impacting the ballistic properties.

The decomposition reactions described above cannot be prevented, but the addition of an organic compound containing secondary amines, such as diphenylamine (DPA), 2-nitrophenylamine (2-NDPA) or urea derivatives (e.g. ethyl or methyl centralyte), absorbs the NO_x gases released during the decomposition of the nitrate esters, thus delaying autocatalytic degradation and preserving the base components in the original composition [7, 11,12]. DPA and 2-NDPA are often added to nitrate ester-based gun propellants at concentrations ranging from 1 to 3% (w/w)[13]. The nitration of DPA during the aging of gun propellants has already been extensively reported[14–18]. The efficiency of DPA as a stabilizer decreases with storage time, and it is therefore necessary to monitor the concentration of DPA in propellants for the better management of safety and ballistic performance[19]. The concentrations of stabilizers and their derivatives are usually determined by extraction using solvents such as diethyl ether, dichloromethane or acetonitrile, followed by analysis with a high performance liquid chromatography (HPLC) equipped with UV absorbance or photodiode array detectors[20–23]. The derivatives of the primary stabilizer generated during aging can act as secondary stabilizers[24]. The isothermal decomposition of nitrocellulose has been investigated at various temperatures and decomposition mechanisms have been proposed[25].

Extending the service life of propellants in this manner can reduce stockpile management costs and maintain performance, but this requires an extensive knowledge of the safety margins and shelf lives of different propellant ingredients[26]. Thus far, research has focused mainly on the decomposition mechanism of nitrate esters and stabilizer depletion in relation to storage safety rather than longevity or ballistic properties[26–29]. The burning rate of propellants is used to design munitions. However, the burning rate of propellants in the high-pressure environment that exists during gun firing (tens or hundreds of MPa) is strongly affected by aging, and this has a knock-on effect on gas production and thus munitions functionality, so these factors must be well understood to assess the variation of ballistic performance with propellant storage time[30].

The burn rate of smokeless propellants in the high-pressure environment during firing is one of the most significant ballistic characteristics, allowing the theoretical analysis of barrel propellant systems[31], but the burn rate can be affected by aging of propellants. The effect of aging on the burning rate of propellants has been widely investigated but most research has focused on single-base and rocket composite propellants[32–42]. Few studies have addressed the link between aging and the burning rate of nitrate ester-based propellants, and the corresponding reports are published in Chinese which limits public access. The effect of wet and hot environments on the ballistic performance of smokeless composite double-base propellants has been reported, suggesting that the mechanical properties of the aged propellants deteriorate without detectable changes in the burning rate[43]. Accelerated aging of lead-free double based rocket propellants demonstrated the effect of lead-free ballistic modifiers, but the burn rate was not reported[44]. In order to provide users with comprehensive information about the condition and performance of double-base gun propellants, it is necessary to understand the relationship between burning rate, dynamic vivacity and aging. This will facilitate the more effective management of stockpiles in terms of obsolescence, performance and safety. However, research in this area has significantly undermined.

We therefore investigated the combustion and ballistic properties of three spherical double-base propellants with diameters ranging from 300 to 800 µm, aged at 80 ºC for 5.3, 10.6 and 21.6 days, which is equivalent to 5, 10 and 20 years of aging at 25 ºC, respectively. We evaluated the burning rates, force (related to peak pressure) and vivacity of the samples using a closed-bomb vessel chamber, and considered the aging characteristics of the samples in relation to grain geometry and calorific values.

2. Theory

Colloidal propellants burn in parallel layers, according to “Vieille’s Affinity Law”, progressing perpendicularly to the surface and maintaining the shape until a given thickness, or web, is consumed[45]. We tested spherical propellants in the current study, and their regression is schematically represented in Fig. 1, where *w* is the web and *r* is the unburnt fraction of the web.

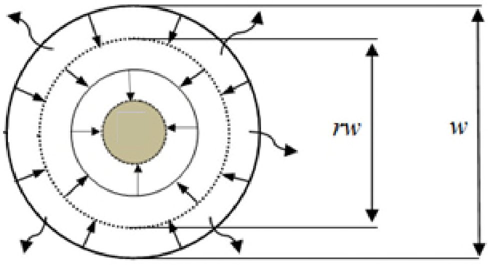

Fig. 1. Schematic representation of the burning surface of a spherical propellant (*w* is the web and *r* is the unburnt fraction of the web).

The rate at which the reacting surface is consumed and, as a consequence, the rate at which gas is produced, is termed the burning rate, generically[46–49] given in the following equations:

$$\mu = k\theta(P) \qquad (1)$$

where μ is the linear regression rate, usually given in mm/s, *k* is an environment temperature function parameter, in practical terms independent of pressure and thus treated as a constant, and $\theta(P)$ is the applicable pressure function.

