Experiments with some KNO3/epoxy composite propellants

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Introduction

This report describes the work done by the Danish Amateur Rocketry Club DARK with composite propellants based on KNO_3 as oxydizer.

KNO_3 is commonly used by amateurs in propellant compositions together with different kinds of sugar. Some work has been done by rocketry amateurs to describe the "candy" propellants behaviour in terms of chemistry, burnrate and expected performance. A classic work on the subject is the booklet " The Potassiumnitrate - Sugar Propellant" written by Antoon Vyverman in 1978. Sugar based propellants have been popular among amateurs for being inexpensive, easy to manufacture and for being relatively safe to operate. Their drawbacks have been however that they are quite brittle and also somewhat hygroscopic. Furthermore, KNO_3 is considered a low performance oxydizer, and as such, it has never attracted the attention of professionals, hence the literature in the field is almost entirely written by amateurs.

When, during the late seventies, rocketry amateurs in Europe started working with "candy" propellants, very little was known on the practical realisation of composite propellant rocket motors. At the time, DARK had most of its experience from gunpowder and Zinc-sulphur propulsion, and “candy” motors were made as simple case bonded coreburners. As shown by Richard Nakka (http://www.nakka-rocketry.net) case bonding of the brittle sugar based propellants is a fairly bad choice and consequently the motor experiments had a rather high failure rate.

To overcome these problems, Kim Vilbour Andersen and Michael Milling Madsen tried replacing the sugar with a polymer binder. The first attempt of replacing sugar was done with polyester resin. Available from a shop across the street, reasonably low priced and simple to work with, it was a convenient choice. Two separate compositions were tried out. One with polyester simply replacing sorbitol in the standard 65/45 KNO3/sorbitol mixing ratio, and one composition that included aluminium powder (details of this composition are unknown). Small batches of both mixes were prepared, and it was decided to do two full scale motor for testing. The motor cases for this experiment shared the same motor casings normally used for zinc-sulphur motors. The propellants were hand mixed without degassing and poured into the cleaned but otherwise unprepared motor casings. The formation of the case bonded core burning geometry was done by rotating the motors on a lathe until the polyester resin had cured. It turned out that the propellant containing aluminium powder was completely unable to cure, and that composition was then given up. The motor with the plain KNO3/polyester propellant did cure however, at it was tested at the Stold artillery proving ground on July 14, 1984. The test firing was completely unsuccessful. Ignition was done by means of a zinc-sulphur charge, however the first two ignition attempts failed. The third attempt with a rather large charge (details unknown) resulted in a large pressure build up followed by a nozzle blow out. Several large pieces of propellant were recovered, and it could be seen, that some burning had occurred leaving a rather rough surface. Also there was clear evidence of trapped air in the grain.

Discurraged from this result no more experiment were done for a couple of years. It turned out however, that there was some propellant left in the motor casing after the test, and that this leftover was rather impossible to remove. In practice this was solved when the motor casing was filled with zinc-sulphur and tested for noise measurements required for the operation of the military proving ground. This motor had a nice after burn, when the KNO3/polyester remains were consumed.

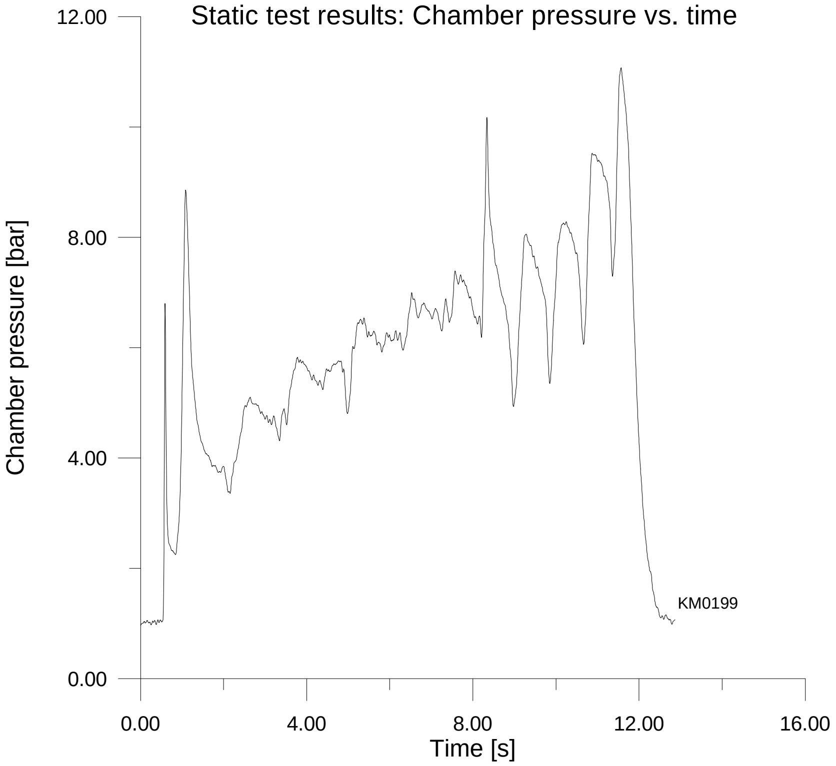
This gave birth to a new experiment, this time using epoxy as binder instead of polyester. The general idea was, that the longer pot-life of epoxy would give the trapped air longer time to leave the propellant. Tests done at atmospheric pressure showed that KNO_3/epoxy compositions were easy to ignite and a nice smooth but rather slow combustion. Finally, in October 1989 a full scale motor was tested with a propellant consisting of 65% KNO3, 43% epoxy and 2% aluminium. The motor ignited, but burnrate was very low, and the motor burned at a very low pressure (no measurements of the chamber pressure was done). Only this single attempt was made, before the KNO_3 based propellants were abandoned, in favour of AP, AN and KP based compositions. Michael Milling Madsen, and later also Kim Vilbour Andersen left DARK and almost 10 years went by until the work on KNO_3/epoxy based propellants was resumed.

