# Combustion Characteristics of Low Flame Temperature, Chlorine-Free Composite Solid Propellants

P. A. O. G. Korting,* F. W. M. Zee,† and J. J. Meulenbrugge‡
*Prins Maurits Laboratory TNO, Rijswijk, the Netherlands*

**Presently, there is an increased interest in composite solid propellants that burn with low flame temperatures and do not contain chlorine or chlorine compounds. Applications for such propellants may be found in solid propellant gas generators and turbine pump starters. Phase-stabilized ammonium nitrate (ANS)-based propellants meet these requirements, but other composite propellant formulations are also feasible, such as propellants based on a rubber binder and nitroglycerin (NG) or trimethylol-ethane-trinitrate (TMETN). In order to compare the combustion characteristics of these propellants, three different families have been developed and tested: 1) Hydroxy-terminated polybutadiene (HTPB) binder with ANS and various catalysts; 2) Polyester-urethane (PU) binder with NG and nitroguanidine (NQ) or guanidine nitrate (GuNi); and 3) PU binder with TMETN and NQ or GuNi. With some exceptions, all propellant formulations have calculated flame temperatures between 1200 and 1400 K. In a special burner, the combustion characteristics of these propellants have been investigated in the pressure region between 1 and 10 MPa. The results of this study show that burning rates up to 7 mm/s at 10 MPa may be obtained, while the burning rate exponent may vary between 0.3 and 0.7. In addition, the importance of catalysts to improve the ignitability of (ANS)-based propellants is confirmed.**

## Introduction

SOLID-PROPELLANT gas generators may be used to start and drive turbines for power generation. For such a purpose, the combustion gases of the solid propellant should not contain corrosive constituents such as chlorine or chlorine compounds, Also, the amount of solid particles in the combustion gases should be kept as low as possible. In addition, the propellants have to burn with low flame temperatures. Such propellants may also be used for rocket propulsion where the energy content of the propellant is not of prime importance but the low signature of the rocket exhaust gases.

Although double base propellants may meet these requirements, composite propellants are preferred because of safety reasons and superior mechanical properties. However, the requirement of no chlorine in the combustion gases excludes the important oxidizer ammonium perchlorate. Therefore, composite propellants based on ammonium nitrate, nitroglycerin (NG), or tri-methylol-ethane-trinitrate (TMETN) have been manufactured and tested in a special burner to investigate the performance of these propellants.

## Propellant Families

Three different families of propellants were manufactured and tested. The first family is based on a hydroxy-terminated polybutadiene (HTPB) binder with phase-stabilized ammonium nitrate (ANS). The other two families consist of a polyester-urethane (PU) binder with either nitroglycerin (NG) combined with nitroguanidine (NQ)/guanidine nitrate (GuNi) or trimethylol-ethane-trinitrate (TMETN) with NQ/GuNi. The (ANS)-based propellant was manufactured by the Prins Maurits Laboratory TNO, whereas the latter two types were manufactured by the Fraunhofer Institute für Treib-und Explosivstoffe in Pfinztal, FRG.

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*Head, Rocket Propulsion Section. Member AIAA.
†Senior Scientist, Rocket Propulsion Section.
‡Head, Pyrotechnics Section.

### ANS-HTPB Propellant

Ammonium nitrate (AN)-based propellants will meet the requirements of low flame temperatures and no chlorine containing combustion gases. The use of AN however is limited by the practical problems encountered when working with it. These problems are, e.g., low burning rates, high hygroscopicity, phase transitions with large volume changes in the temperature range −40 to +60 °C, and ignition difficulties.

One of these problems, phase stabilization, can be solved by incorporating certain compounds in the AN crystals. Nickel oxide is one of them and gives good phase stabilization by forming nickel-diamine-dinitrate complexes[1]. Figure 1 shows the volume expansion for pure AN and AN with various amounts of nickel oxide. For demonstration purposes, only the curves are shifted along the $y$ axis and therefore do not indicate an absolute value of the specific volumina.