Experimentally, Eq. (1) assumes the Saint Robert – Vieille form, as shown in Eq. (2) [50]

$$\mu = kP^n \qquad (2)$$

where *n* is the pressure exponent, ranging from 0 to 1, typically restricted to the range 0.6–0.8 for double-base powders.

Using these formulae, it is necessary to have prior knowledge of *k* and *n* in order to determine the burning rate. In turn, this would require many Crawford Bomb tests in order to cover the range of pressures involved in closed bomb shots. Such a time consuming set of experiments is beyond the scope of this work, so we used a simplified approach that does not invalidate our conclusions because they are based on comparative results.

At an arbitrary time *t* during combustion, the amount of gas produced may be related to the solid mass as shown in Eq. (3) [51]:

$$m_g = \phi(t) m_s \quad (3)$$

where m_g is the mass of solid propellant transformed to the gas phase, t is the time, Ø is the time-dependent fraction of propellant burnt within $0 \leq Ø \leq 1$ and m_s is the mass of solid propellant, also related to Eq. (4):

$$m_s = \rho V_s \quad (4)$$

where ρ is the propellant density and V_s is the volume.

Given a spherical propellant, V_s can be determined as shown in Eq. (5):

$$V_s = \frac{\pi}{6} W^3 \quad (5)$$

where W is the sphere diameter, which is also the web to be burned.

Considering the time-dependent solid volume of the propellant, we have, for a given time during combustion, the volume determined using Eq. (6):

$$V_s(t) = \frac{\pi}{6} [w(t)]^3 \quad (6)$$

where $w(t)$ is any diameter smaller that the starting value.

Eq. (4), Eq. (5) and Eq. (6) can be combined to yield Eq. (7):

$$m_g(t) = \rho[V_s - V_s(t)] = \rho \frac{\pi}{6}\left[W^3 - w(t)^3\right] \quad (7)$$

And given the definition of $\phi(t)$ in Eq. (3), we can use Eq. (5) and Eq. (7) to derive Eq. (8):

$$\phi(t) = \frac{m_g(t)}{m_s} = \left\{1 - \frac{w(t)^3}{W^3}\right\} \quad (8)$$

By considering $w = rW$ (Figure 1), Eq. (8) can be rearranged to yield Eq. (9):

$$\phi(t) = \left\{1 - \frac{(rW)^3}{W^3}\right\} = 1 - r^3 \quad (9)$$

And given that r is the remaining web fraction and $1 - r$ is the burnt fraction, differentiation can be used to derive the regression rate as shown in Eq. (10) and Eq. (11):

$$-W\frac{dr}{dt} = \frac{W}{3}.\left\{\frac{1}{\sqrt[3]{[1-\phi(t)]^2}}\right\}.\frac{d\phi(t)}{dt} \quad (10)$$

where $-W\frac{dr}{dt} = \mu$ (11)

In order to obtain this regression rate from closed bomb tests, we use Eq. (12):

$$P(t).[V-\eta] = m_g(t)RT_o \tag{12}$$

where $P(t)$ is the pressure attained in the closed bomb chamber at time t, V is the closed bomb chamber volume and η is the co-volume correction of the ideal gas law to match the real gas scenario applicable in closed bomb experiments.

Given the combustion test event is in the order of milliseconds, it can be assumed to be adiabatic and will thus lead at the end of combustion to Eq. (13):

$$P_{max}.[V-\eta] = m_s RT_o \tag{13}$$

where P_{max} is the peak pressure (maximum pressure attained at the end of the experiment) and the co-volume is assumed constant, given it is function of T_o.

The piezoelectric sensor of the closed bomb device directly records the evolution of pressure versus combustion time, often presenting this record in terms of the ratio $P(t)/P_{max}$. Thus, the division of Eq. (12) by Eq. (13) yields Eq. (14):

$$\frac{P(t)}{P_{max}} = \frac{m_g(t)}{m_s} = \phi(t) \tag{14}$$

And the differentiation of Eq. (14) yields Eq. (15):

$$\frac{1}{P_{max}}.\frac{dP(t)}{dt} = \frac{1}{m_s}.\frac{dm_g(t)}{dt} = \frac{d\phi(t)}{dt} \tag{15}$$

where $dP(t)/dt$ is also available from the closed bomb tests.

Based on the above, we conclude that closed bomb tests can provide the burning rate if we use Eq. (10), Eq. (14) and Eq. (15).