It was not until the late 90's that Claus Nielsen and the author started doing small batches of different KNO_3 based compositions. These batches were hand mixed and evaluated by burning them at ambient pressure. It was generally found, that different compositions containing KNO_3, epoxy and non metallic additives were easy to ignite and had smooth but rather slow combustion. No miracles were discovered, but it was found, that the addition of sulphur had some increasing effect on the burnrate. Addition of aluminium was also tried, however this had the effect of making the propellant samples virtually unignitable (although this basically contradicts the 1989 static test - indicating that ignition could possibly occur at higher pressure). Surpricingly, the combination of sulphur and aluminium turned out to be very promising. Several different mixing rations were tried out, but in the end the composition settled at:

64% KNO3
26% Epoxy
5% Sulphur
5% Aluminium

This composition showed good ignition characteristics and had smooth, almost violent combustion when compared with the non-aluminized samples. It should be noted, that similar results were obtained by replacing Aluminium with Iron, but aluminium was preferred for its promise of higher specific impulse, according to PROPEP simulations.

After having stayed as a low priority project, the first real test firing of this proposed propellant took place in April 1999. The test, designated KM0199, was done as a characterisation of burnrate in accordance with the methods that had been developed for work with other (mainly AP based) composite propellants. One test firing took place. Ignition was good, but the combustion showed severe chuffing. The maximum "stable" chamber pressure was only some 10 bar at Ab/At of 400. The test was considered a partial success. Even though performance had been poor, it was generally believed, that the chuffing could be eliminated by either changing the type of aluminium or by increasing the chamber pressure. In the end however it should turn out that the nature of the chuffing was completely different from "normal" chuffing, but that was not to be discovered until a year later.



KM0199 pressure recordings

Propellant burnrate testing

This chapter describes the method that DARK uses for characterisation of composite propellants.

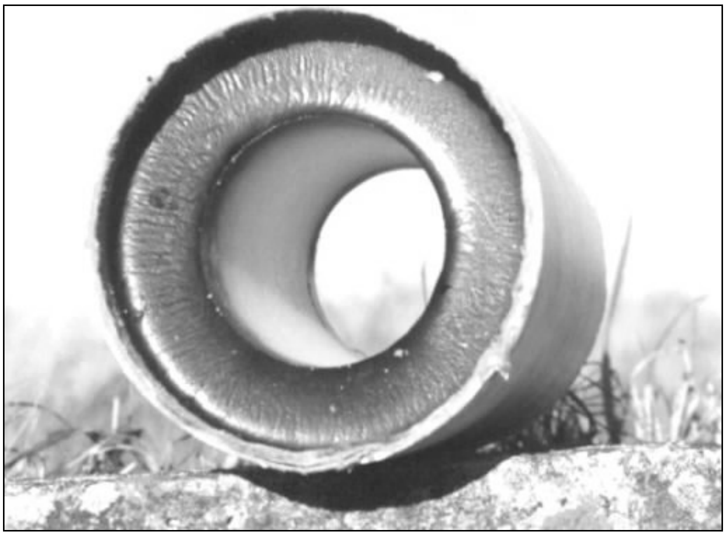
Characterisation of a propellant is done by firing a grain of the desired composition in a characterisation motor while monitoring the chamber pressure and thrust produced during the burn.

The characterisation motor is a small and robust all steel rocket motor designed to withstand high pressures and high temperatures. It has a sortiment of nozzles for operation at a large span of Kn values – the practically achievable range is in the order of 100 up to 1500. The characterisation motor is intended for determination of purely propellant specific data such as burnrate at different operating conditions and of the characteristic velocity c*. Generally, the characterisation tests are done with nozzles that have no divergent part, causing severe under expansion. Hence, the measured thrust data are of limited use and does not lead to any realistic values of specific impulse for the propellant in question. Realistic values of Isp may be calculated from thermodynamic data from theoretical considerations, computer simulations or by fitting data from other tests.

The test grains are shaped as free standing coreburners, inhibited on the outside and at both ends, thus resulting in a burning surface that increases linearly with the regression length. The core diameter is 50mm at ignition, expanding to 90mm at burnout resulting in an increase of burning surface by a factor of 1.8 during the burn. The preferred size of the characterisation grain is 600g. Both smaller and larger segments are possible.

The variation in burning surface causes the chamber pressure to increase during burn. Chamber pressure and thrust is measured during burn, usually at a rate of 2-300Hz. The recorded data is processed numerically together with the dimensions and weight of the grain and the diameter of the nozzle to give estimates of c*, Ab/At versus time and burnrate versus time. The result of the test is a dataset containing corresponding values of time, pressure, thrust, Kn and burnrate and may be turned directly into design charts by plotting burnrate versus chamber pressure and chamber pressure versus Kn.

By selecting the nozzle with great care - or great luck – new propellants may be characterized within the complete pressure range of practical interest by only one or two tests.



Characterisation propellant segment

Estimation of burnrate

This method of burnrate estimation enables the calculation of burnrate versus chamber pressure for rocket motors of virtually any grain geometry of known properties. It is based on the assumption that the rocket motor operates in equilibrium conditions, i.e. the mass flow through the nozzle equals the propellant consumption rate.

For a propellant with density ρ, burnrate r, characteristic velocity c* and exposed propellant surface A_b, placed in a rocket motor with nozzle throat area A_T and chamber pressure P_c, the equilibrium condition – at any given time t during the burn - may be written as:

$$r(t)A_b(t)\rho = \frac{A_T P_c(t)}{c^*}$$

Or, if burnrate is isolated:

$$r(t) = \frac{A_T P_c(t)}{\rho c^* A_b(t)}$$

this equation makes it possible to calculate the burnrate as function of time – in principle. One drawback is that $A_b(t)$ is not known as such. For this reason we define the regression length s from the following relation:

$$r(t) = \frac{ds(t)}{dt} = \dot{s}$$

The reason for doing this is that $A_b(s)$ is known by design, so rewriting the burnrate equation, introducing the regression length, it ends up as:

$$r(t) = \dot{s} = \frac{A_T P_c(t)}{c^* \rho A_b(s(t))}$$

This equation may be solved numerically from recorded chamber pressure data, when c* is known.

c* itself may also be calculated from the pressure readings when the propellant mass M_p is known:

$$c^* = \frac{1}{M_p}\int_0^{t_{burn}} A_T P_c dt$$

The calculation of burnrate may actually be extended to also cover the transient phases where equilibrium does not apply. This requires the addition of an extra term to the mass balance:

$$rA_b\rho = \frac{d}{dt}(\rho_{gas}V) + \frac{A_T P_c}{c^*}$$

Again, this expression may be reordered to facilitate the numerical calculation of the burnrate, but the thermodynamical properties of the combustion gas has to be known.