A welcomed side effect of stabilized AN (ANS) is reduced hygroscopicity. However, moisture remains a problem because water reduces the stabilizing effect of nickel oxide and

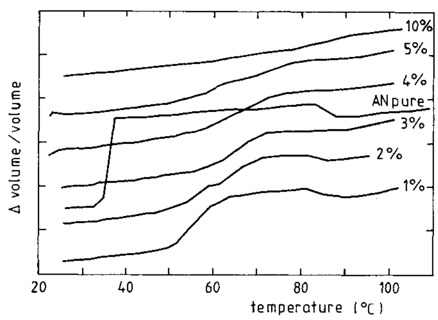


**Fig. 1 Volume expansion of AN and phase-stabilized AN by various percentages of nickel oxide vs temperature (Ref. 1).**

**Table 1 Average particle size of solid-propellant components**

| Compound | Average particle sizes, μm |
|---|---|
| ANS | 160 and 60 |
| $(NH_4)_2Cr_2O7$ | ≈30 |
| $Cu_2Cr_2O7$ | ≈30 |
| $Fe_2O_3$ | 0.7 |

interferes with the hardening reaction of the binder, thereby producing carbon dioxide gas.

The AN is also difficult to ignite because of the relatively small quantity of heat released by decomposition. Gorbanov and Shidlovski[2] found that transition metals/metal compounds increase the heat of the reaction and thus are capable of increasing burning rates and ignitability of AN propellants. So phase stabilizing of AN with NiO is also beneficial with respect to burning rates, ignition, and hygroscopicity.

### Ingredients

HTPB-R 45HT is used as a binder for the (ANS)-based propellants, cured with isophorondi-isocyanate (IPDI). Plasticizers, such as di-octylphtalate (DOP) and isodecylpelargonate (IDP), wetting agents, and antioxidants are used to improve castability and aging properties of the propellant.

As solid ingredients, ANS and several burning catalysts are used. Different combinations of ammonium dichromate (AD), copper-I-chromite (CC), and iron-II-oxide ($Fe_2O_3$) with ANS have been produced. Formulations have not been optimized as the aim was to investigate the influence of additives on the burning properties. The solids are all monomodal mixtures, with average particle sizes as shown in Table 1. With these monomodal mixtures, a solid load of around 80% turned out to be the maximum of castable compositions.

The ingredients were mixed in a vertical planetary Baker Perkins mixer under vacuum at elevated temperatures (40-60 °C). Casting and mixing was performed in a conditioned room with a relative humidity of less than 30%. The propellants were cured at the same temperature as the mixing temperature. The different formulations manufactured are listed in Table 2. This table also contains the theoretical flame temperature of the various formulations. Calculations were performed using the NASA SP 273 code.[3]

### NG/TMETN-PU Propellant

A propellant with NG or TMETN as oxidizer will neither produce chlorine-containing nor corrosive combustion products. Both NG and TMETN are energetic compounds, so addition of coolants such as nitroguanidine (NQ) or guanidine nitrate (GuNi) will be necessary to adjust the flame temperature to the required low value.

Because NG and TMETN are immiscible with HTPB, a polyesterdiol prepolymer cured with hexamethylenediisocyanate (HMDI) is used with a polyether-polyol as crosslinker. NG and TMETN act as plasticizers so that additives to improve castability were not necessary.

The average particle sizes of NQ and GuNi are 30 and 50 $\mu$m respectively.