In turn, we may calculate the dynamic vivacity by combining Eq. (1) and Eq. (10), assuming $\theta(P)$ is a linear function of $P(t)$, yielding Eq. (16):

$$\frac{d\phi(t)}{dt} = \frac{3\sqrt[3]{[1-\phi(t)]^2}}{W}\omega P(t) \tag{16}$$

where ω is a modified pre-exponential constant that compensates for the linearization of $\theta(P)$.

Now, if we define $L(\phi)$ as shown in Eq. (17):

$$L(\phi) = \frac{3\sqrt[3]{[1-\phi(t)]^2}}{W}\omega \qquad (17)$$

Eq. (16) may conveniently be expressed as shown in Eq. (18):

$$\frac{d\phi(t)}{dt} = L(\phi)P(t) \qquad (18)$$

where L is the dynamic vivacity, a quantity encompassing both chemical and physical burn properties of the powder grain, as well as compensating for the adoption of linear dependence for the burn pressure in Eq. (17).

L varies according to ϕ because the other quantities in its relation are constants. Thus, if we take into account the relations of Eq. (14) and Eq. (17), we derive Eq. (19):

$$L[\phi] = \frac{1}{P_{max}} \cdot \frac{d[P(t)]}{P(t)dt} = \frac{1}{\phi} \cdot \frac{d[P(t)]}{P_{max}^2 dt} \qquad (19)$$

Thus, it becomes clear that L may be derived from the results of closed bomb tests, being expressed as a weighted derivative of the pressure raise slope.

3. Materials and methods

3.1 Source of propellants and physical/chemical properties

Three batches of different spherical ball powders used in small-caliber weapons were subjected to artificial aging. The powders were manufactured by the MKE Propellant Factory, Kırıkkale, Turkey. The compositional and physical characteristics of the powders are listed in Table 1.

Table 1. Grain sizes, compositions and physical properties of the three different caliber propellants

Propellant grain diameter	300–800 µm		
Application *	5.56 x 45 mm	7.62 x 51 mm	9 x 19 mm
Nitrocellulose	80.45%	82.32%	78.36%
Nitrogen of nitrocellulose	13.06%	13.06%	13.04%
Nitroglycerin	13.72%	11.59%	19.91%
Diphenylamine	1.44%	1.42%	1.48%
Dibutylphthalate	4.16%	4.46%	0.0%

Sodium sulfate	0.23%	0.21%	0.25%
Litre weight	958 g/L	965 g/L	852 g/L
Calorific value	944 cal/g	926 cal/g	1121 cal/g
Density	1.55 g/cm^3	1.57 g/cm^3	1.42 g/cm^3

*Note: *The full nomenclature of a round includes the length of the cartridge. For example, 5.56 x 45 mm implies that the weapon caliber is 5.56 mm and cartridge length 45 mm.*

3.2 Closed bomb chamber

We used a 200-cm^3 Closed Bomb W/Jacket (Design Integrated Technology, Inc., Warrenton, Virginia, USA) combined with a Kistler 6213B and Kistler Charge Meter 5015 (Kistler Group, Winterthur, Switzerland) as shown in Fig 2. When the propellant was ignited in the chamber, the transducer reported a voltage proportional to the pressure. The closed bomb contained a constant volume reaction and was able to withstand pressures of up to 6895 bar. Pressure versus time plots were constructed to determine the rate at which gases were produced, and the rate of change of pressure was used to calculate burning rate and vivacity as described in the theory section.

(a) (b) (c) (d)

Fig. 2. Closed bombs and associated apparatus: (a) closed bomb main unit, (b, c) data recorder, (d) piezoelectric transducer.

The closed bomb tests were carried with a loading density of 0.125 g/cm^3. We weighted out 25 g aliquots of each sample using a calibrated scale with a precision of ±0.001 g. Five replicates of each of the 12 samples were tested (nine artificially aged and three controls from three different grain granulometries). The temperature on the inner surface of the vessel during loading was maintained at 294 ± 2K [30]. The closed bomb was operated with two samples per day to comply with the temperature standards in the vessel.

3.3 Accelerated aging and stabilizer quantitation

Under normal storage conditions, propellants decompose slowly and the analysis of decomposition would take many years. Artificial aging was therefore performed by heating the samples in an HBA 40 Heating Block (OZM Research, Hrochův Týnec, Czech Republic) to accelerate their decomposition. A 1-kg sample of each propellant was divided into four portions of 250 g, which were aged at 80 ºC for 5.3, 10.6 and 21.6 days, respectively, according to STANAG 4582[52]. The fourth portion from each sample was used as an unaged control. Each heating tube accommodated 25 g of propellant, so propellants in 10 tubes were heated simultaneously and the aliquots were combined after aging to reconstitute a 250 g sample.