Experiments with “crusted” propellants

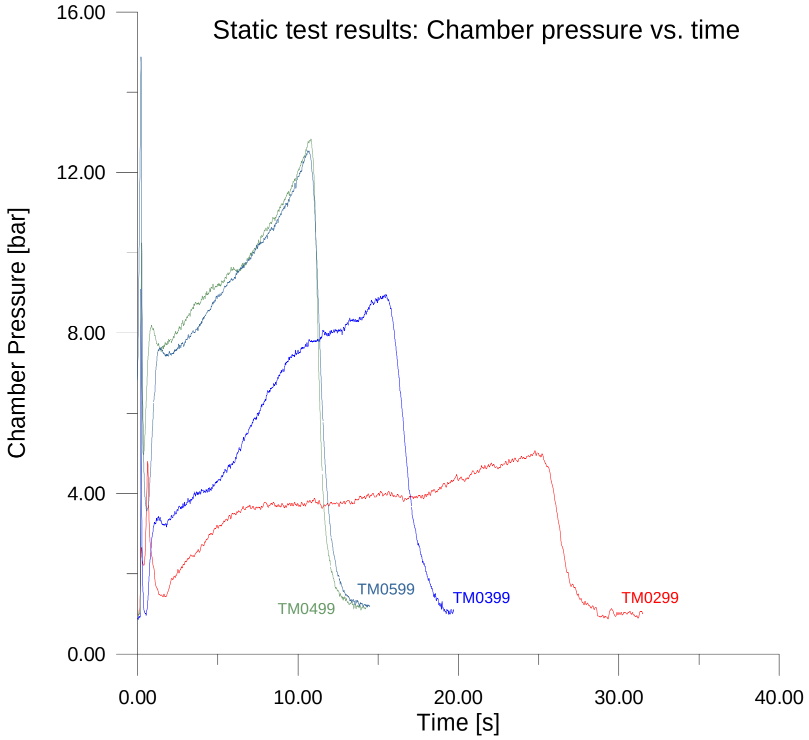
Although the test of KM0199 had not been very successful, it attracted the attention of others, namely Theis Brock-Nannestad and Henrik D. Nissen, and soon it was decided to try a couple of new compositions. It was clear from the preliminary work, that compositions that included aluminium required some form of catalyst. Sulphur did work, but was it the best or the only solution?

Bearing in mind, that Ammoniumnitrate propellants quite often use Ammoniumdichromate as catalyst, this would maybe also work for Potassiumnitrate. Another candidate catalyst would be Ammoniummolybdate.

3 different compositions were tried:

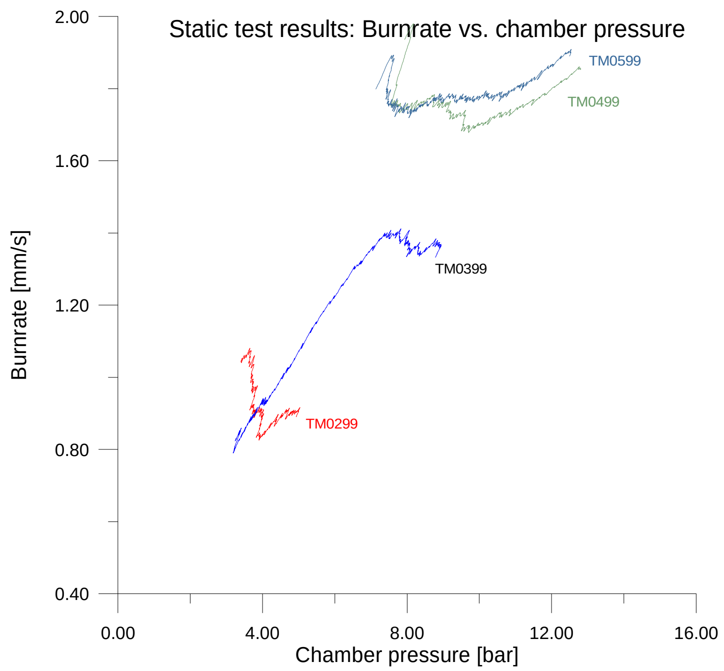
1: 64% KNO3, 26% epoxy, 5% Aluminium and 5% Ammoniumdichromate (TM0499 & TM0599).
2: 64% KNO3, 26% epoxy, 5% Sulphur 5% Ammoniumdichromate (TM0399).
3: 64% KNO3, 26% epoxy, 5% Sulphur and 5% Ammoniummolybdate (TM0299).

The test results are shown below:



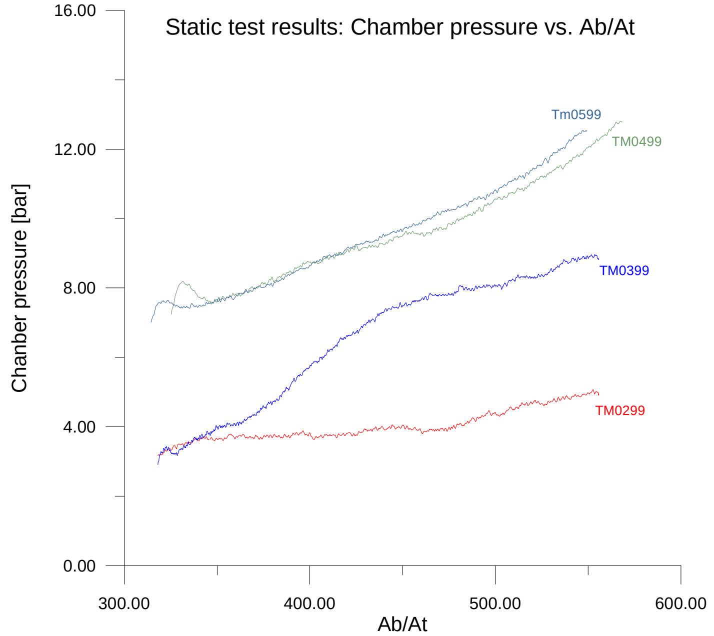
Pressure recordings for TM0299, TM0399, TM0499 & TM0599

The corresponding burnrate estimates are shown of the following graph:



Burnrate estimates for TM0299, TM0399, TM0499 & TM0599

Finally, the relation between Ab/At and chamber pressure:

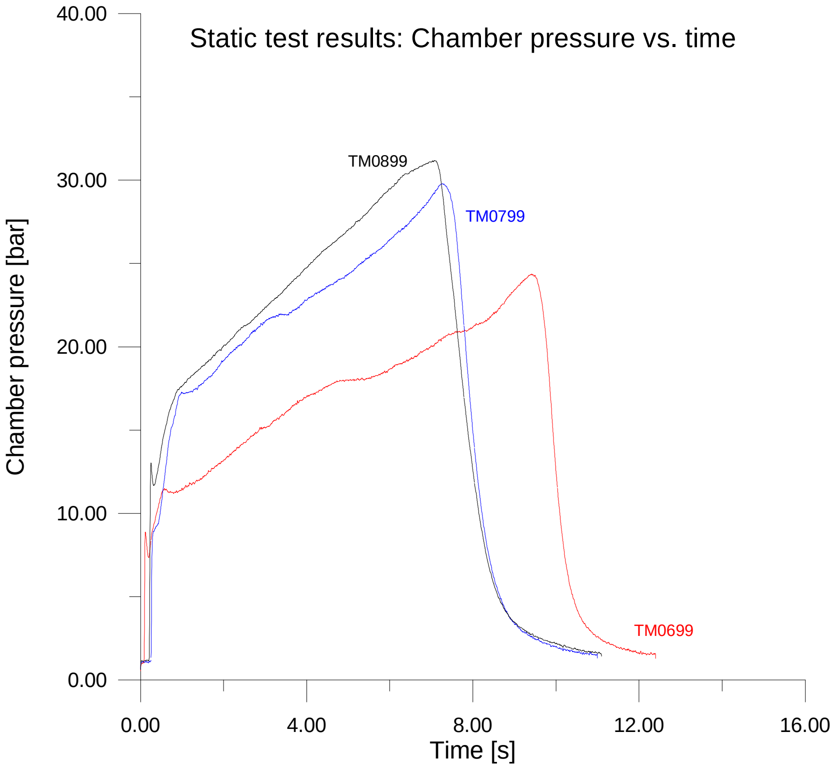


Effect of nozzle on chamber pressure for TM0299, TM0399, TM0499 & TM0599

The composition containing Ammonium molybdate clearly is the slowest of the 3 tested compositions and Ammonuiummolybdate seems like a poor choice of burnrate modifier for this type of propellant. The combination of Sulphur and Ammoniumdichromate does increase the burnrate, but the prescense of Aluminium in combination with Ammoniumdichromate increases burnrate even further. It is believed, that when Aluminium acts as a strong burnrate modifier, it is mainly because it raises the combustion temperature, thereby increasing the evaporation rate for the epoxy binder.

The composition containing aluminium had one negative surprice however: Nearly 1/3 of the original propellant mass was left in the burning chamber as residue. Not only was the amount of residue surpricingly high, but also the fact that the residue had totally preserved the original shape of the propellant grain, simply replacing the original solid propellant with a porous substance of. Also, the residue had the unfortunate characteristic of trapping a significant amount of heat - in fact, the residue was able to sustain the evaporation and external combustion of coating and liner materials for more than one minute.

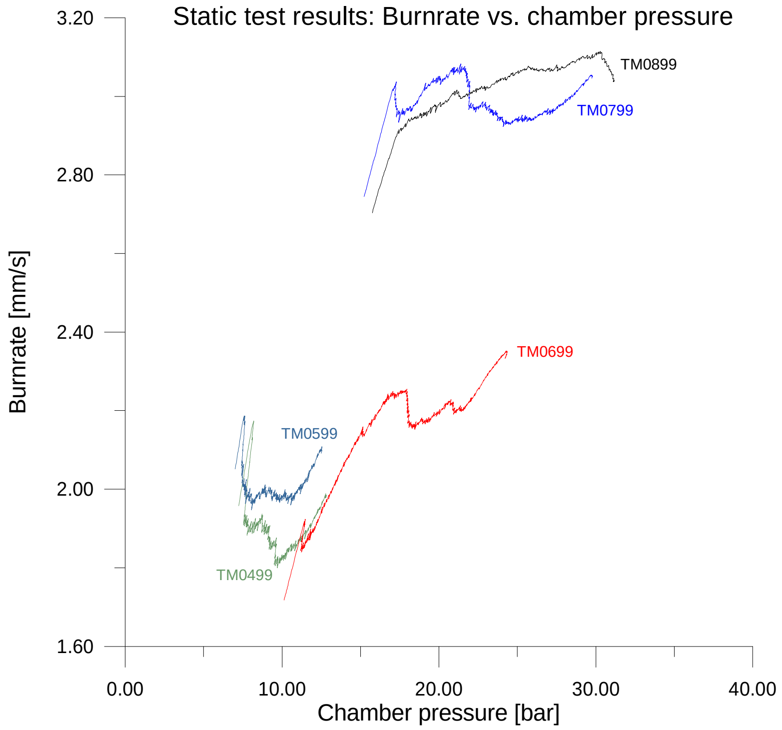
Still, the general results were incurraging, and it was decided to continue tests with the Aluminium/Ammoniumdichromate composition, but at a higher Ab/At – in the order of 1000 in an attempt to establish chamber pressures and burnrates suitable for flight. It was also believed, that the "crusty" effect would disappear at higher chamber pressures. The increased Ab/At, however only created a moderate increase of chamber pressure, and it did not solve the crust issue.



Pressure recordings for TM0699, TM0799 & TM0899

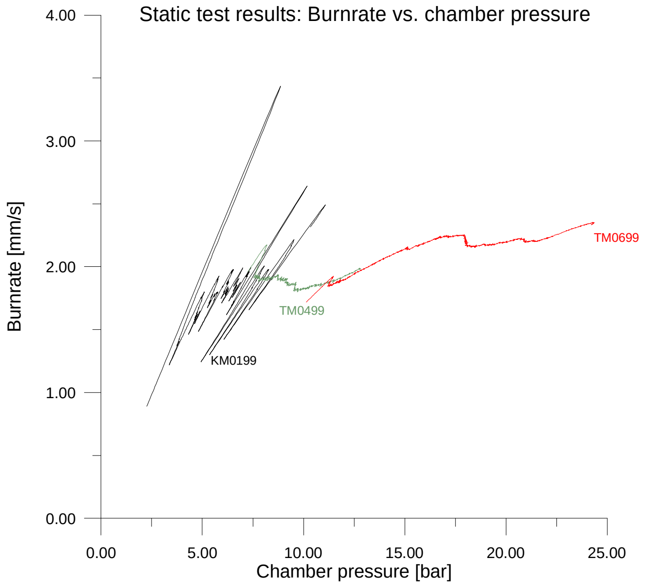
It should be noted, that of the three propellant segments (designated TM0699, TM0799 and TM0899), only TM0699 had been manufactured with degassing during the mixing process. The density of TM0799 and TM0899 propellant segments were somewhat lower than for the TM0699, resulting in a higher Ab/At. This was also reflected in the estimated burnrate, which was higher for the lower density grains. It is believed, that bubbles of trapped air inside the propellant may have caused this effect. A more detailed study of the effect of trapped air in composite propellants may be found in Appendix.