**Table 2 Formulations of (ANS)-based propellants**

| Formulation code CK | ANS, wt% | Average particle size, $\mu$m | AD, wt% | CC, wt% | $Fe_2O_3$, wt% | Solid load, wt% | Adiabatic flame temperature, 10 MPa, K |
|---|---|---|---|---|---|---|---|
| 1001 | 76.2 | 160 | — | — | — | 76.2 | 1251 |
| 1101 | 76.2 | 60 | — | — | — | 76.2 | 1251 |
| 1102 | 74.1 | 60 | 1.8 | — | — | 75.9 | 1244 |
| 1103 | 72.7 | 60 | — | — | 0.4 | 73.1 | 1217 |
| 1104 | 72.0 | 60 | — | 2.0 | — | 74.0 | 1218 |
| 1105 | 74.0 | 60 | — | — | 1.0 | — | 1233 |
| 1107 | 71.0 | 60 | — | — | 4.0 | 75.0 | 1219 |
| 1108 | 70.0 | 60 | 2.0 | 2.0 | — | 74.0 | 1215 |
| 1109 | 72.0 | 60 | — | 2.0 | 1.0 | 75.0 | 1223 |
| 1110 | 70.0 | 60 | 2.0 | 2.0 | 1.0 | 75.0 | 1217 |
| 1112 | 72.0 | 60 | 1.0 | 1.0 | 1.0 | 75.0 | 1232 |
| 1113 | 73.0 | 60 | 1.0 | 1.0 | — | 75.0 | 1236 |
| 1115 | 77.0 | 60 | 1.0 | 1.0 | 1.0 | 80.0 | 1287 |
| 1116 | 80.0 | 60 | — | — | 0.5 | 80.5 | 1365 |
| 1117 | 80.0 | 60 | 0.5 | — | — | 80.5 | 1367 |
| 1118 | 80.0 | 60 | 0.25 | — | 0.25 | 80.5 | 1366 |
| 1119 | 79.2 | 60 | 1.0 | — | 0.5 | 80.7 | 1364 |
| 1120 | 78.0 | 60 | 2.0 | — | 0.5 | 80.5 | 1347 |
| 1121 | 80.0 | 60 | — | — | 0.25 | 80.25 | 1356 |

**Table 3 Formulations of NG/TMETN-based propellants**

| Formulation code CK | NG, wt% | TMETN, wt% | NQ, wt% | GuNi, wt% | Binder, wt% | Adiabatic flame temeprature, 10 MPa, K |
|---|---|---|---|---|---|---|
| 5015 | — | 20 | 60 | — | 20 | 1308 |
| 5016 | — | 40 | 40 | — | 20 | 1374 |
| 5014 | — | 40 | 45 | — | 15 | 1497 |
| 5019 | — | 20 | — | 60 | 20 | 1205 |
| 5020 | — | 40 | — | 40 | 20 | 1292 |
| 5018 | — | 40 | — | 45 | 15 | 1356 |
| 5003 | 20 | — | 55 | — | 25 | 1308 |
| 5001 | 20 | — | 60 | — | 20 | 1375 |
| 5005 | 40 | — | 30 | — | 30 | 1375 |
| 5004 | 40 | — | 35 | — | 25 | 1500 |
| 5002 | 40 | — | 40 | — | 20 | 1736 |
| 5013 | 40 | — | 45 | — | 15 | — |
| 5008 | 20 | — | — | 55 | 25 | 1214 |
| 5006 | 20 | — | — | 60 | 20 | 1248 |
| 5010 | 40 | — | — | 30 | 30 | 1312 |
| 5009 | 40 | — | — | 35 | 25 | 1385 |
| 5007 | 40 | — | — | 40 | 20 | 1557 |

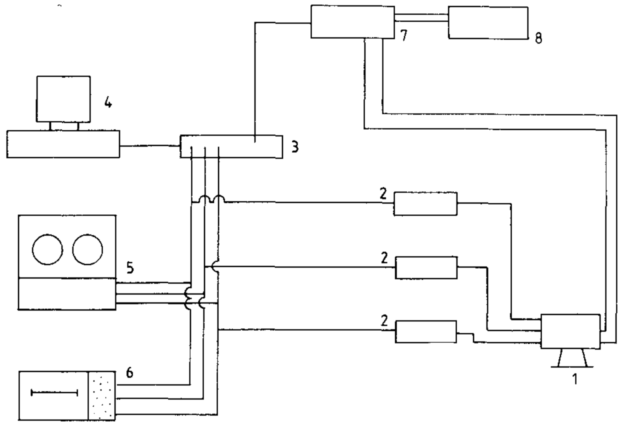


**Fig. 2 Schematic of the experimental setup: 1) Combustion chamber; 2) amplifiers for pressure transducers; 3) AD converter; 4) personal computer; 5) tape recorder for backup of signals; 6) ultraviolet recorder for quick look; 7) ignition system; and 8) power supply.**

Mixing was performed in a vertical planetary mixer at 40–50 °C. Iron-acetyl-acetonate was used as a curing catalyst. The propellant was cured at 60° C for 5 days. Formulations and flame temperatures are given in Table 3.