An arbitrary temperature of 80 ºC was selected to reduce the experimental time. Temperatures of 80 ºC, 85 ºC and 90 ºC were previously used to age double-base rocket propellants in order to evaluate the stabilizer concentration by HPLC [37]. Aging at 80 ºC might alter the nitrate ester decomposition mechanism but the ballistic performance should not be affected by different aging kinetics. The duration of heating at 80 ºC was converted to natural aging at 25 ºC using Eq. (20) based on an earlier study[52]:

$$\mathrm{t_m} = \mathrm{t_{25}}{*}\mathrm{e}^{\left[E_1\cdot\left(\frac{1}{T_m}-\frac{1}{T_{60}}\right)+E_2\cdot\left(\frac{1}{T_{60}}+\frac{1}{T_{25}}\right)\right]/R} \tag{20}$$

where $\mathrm{t_m}$ = test duration (days), $\mathrm{t_{25}}$ = duration of storage at 25 ºC (3652.5 days = 10 years), T_m= test temperature (K), T_{60} = temperature of change of the activation energy (AE) (333 K = 60 °C), T_{25} = storage temperature (298 K = 25 °C), E_1= AE at higher temperature range (120 kJ/mol), E_2= AE at lower temperature range (80 kJ/mol) and R = molar gas constant (0.0083143 kJ/K/mol). By introducing the constant values T_{25} = 298 K, T_{60} = 333 K and E_2 = 80 kJ/mol, Eq. (20) can be simplified to Eq. (21)[52]:

$$\mathrm{t_m} = \mathrm{t_{25}}{*}e^{E_1/(R*T_m)-c} \tag{21}$$

where the constant C = 46.713.

Substituting the values in Eq. (21), the aging times of 5.3, 10.6 and 21.6 days at 80 °C (T_m) are equivalent to 5, 10 and 20 years, respectively, at a storage temperature of 25 ºC.

The chemical aging of the propellant samples was confirmed by monitoring the loss of stabilizer (DPA) during accelerated aging by HPLC using an Agilent Technologies 1200 series [30]. The stabilizer was extracted using the procedure described in AOP-48 Edition 2. Approximately 500 mg of propellant grain was dissolved in 125 ml acetonitrile by shaking for 4 h at room temperature using a KS501 IKA-WERKE orbital bench shaker at 250 rpm. A portion of the extract was passed through a 0.2 μm nylon filter in a glass syringe. Using a micropipette, 5 ml of the solution was transferred to a 25 ml volumetric flask containing 1 ml 2% $CaCl_2$ and was made up to 25 ml with acetonitrile. The contents of the flask were allowed to settle for 1 h at room temperature. The supernatant was filtered as above and transferred to a vial for immediate HPLC analysis. The flow rate was 1.5 ml/min using a mobile phase comprising 55% acetonitrile and 45% water. The injection volume was 10 μl and the UV detector wavelength was 254 nm.

Where the propellant was stabilized using DPA alone, the effective stabilizer content[53] was calculated using Eq. (22):

Effective stabilizer = (diphenylamine content + 0.85 N-nitrosodiphenylamine content) (22)

4. Results and discussion

4.1 Artificial aging and stabilizer concentrations

The physical appearance of the samples after the artificial aging process (and the corresponding controls) is shown in Fig. 3.

Fig. 3. Physical appearance of the aged propellant samples compared to the unaged control.

During accelerated aging, all the propellants turned dark brown in color, which is distinct from the lighter color of the unaged control samples. Visible color changes as a result of accelerated aging at

80 ºC are probably caused by the reaction products of DPA and NO_x. Similar color changes in aged nitrate ester propellants have been reported previously [15, 26, 37, 54–57]. Furthermore, the blackening of nitrocellulose was reported during aging at 90 ºC and was attributed to the cool burning of the nitrocellulose without ignition[58].

The loss of stabilizer in the nine propellant samples aged at 80 ºC for 5.3, 10.6 and 21.6 days was measured by HPLC. A calibration curve was constructed by injecting DPA solutions at four concentrations ranging from 5.5×10^{-6} to 4.4×10^{-5} mg/ml, which spanned the concentration range of the propellant in our samples. Stabilizer levels were calculated by integrating the peak areas as shown in Table 2.

Table 2. Effective stabilizer content as a function of aging time (grain size 300-800 µm).

Aging time (days)	Stabilizer content (%)		
0	1.36	1.32	1.35
5.3	0.926	0.9505	0.8725
10.6	0.593	0.605	0.497
20.6	0.447	0.476	0.471

Note: The stabilizer levels reported in Tables 1 and 2 are slightly different because Table 1 refers to recently manufactured propellants whereas Table 2 refers to the same propellants after 6 months of storage.