Except from the low density segments, the burnrate estimates for the KNO3 / epoxy / Aluminium / Ammoniumdichromate propellants are in good agreement. They even match the test of KM0199 fairly well, even though the propellant for KM0199 contained sulfur instead of ammoniumdichromate. This, together with the burnrate measurements without aluminium indicated that the aluminium content was the main factor in the burnrate regulating mechanism for this type of propellants.

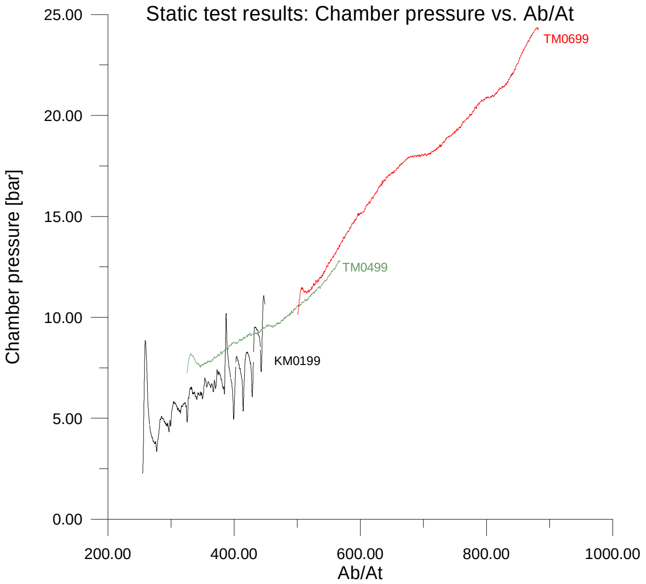


Burnrate estimates of KNO3/epoxy/Aluminium/Ammoniumdichromate propellants.

As a result of the crustiness of this propellant, and the fact that none of the other propellant compositions had suffered from this effect, it was decided to return to the original composition of 64% KNO3, 26% epoxy, 5% Aluminium and 5% Sulphur. If the assumptions were correct, that the burnrate was depending mainly on the content of Aluminium, then the switch to the original composition would not affect the burnrate at all. This may be illustrated by the somewhat uncertain burnrate estimates of the KM0199 test firing when plotted together with the results from TM0499 and TM0699.



Burnrate estimates, combined



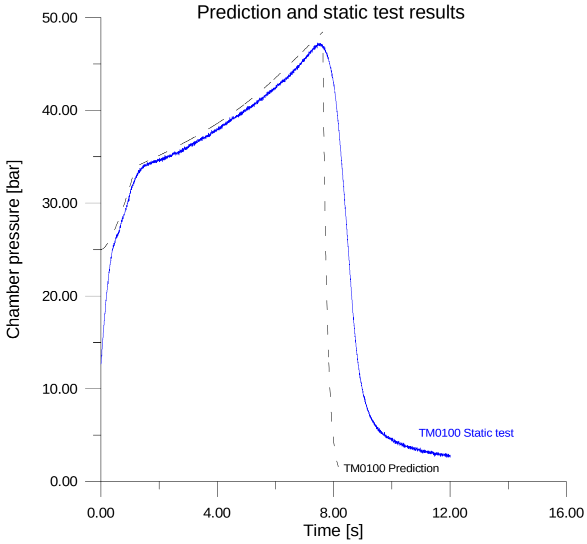
Effect of nozzle on chamber pressure, combined

The combined results of TM0499 and TM0699 was turned into a burnrate model assuming the following relationship between pressure and burnrate:

$\log(r) = a + n^*\log(P_c) + n_2^*\log(P_c)^2 + n_3^*\log(P_c)^3 + n_4^*\log(P_c)^4$

After fitting suitable values of (a, n, n_2, n_3, n_4) to the existing burnrate estimates, some time was spent on simulated burns. As the simulations seemed to mimic the tests fairly well, and the extrapolated burnrate at higher pressures looked “reasonable”, this burnrate model was used for the somewhat daring project of designing a flight motor with 4kg of propellant even before reliable burnrate data existed.

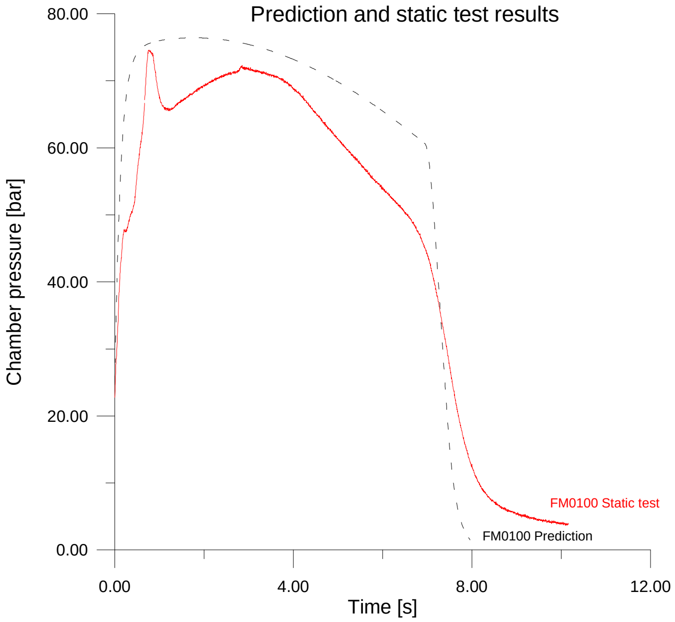
The flight motor was a 4-segment BATES grain design operating at Ab/At of around 1700 corresponding to an expected chamber pressure of around 75bar. None of the already conducted tests had utilised such a high value of Ab/At, and to make sure, that the burnrate estimates were not far out, and that the old chuffing problem was under control, the first test in this test series was done with a standard characterisation segment operating at Ab/At of 800-1500. This test, designated TM0100 turned out to be in very close agreement with the predictions. Surpricinly, it was discovered that the crust problem was also prescent with this propellant composition, even though it had not been observed at the original KM0199 test.