## Experimental Setup and Data Reduction

### Description of Propellant Samples

All propellants were cast in plastic hollow cylinders made of Plexiglas or polyamide with an outer diameter of approximately 100 mm and a wall thickness of about 2 mm. The height of these cylinders varied between 100 and 150 mm. These cylinders were sawed into slices by means of a numerically controlled milling machine, the height of each slice being about 10 mm. As the wall of the plastic cylinder was still present at the circumference of each slice, this served as an inhibitor during combustion.

For a smooth ignition, the top surface of the propellant disk was coated with a compatible pyrotechnic lacquer. This method has been described in more detail in Ref. 4.

### Experimental Apparatus

A schematic of the experimental setup is given in Fig. 2. The various components of the test installation are described below.

The combustion chamber itself consists of a 10-cm-i.d. cylinder ($L^*$ burner). At one end, the chamber is closed by a piston to which a propellant disk is bonded. The position of the piston is adjustable so that the free inner volume may be changed as desired. At the other end, the combustion chamber is closed by a nozzle endplate. A great variety of nozzles is available so that combustion experiments at various chamber pressures up to 10 MPa are feasible. The nozzle end plate is provided with a small plug so as to allow the mounting of a pressure transducer. In addition, two other holes in the nozzle end plate allow the mounting of two igniter squibs. Figure 3 shows a cross section of the 10-cm i.d. $L^*$ burner. During all of the test runs, the initial free volume of the 10-cm $L^*$ burner was kept at about 235 cm$^3$.

The propellant disks were ignited by means of two simultaneously actuated squibs. These squibs were manufactured by Davey Bickford, France, whereas the booster charges were manufactured by the Prins Maurits Laboratory and consisted of 0.5 g $B/KNO_3$ for each squib. As the surface of the propellant disk was coated with pyrotechnic lacquer, this ignition method guaranteed a smooth ignition of the propellant.

Only when ANS propellant without additives was tested (propellants CK 1001 and CK 1101), ignition failed and a different approach was taken. In these cases, the propellant surface was covered with a thin layer of an ammonium perchlorate-based composite propellant. On top of this layer a pyrotechnic lacquer was applied.

Combustion of a propellant disk provides a constant pressure level during combustion. By defining the burning time as the time interval between a significant rise and decrease in pressure, a computer program calculated the burning rate and the mean pressure level after each test run. As it was verified that all propellant has been consumed after each test run, no correction on the web thickness of the propellant was necessary.

## Results

### Ignition

In general, ignition of the propellant that was covered by pyrotechnic lacquer could easily be accomplished by means of the two squibs. Only those ANS propellant formulations that did not contain any catalysts, propellants CK 1001 and CK 1101, respectively, could not be ignited by this method. Obviously, catalysts have a great effect on the ignitability of ANS propellants, even when applied in very small quantities.

### Combustion Behavior

In general, a smooth burning of the propellant was observed. However, some ANS propellants exhibited an oscillatory combustion behavior. A typical example is shown in Fig. 4. Table 4 is a compilation of all propellant formulations that to a certain extent suffered from combustion instability, together with the frequencies and the amplitudes of the oscillations observed. The (relatively) low-pressure/low-frequency character of these oscillations are possibly $L^*$ oscillations. Note that the frequency decreases with increasing pressure.

Formulations that contain copper chromite and no iron oxide seem to be liable to combustion oscillations; when iron oxide is also present, combustion oscillations are suppressed. Ammonium dichromate or iron oxide only seem to evoke