The DPA content in all three unaged samples was ~1.3%. After 5.3 days of accelerated aging, the stabilizer level had fallen below 1% in all the samples, reflecting the reaction of DPA with NO_x released during the decomposition of the $O–NO_2$ bond, leading to the formation of DPA derivatives[14, 26, 58]. After further aging of the samples for 10.6 and 21.6 days, the DPA level fell below 0.5%. The greatest loss of DPA was observed in the propellant with the highest amount of nitroglycerin content (19.91%) suggesting that a nitroglycerin has a direct impact on the stability of propellants stabilized with DPA. Most manufacturers do not use DPA in double-base powders because it has poor compatibility with NG, therefore, the propellant stability decreases as the nitroglycerin content increases, which could lead to spontaneous ignition at higher temperatures[59]. Given the potential for spontaneous ignition by self-heating, experimental aging was terminated once the stabilizer level fell to ~0.4%, although according to AOP-48, the minimum percentage of stabilizer remaining after aging should be ≥ 0.2%.

Table 2 also shows that the rate of stabilizer loss was the highest during the first 5.3 days, with most of the DPA undergoing at least mono-nitration. Further nitration of unreacted DPA is sterically hindered by nitro groups in the mono-nitrated derivatives, so the rate of DPA loss is much slower during the second and especially the third substitution reactions. In the latter case, successive nitration to form derivatives nitrated at two or three positions increases the steric hindrance and slows down the nitration of unreacted DPA even further [14, 60]. The aging reaction paths of nitrate ester-based propellants stabilized with DPA are illustrated in Fig. 4, showing derivative substances formed during the aging process.