Pressure recordings for TM0100

TM0100 was followed by an apparently successful test of a single segment BATES grain motor. Unfortuneatly however, all data recordings from this test were lost due to a communication error.

Then, after the two successful test firings, the flightmotor designated FM0100 was readied for test and fired. As the largest motor so far based on the KNO3/epoxy family of propellants it made an impressive and completely flawless burn.



Pressure recordings for FM0100

As shown on the graph, agreement between predicted and recorded pressure is fairly good considering that the predictions are based on heavily extrapolated burnrates of a different propellant. One interesting feature of the burn is the pressure peak at the beginning of the burn. This looks like an unmistakeably sign of erosive burning, but that would be a huge surprice considering the large Ab/At. Also in this test, some post burning was observed. The heat trapped in the residue was causing liner material, O-rings, grease etc. to evaporate and even combust with atmospheric oxygen. The motor itself was far too hot to be removed from the test bench for some 10 minutes. It had to be cooled with water before it could be opened for inspection.

Static test of FM0100

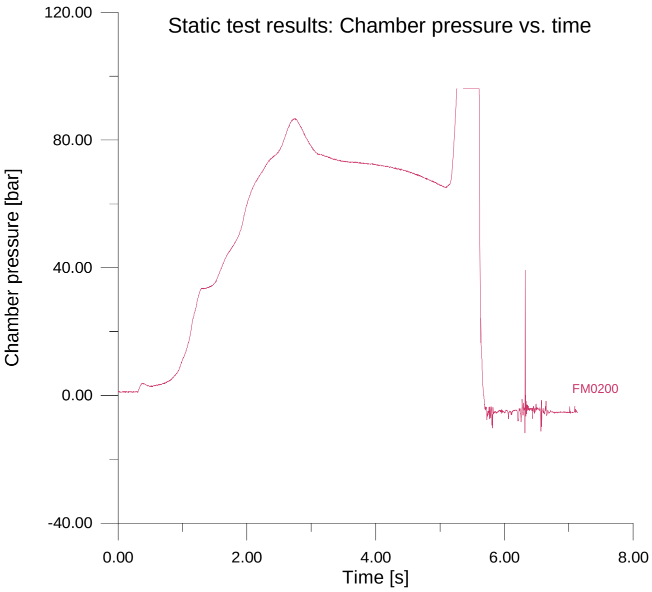
Despite this large afterheating/afterburning problem caused by massive residue, the test was considered successful, and the motor was reloaded with four fresh propellant segments for a da capo. This 2'nd test, designated FM0200, turned out apparently well for the first approximately four seconds of burn. Then suddenly the motor chuffed a couple of times at very short intervals and disintegrated.

There had been some concern, that the aluminium motor casing had been degraded by the large heat exposure during the first test, and the immidiate conclusion was that this was a simple casing failure. However, a closer inspection of the thrust and pressure readings told a completely different story.

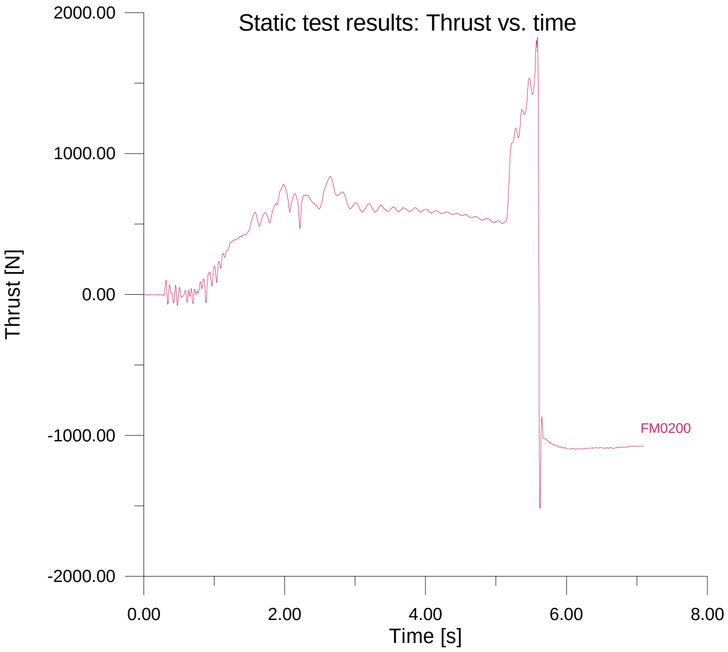
FM0200 CATO

At first glance, the pressure readings of FM0200 are "similar" to those of FM0100, however there are some differences. The startup of the FM0200 is significantly slower than the startup of FM0100, which is likely due to the somewhat improvised ignition system. It is very likely, that ignition did not occur simultaneously on the entire burning surface. Especially, ignition of the top end of FM0200 could have been delayed approximately 1 second. Again, FM0200 has the initial pressure peak indicating erosive burning, but as this peak goes away, the operating pressure settles at a level some 10 bar higher than the FM0100.

Also the final 0.5 second prior to termination are interesting. The pressure increases rapidly, but not instantly until the pressure reading saturates at 95 bar. The pressure readings stays saturated during the final 0.5s until the casing fails. The pressure level during this period is unknown, but some indications are given by the thrust readings, that shows a rapid increase of thrust from approximately 500N to 1000N, then followed by a slower increase until termination occurs at 1800N. This indicates, that the pressure at the time of termination must have been roughly twice the value of saturation, i.e. 180-200bar. On a hydrostatic test of a similar motorcasing, failure occured at roughly 180 bar. Consequently, the motor casing performed nominally, and this was not a casing failure.