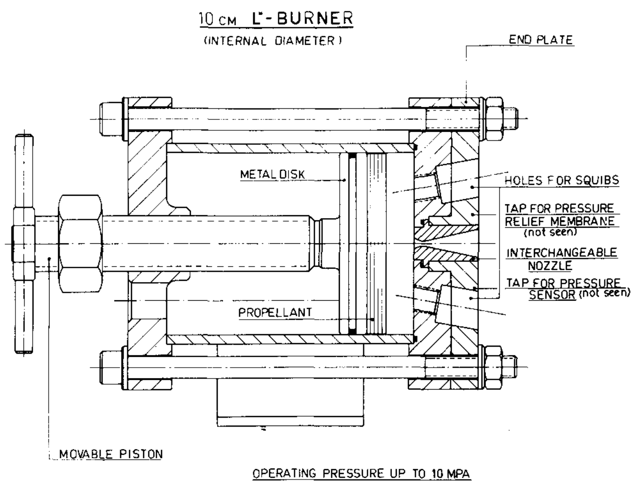


**Fig. 3 Crossection of the 10-cm i.d. $L^*$ burner.**

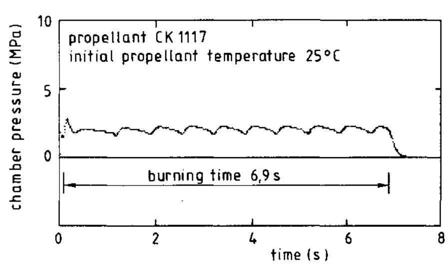


**Fig. 4 Typical pressure history during oscillatory combustion.**

**Table 4 Compilation of oscillatory combustion behavior of ammonium nitrate-based propellants**

| Propellant CK | Mean pressure level, MPa | Amplitude/ mean pressure (−) | Frequency mode, Hz |
|---|---|---|---|
| 1104 | 2.4 | 0.09 | 1.4 |
| | 4.4 | 0.10 | 1.0 |
| | 5.7 | 0.10 | 0.8 |
| | 5.8 | 0.10 | 0.8 |
| 1108 | 6.2 | 0.03 | 1.9 |
| | 6.2 | 0.03 | 1.9 |
| 1113 | 4.3 | 0.08 | 1.0 |
| | 6.1 | 0.09 | 0.8 |
| | 8.3 | 0.06 | 0.6 |
| 1117 | 2.1 | 0.15 | 1.5 |
| | 3.8 | 0.17 | 1.2 |
| | 5.0 | 0.19 | 1.3 |
| | 6.9 | 0.11 | 1.2 |
| 1121 | 2.1 | 0.12 | 1.8 |

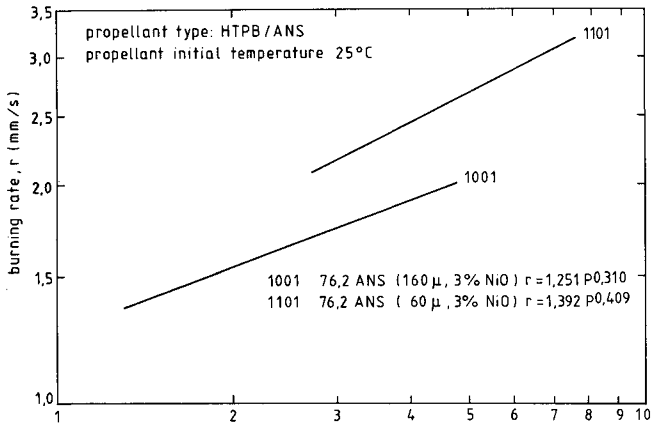


**Fig. 5 Burning-rate behavior of ANS propellants; effect of ANS particle size.**

combustion oscillations when it is applied in very small amounts (0.5 and 0.25%, respectively).

### Burning-Rate Measurements

All burning-rate measurements have been performed at an initial propellant temperature of 25°C and at least four different pressure levels in the pressure range 0.1–10 MPa. All results have been correlated according to the De Vieille burning rate law. In all cases, the correlation coefficient exceeded 0.99, indicating a high reliability of the results.

#### *ANS Propellants*

To examine the results in detail, the propellants may be divided into groups; in each group the effect of the following parameters on the burning rate has been investigated: 1) particle size of ammonium nitrate crystals; 2) amount of iron oxide as a catalyst, also in combination with other catalysts; 3) amount of ammonium dichromate and/or copper chromite as a catalyst; and 4) amount of iron oxide, ammonium dichromate, and copper chromite as catalysts at high solid loading.

*Particle size of ANS crystals.* Two particle sizes were selected, 160, and 60μm. No additives were used. The results are shown in Fig. 5. It is clearly visible that the particle size affects not only the burning rate but also the burning-rate exponent. From this result, the highest burning rates may be expected when using small particle size AN crystals. All other propellant formulations were based on 60-μm particle size AN crystals.