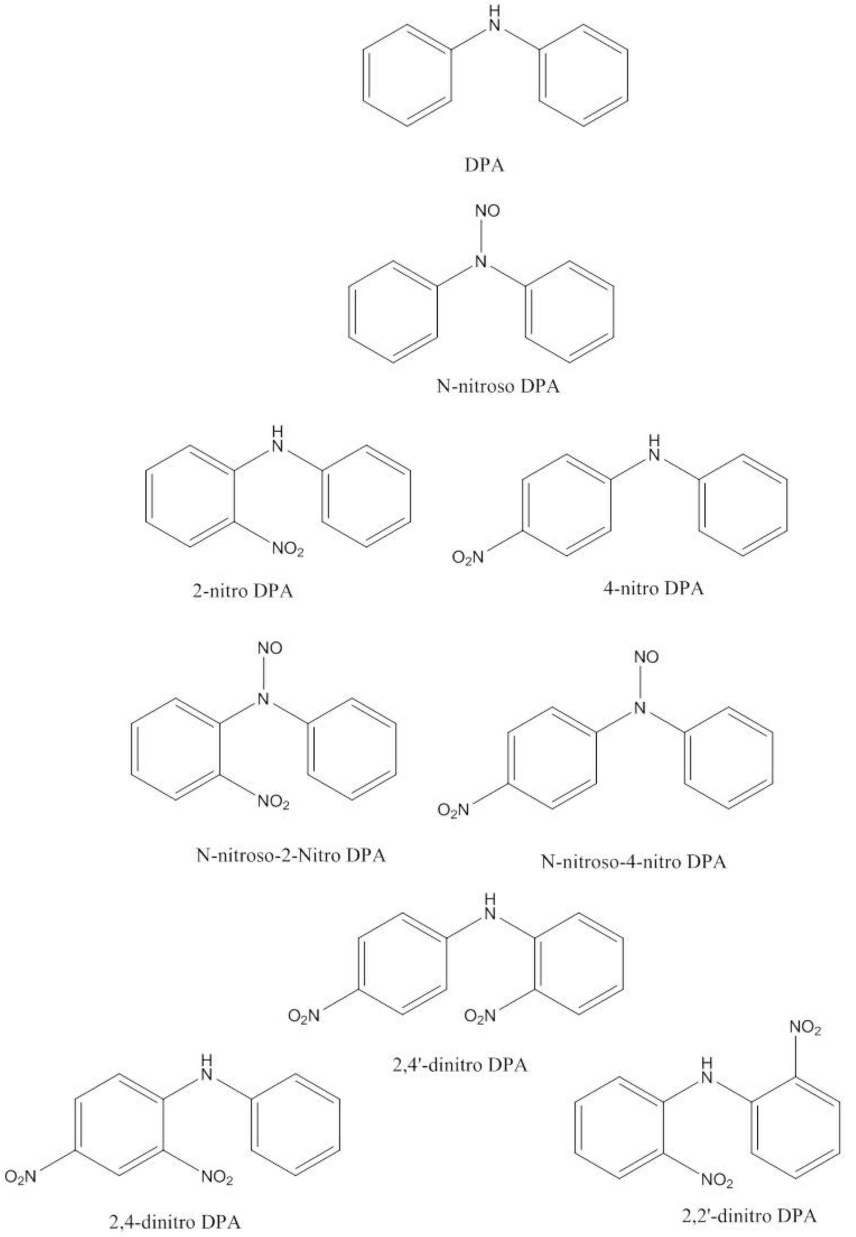

Fig. 4. DPA derivatives formed during the aging of propellants [57].

4.2 *Measurement of the vivacity and burning rate*

For the closed bomb tests, 25 g aliquots of each sample were weighed out and five aliquots of each of the 4 samples were tested (nine artificially aged and three controls representing three different grain geometries). The grain geometry and combustion properties of each lot of samples were determined before and after aging.

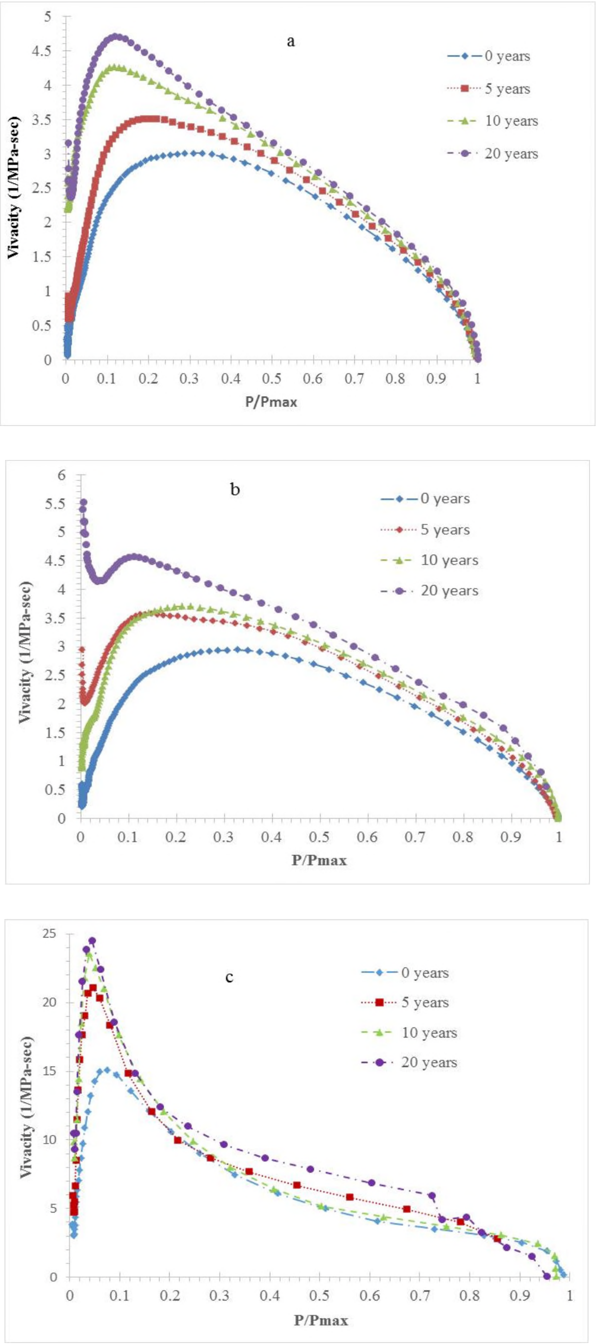

Fig. 5. Vivacity of double-base propellants measured in a closed bomb as functions of pressure and artificial age: (a) 5.56 x 45 mm; (b) 7.62 x 51 mm; (c) 9 x 19 mm.

The sieve shaker was used for equal grain geometry. Grain counts were determined according to the average spherical diameter of the propellant particles. The temperature on the inner surface of the vessel during loading was maintained at 294 ± 2K [30]. The calculations of vivacity (Fig. 5) and burning rate (Fig. 6) for each sample were based on the average of the recorded values for each aliquot. Furthermore, the pressure ratio was maintained within the range 0.3–0.8 to avoid transients of ignition (which occur when $P/P_{max} < 0.3$) and combustion extinction (which occurs when $P/P_{max} > 0.8$).