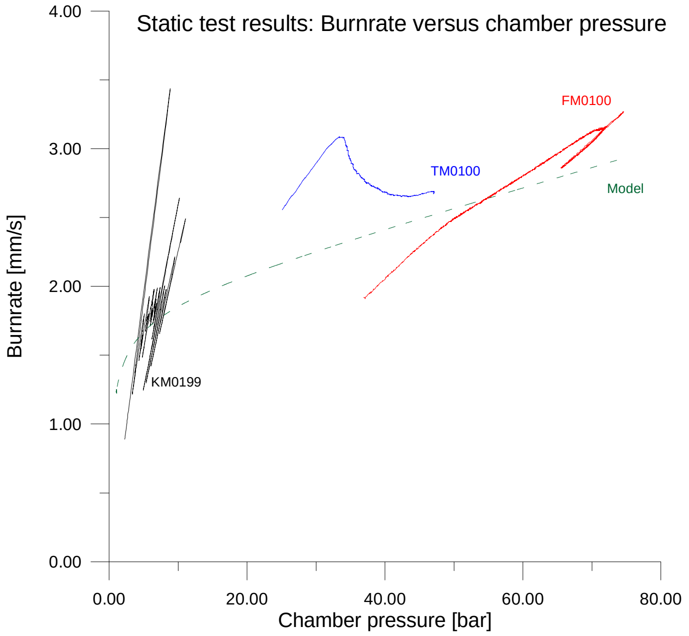


Saturated pressure readings for FM0200



Thrust readings with sudden increase for FM0200

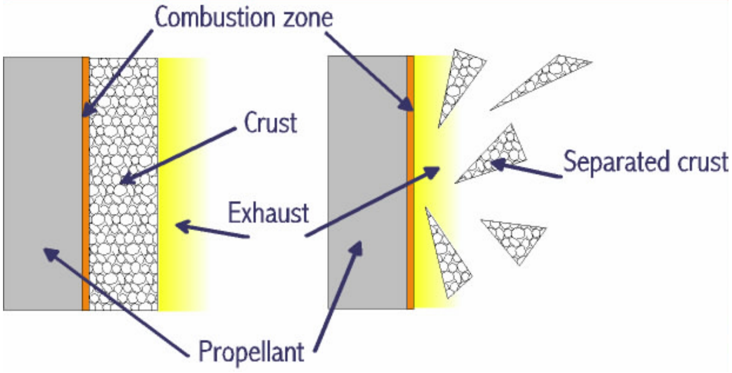
If the casing was not to blame for the failure of FM0200, and as it was clearly not a failure caused by a blocked nozzle, then the only possible explanation would be that it had something to do with the propellant. The previous tests had not indicated any kind of problems, but the estimated burnrate from the TM0100 test showed a rather unexpected peak at around 30 bar. Also, when compared to the burnrate estimates from KM0199 and FM0100, burnrate data did not seem to match.



Burnrate estimates and model for 5% S - 5% Al composition

It should be remembered, that the burnrate is estimated as a function of time and then correlated with the pressure assuming that burnrate is a well defined function of pressure only. However, plotting burnrate versus time for TM0100 showed, that the unexpected high burnrate occured in the beginning of the burn. For the FM0100 burnrate also peaked during startup causing the apparent erosive burn. This led to the theory, that burnrate is depending not only of the chamber pressure, but also on the crust layer. The theory is, that the buildup of crust reduces the burnrate. This explains both the unexpected high initial burnrate of TM0100 and the “erosive burn” pressure peak of FM0100 and FM0200. A closer look on some of the earlier tests reveals that they also shows signs of this effect, although to a lesser extent.

This also explains why FM0200 failed: If somehow the crust layer separated during the burn, the burnrate would certainly increase. At lower surface mass flux, the crust layer could possibly recover, but at the surface mass flux of FM0200, the crust layer could not recover, and instead the motor worked itself towards the equilibrium conditions of the new increased burnrate. As the mass that otherwise would have been piling up in the crust layer now contributed to the exhaust, a crust separation should result in a significant thrust increase, as was observed. Also the separated crust could break up in chunks resulting in thrust spikes - which was observed as “chuffing”.



Crusted propellants - nominal behaviour and crust separation

The chuffing of the original KM0199 test most likely also originates in crust separation. At the significantly lower surface mass flux, the crust layer recovered to some extent, but then, as burnrate decreased, it separated again due to the stresses of the rapid depressurasation. This led to the cyclic behaviour that was observed, and it also explains why KM0199 had very little residue.

How to eliminate the crust layer?

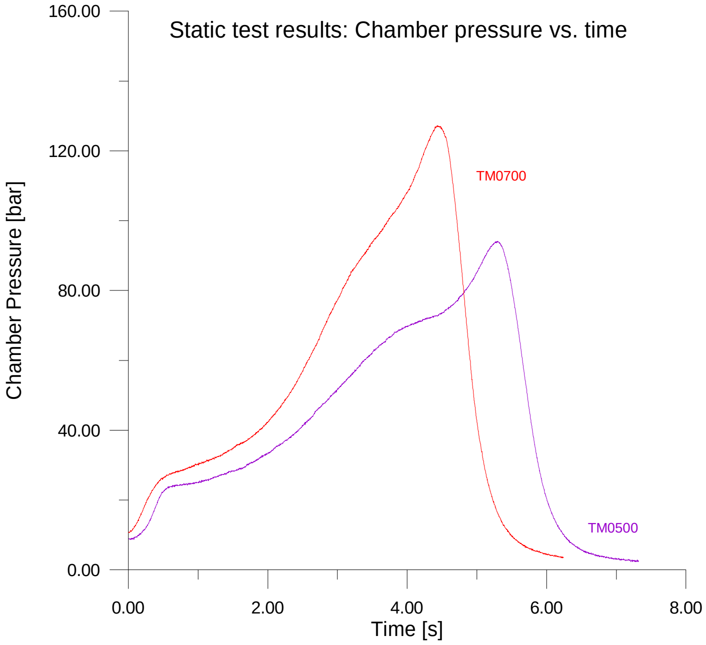
The problems with the crustation and residue seemed to be closely related to the aluminium content of the propellant. To reduce this it would be natural to reduce the aluminium content. As the aluminium would probably speed up the combustion, the reduction of aluminium would possibly lead to a considerably reduced burnrate. It was however not really known how much the aluminium influenced the burnrate, and the results from the FM0200 actually indicated that eliminating the crustation would actually result in higher burnrate.

To investigate this, two experiments were made: In one experiment (TM0500 & TM0700) the aluminium content was reduced to 2%, while in the other (TM0600), the aluminium was completely removed. These experiments yielded excactly the results that we had hoped for: The 2% composition showed increased burnrate in comparison with previous compositions, and even though there was still some residue, it was no longer one third of the original propellant mass, and it was completely reduced to rubble, indicating that the residue no longer had the mechanical properties to sustain the previously experienced crust layer. The second experiment (TM0600) without aluminium was a complete failure in terms of a usable propellant as the burnrate was very low. This however proved the basic theory that the sulfur functions only to reduce ignition temperature while the burnrate is basically depending on the aluminium content.