*Iron oxide.* Iron oxide is known to have an effect on the burning rate of AN propellants. It was therefore investigated to what extent the amount of iron oxide determines the burning rate and the burning-rate exponent in particular. The results are shown in Fig 6. It is evident that the amount of iron oxide greatly influences the burning-rate exponent. Apparently, small amounts of $Fe_2O_3$ yield the highest burning-rate exponent, whereas the burning-rate exponent decreases with increasing iron oxide content. In addition, increasing the amount of iron oxide also seems to decrease the burning rate itself; although propellant formulation CK 1105 (1% $Fe_2O_3$)

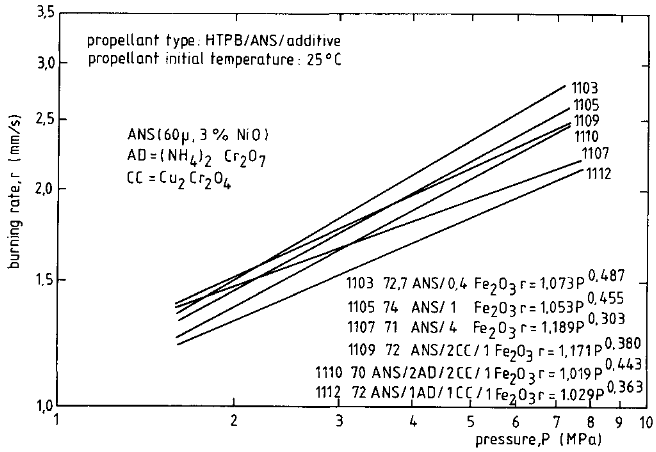


**Fig. 6 Burning-rate behavior of ANS propellants; effect of iron oxide as a catalyst.**

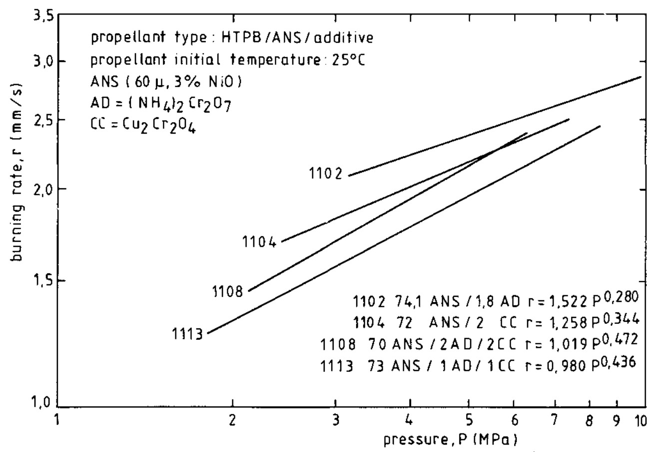


**Fig. 7 Burning-rate behavior of ANS propellants; effect of ammonium dichromate and copper chromite as catalysts.**

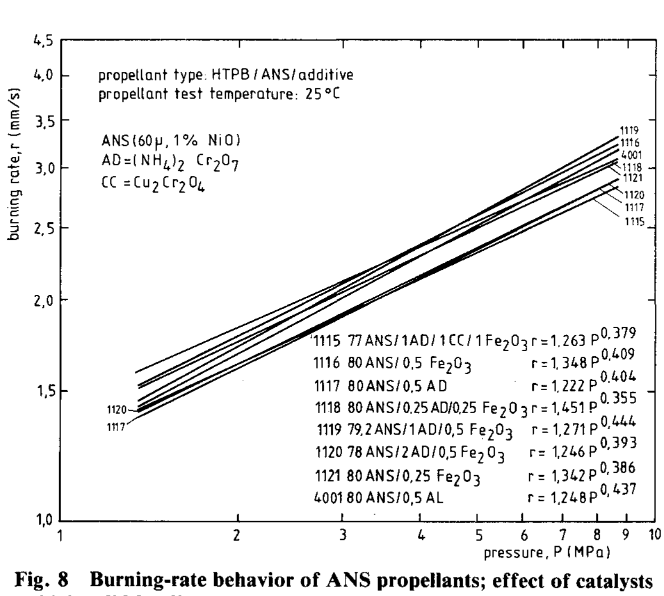


**Fig. 8 Burning-rate behavior of ANS propellants; effect of catalysts at high solid loading.**

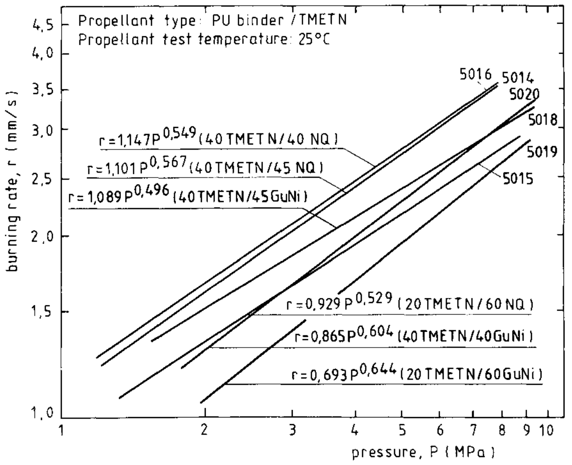


**Fig. 9 Burning-rate behavior of TMETN-PU propellant.**

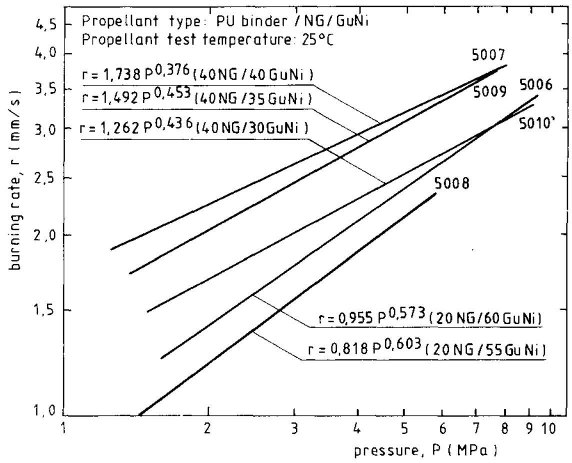


**Fig. 11 Burning-rate behavior of NG-PU propellants with GuNi as coolant.**

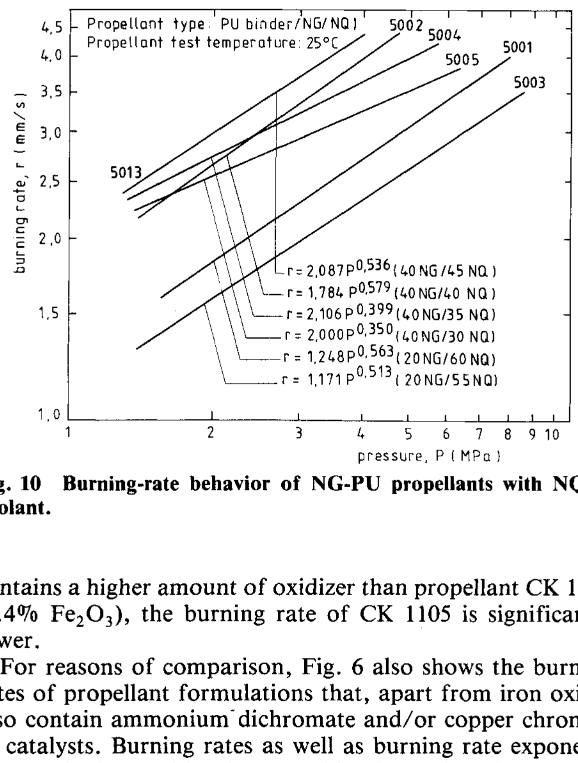


**Fig. 10 Burning-rate behavior of NG-PU propellants with NQ as coolant.**

contains a higher amount of oxidizer than propellant CK 1103 (0.4% $Fe_2O_3$), the burning rate of CK 1105 is significantly lower.

For reasons of comparison, Fig. 6 also shows the burning rates of propellant formulations that, apart from iron oxide, also contain ammonium dichromate and/or copper chromite as catalysts. Burning rates as well as burning rate exponents seem to be lowered by these combinations of additives.

*Ammonium dichromate and copper chromite.* The effect of the catalysts ammonium dichromate (AD) and copper chromite (CC) without iron oxide on the burning rate exponent has been investigated. The results are shown in Fig. 7. Using only AD or CC as an additive apparently yields low values for the burning rate exponents. Only combinations of AD and CC show a significant increase in burning rate exponent. It is worth noting that burning-rate exponents of about 0.5 can only be achieved by considerable amounts of AD and CC (together more than 4%), whereas such a burning-rate exponent can also be achieved by very small amounts of iron oxide (cf. propellant formulation CK 1103, Fig. 6). At higher pressure levels, the burning rates of these formulations fall below those of the formulations where also iron oxide is incorporated.