The vivacity of the 5.56 x 45 mm and 7.62 x 51 mm caliber propellants increased in direct proportion to the aging time, resulting in similar curve shapes (Fig. 5a and 5b). The increase in vivacity at lower pressures correlated with a higher sensitivity to ignition, as anticipated. The similar slopes (Fig. 5a and 5b) indicate that DPA fulfilled its role as a stabilizer for a while, but did not maintain the vivacity ratio between aged and unaged propellants within the recommended range after 5 or more years of aging. The vivacity ratio between aged and unaged propellants is known as the relative quickness (RQ), and is allowed to differ by up to ±5% before falling outside the regulations stipulated by MIL-STD 286C[61]. Our data showed that the average RQ of 5.56 x 45 mm caliber propellants artificially aged for 10 and 20 years was 14% and 16%, respectively, and the equivalent values for the 7.62 x 51 mm caliber propellants were 5.5% and 12%, respectively. Powders that begin to deviate from the recommended standards after only 5 years have a poor shelf life and limited stability, which is possibly due to the aforementioned incompatibility between DPA and nitroglycerin.

The increase in dynamic vivacity with aging may reflect changes in the grain properties. During aging, the escape of NO_x gases from the propellant grains and potentially also the migration of stabilizer and nitroglycerin at higher temperatures can generate microscale pores, increasing the burning surface area. All aging-related physical and chemical changes increase the surface area of the burning propellants, ultimately increasing the dynamic vivacity and peak pressure in the combustion chamber compared to the less-porous unaged propellants, as reported elsewhere [62], [63]. It is assumed that the porosity of the aged propellants also causes oxygen to become trapped in the pores, which eventually increases the oxygen balance and thus facilitates the combustion reaction, forming more CO_2, thus releasing more energy. Furthermore, the unaged propellants burned in a stable and linear manner, but aging resulted in faster burning at lower pressures.

In contrast to the results described above for the 5.56 x 45 and 7.62 x 51 mm caliber propellants (Fig. 5a and 5b), the 9 x 19 mm caliber propellants showed more erratic behavior (Fig. 5c). Although the sensitivity increased with aging as expected, the vivacity showed no clear trend. The average RQ after 5 years was 6%, but after 10 years the RQ fell to just above 5% and then increased substantially to 21% after 20 years. The unexpected fall in vivacity after 10 years highlights the contraindication of DPA as stabilizer in double-base propellants, and probably reflects the depletion of nitroglycerin which is attacked by DPA and its degradation products. Importantly, the 9 x 19 mm caliber propellant contained the highest nitroglycerin content among the samples we tested (~19.91% w/w).

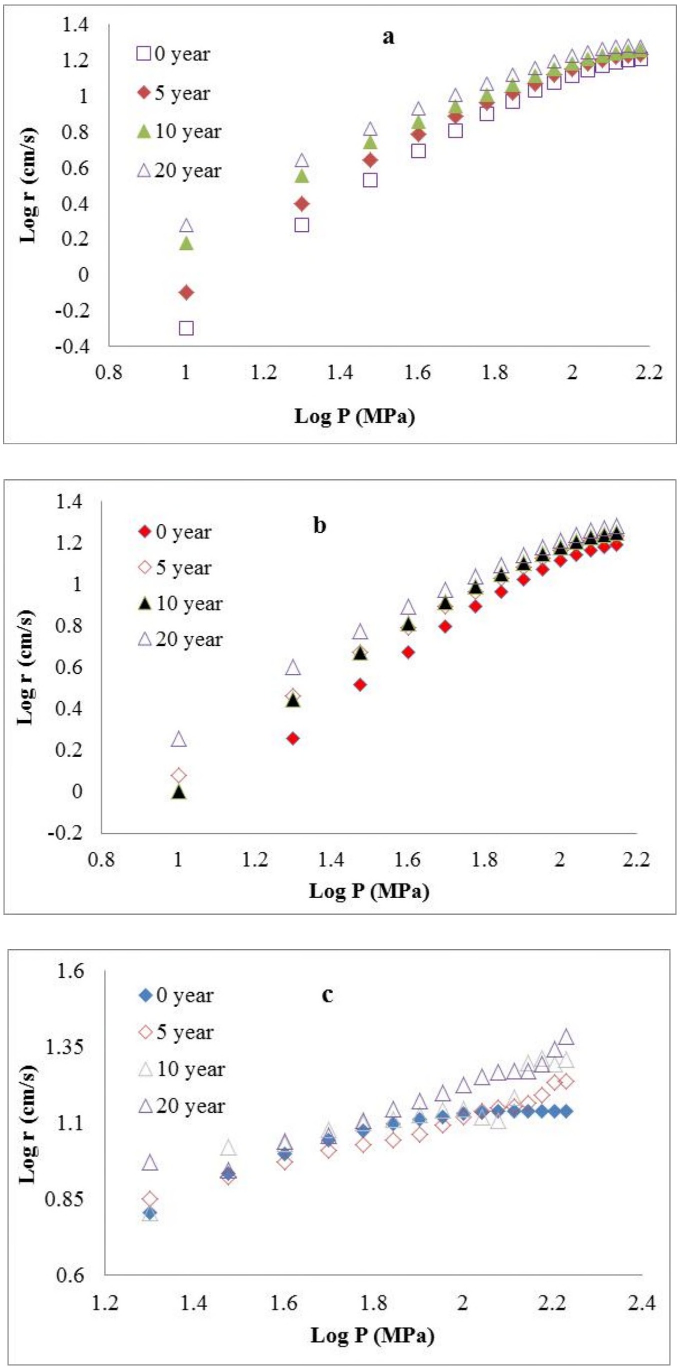

Fig. 6. Burning rates of double-base propellants measured in a closed bomb as functions of pressure and artificial age: (a) 5.56 x 45 mm; (b) 7.62 x 51 mm; (c) 9 x 19 mm.

Fig. 6 shows the burning rates of the three propellants and the results broadly support the vivacity data shown in Fig. 5. For the 5.56 x 45 and 7.62 x 51 mm propellants, the burning rate increased with aging and the curves were similar (Fig. 6a and 6b). The only variation was in the pre-exponential parameter of Eq. (2) which encompasses the sensitivity to initial temperature, but the pressure slopes were similar, indicating only small differences in chemical composition. In both cases (Fig. 6a and 6b) the burning rate increased with aging upto a pressure of range of 130 MPa but at higher pressures it remains constant. In contrast, the 9x19 mm caliber propellant presents an uncommon variation with different slopes, denoting changes in the *k* and *n* parameters of Eq. (2) probably reflecting differences in mass composition and potentially also unanticipated changes in the burning surface (Fig. 6c).

Note that for the composition 9 mm, there is no dibutylphthalate which plays three detached functions in the composition of NC- NG based propellants playing as a burn rate moderator – its essential function – plasticizer and coolant. In the case of propellant 5.56 and 7.62: a two-step surface coating process is mainly used in the production of double base propellants. The impregnation of single base propellant grains with blasting oil (nitroglycerin) forms an outer layer with a thickness up to several hundred micrometers and almost uniform blasting oil concentration. Following the impregnation process, the propellant grains are impregnated in a second step by the deterrent (dibutylphthalate) causing a nitroglycerine front movement towards the center of the grains by some tens of micrometers. In the case of the composition 9 mm: Only the previous first step surface coating process is used in the production of double base propellants (no impregnation process by deterrent). So, the burning rate of propellant 3 containing ~20% nitroglycerin exceeds the burning rates of the samples 1 and 2 containing 12-14% nitroglycerin, only in the pressure range of 20–50 MPa. This is thought to be due to a higher nitroglycerin concentration in the grain surface. But in the case of samples 1 and 2, nitroglycerin is present deeper in the grain, which explain the fact that burning rate of powder 1 and 2 are greater towards high pressures [64].

5. Conclusion

The loss of stabilizer poses safety issues during prolonged storage of propellants because aged propellants found to burn more rapidly than unaged propellants due to an increase in the burning surface area. DPA was found to stabilize double-base propellants with a nitroglycerin content of less than 14% by mass, but failed to stabilize compositions in which the nitroglycerin content was nearer to 20%. The increase in the vivacity of the 5.56 x 45 mm and 7.62 x 51 mm propellants is directly proportional to aging time at lower pressures suggesting that DPA fulfilled its role as a stabilizer for a while, but failed to maintain the vivacity ratio between aged and unaged propellants within the recommended range after 5 or more years of aging. This supports recommendations that DPA should not be used as a stabilizer in double-base propellants. The burning rate of the propellants with a lower than 15% NG increases proportionally with aging time upto 130 MPa, but at higher pressures it remains unchanged. The burning rate of the propellant containing a higher nitroglycerin (in this case ~20%) exceeds the burning rates of propellants with 12-14% nitroglycerin in the pressure range of 20–50 MPa. The experimental data indicate that the increase in barrel pressure caused by the combustion of aged propellants must be taken into account in design calculations related to barrel strength, barrel fatigue and barrel life expectancy. Furthermore, appropriate precautions should be taken when storing or transporting propellants that have been stockpiled for any significant length of time. Ideally, inventories should be maintained according to operational requirements to avoid the risks of extended storage, particularly storage periods exceeding 20 years.

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