*Iron oxide, ammonium dichromate, copper chromite at high solid loading.* Combustion experiments showed a burning-rate pressure behavior for the various propellants as shown in Fig. 8.

Propellant CK 1119 couples a (relatively) high burning-rate exponent to the highest burning rate in the pressure region between 6 and 10 MPa. When comparing propellant formulations CK 1103 and CK 1116 (having almost the same amount of $Fe_2O_3$ as catalyst but a different oxidizer content), it is remarkable to see that the burning-rate exponent, being 0.487 at 73% ANS, seems to decrease to 0.40 at 80% ANS. Combinations of $Fe_2O_3$, AD, and CC do not show such a tendency because the burning-rate exponent remains (almost) constant (cf. CK 1115 and CK 1112).

Propellants CK 1116 and CK 1117 contain 0.5% additive, being $Fe_2O_3$ and AD, respectively. From these additives, AD causes the smallest burning-rate enhancement, whereas $Fe_2O_3$ causes the highest burning rate.

Smaller amounts of $Fe_2O_3$ than 0.5% as used in propellant CK 1121 only result in lower burning rates and lower burning rate exponents. The same applies to combinations of small amounts (0.25%) of AD and $Fe_2O_3$ (CK 1118) at pressure levels above 6 MPa.

### *TMETN-PU Propellants*

Figure 9 shows the burning-rate pressure behavior of the TMETN-PU propellants. For propellants CK 5015, CK 5016, CK 5019, and CK 5020, which all contain 20% binder, it is clearly seen that the burning rate decreases with increasing NQ or GuNi content while the burning rate remains about constant (NQ) or is increased (GuNi) when the binder content is lowered to 15, and the NQ or GuNi content is raised to 45%.

TMETN propellants exhibit burning rate values comparable to ANS propellants; the burning-rate exponent, however, is significantly higher, ranging from 0.50–0.64.

### *NG-PU Propellants*

To the NG-PU based propellants either NQ or GuNi is added as a coolant. Figure 10 shows the burning-rate pressure behavior for the NQ-containing propellants, whereas in Fig. 11 the burning rate data of the GuNi-containing propellants are presented.

Both the NQ- or GuNi-containing NG propellants show the same burning-rate behavior. When the NG content is lowered, the burning rate decreases as well. The burning rate also decreases when the binder content is raised (and the NQ or GuNi content is lowered) From the three families tested, the NG-PU propellants exhibit the highest burning rates, when NQ is used as coolant. When GuNi is employed, the values of the burning rate are comparable to those of ANS or TMETN propellants.

## Conclusions

The following conclusions may be drawn:

1) The mean particle size of the AN crystals has an effect on the burning rate. Propellant based on 60 μm AN showed a significantly higher burning rate than propellants containing 160 μm AN crystals.

2) Iron oxide, ammonium dichromate, and copper chromite all improve the ignitability of AN propellants.

3) When iron oxide is the only catalyst used, an increase in the amount of this substance causes a decrease in the burning rate (at pressures above 2 MPa) and a decrease in burning-rate exponent.

4) When only ammonium dichromate or copper chromite is used as a catalyst, the burning-rate exponent proves to be low (0.28–0.35). A combination of these two catalysts greatly increases the burning-rate exponent (0.45). Considerable amounts of these two catalysts are necessary to enhance the burning rate.

5) When in addition to AD and CC iron oxide is also used, a decrease in both burning rate and burning-rate exponent is observed. Iron oxide in combination with AD or CC alone, however, couples an increase in burning-rate exponent with a decrease in the burning rate itself.

6) Some formulations based on copper chromite as a catalyst or formulations that only contained small amounts of AD (0.5%) or iron oxide (0.25%) suffered from combustion oscillations.

7) TMETN-PU propellants have significantly higher burning-rate exponents than ANS propellants (typically 0.5–0.6 compared to 0.3–0.5).

8) NG propellants exhibit the highest burning rates, up to 7 mm/s at 10 MPa, when NQ is used as a coolant. When NQ is replaced by GuNi, burning rates are comparable to those of ANS or TMETN propellants.

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