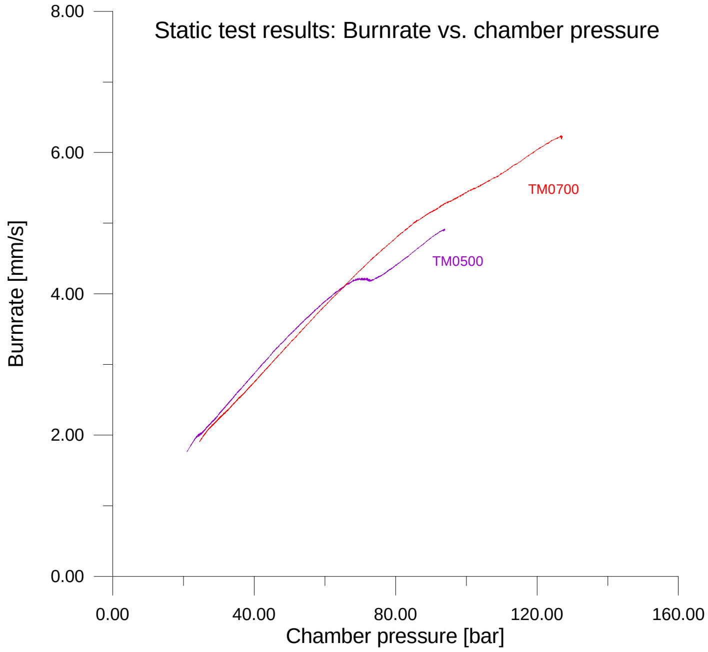
The compositions for the tests were:

1: 66% KNO3, 27% epoxy, 2% Aluminium and 5% Sulfur (TM0500 & TM0700).
2: 68% KNO3, 27% epoxy, 5% Sulphur (TM0600).

The results of the tests are shown below:

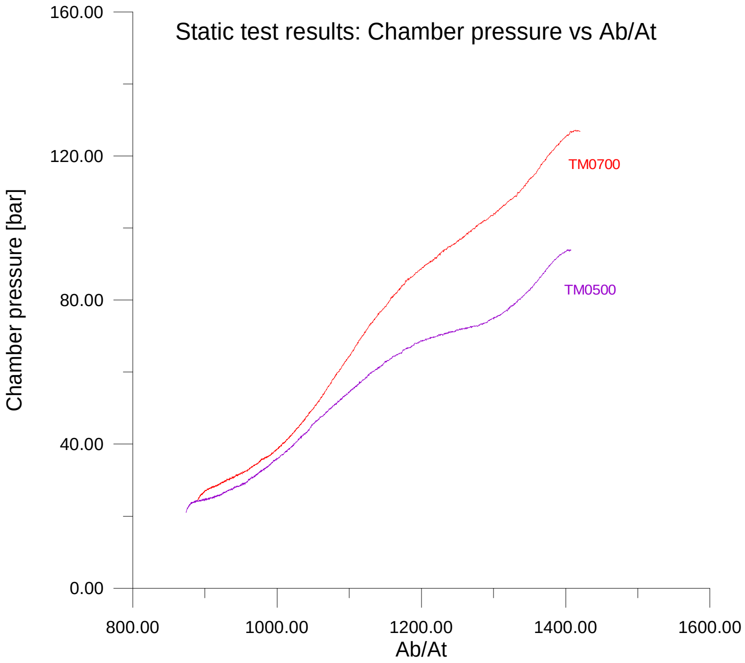


Pressure recordings for 2% Al composition



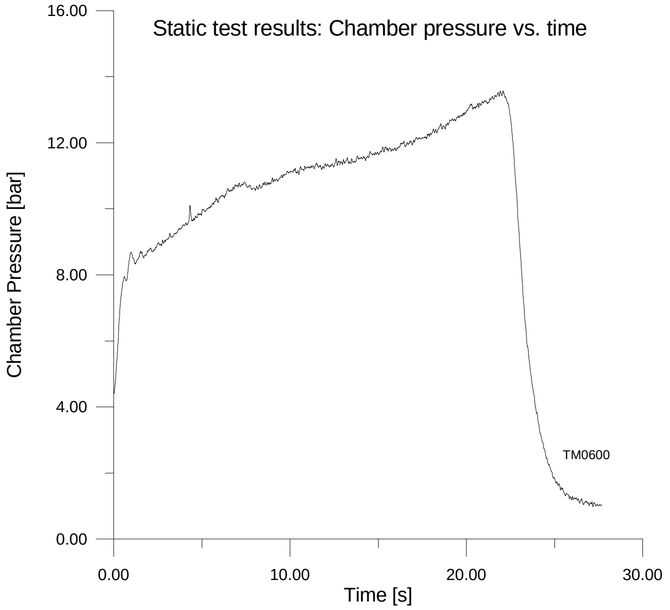
Burnrate estimates for 2% Al composition

It can be seen that there is some difference in the behaviour of the two tests, especially at the higher end of the pressure range. The reason for this is not known, although the TM0700 apparently has a density that exceeds the theoretical, indicating that perhaps the dimensions of the grain have been incorrectly recorded. The trace from TM0500 shows a plateau around 70 bar that is not present for TM0700. One possible explanation is that there could have been a bonding failure between propellant and parts of the end coating of the TM0500 segment.



Effect of nozzle on chamber pressure for 2% composition

Difference between TM0500 and TM0700 is even more visible at this plot. The estimated c* however is almost identical for the two tests, indicating the difference must have some sort of geometrical origin.



Pressure recording for composition without Al

The slow burn of TM0600 was very slow, lasting almost 20 seconds longer than TM0500/TM0700. In terms of a viable rocket motor, TM0600 is a complete failure (except that this particular test achieved the largest c* of all tests covered by this report). This is a clear indication that the burnrate mechanism of KNO_3/epoxy/aluminium/sulfur propellants is gouverned by the addition of even a small amount of aluminium and not by sulfur.

In terms of c*, this test is actually very puzzling. The addition of aluminium is thought to increase c*, while addition of sulfur is expected to have the opposite effect. Still, TM0600 outperforms all the tested compositions that includes aluminium.

Conclusion on “crusted” propellants

Several compositions of KNO3/epoxy propellants has been tested. In general, the compositions without aluminium were fairly easy to ignite, but had too low burnrates for any practical rocketry use. The compositions containing aluminium had much improved burnrate, but required the addition of a sensitizer to aid the ignition process. Compositions with aluminium and no sensitizer turned out to be very hard to ignite, at least at ambient pressure, but this may depend on the particle size of the aluminium powder.

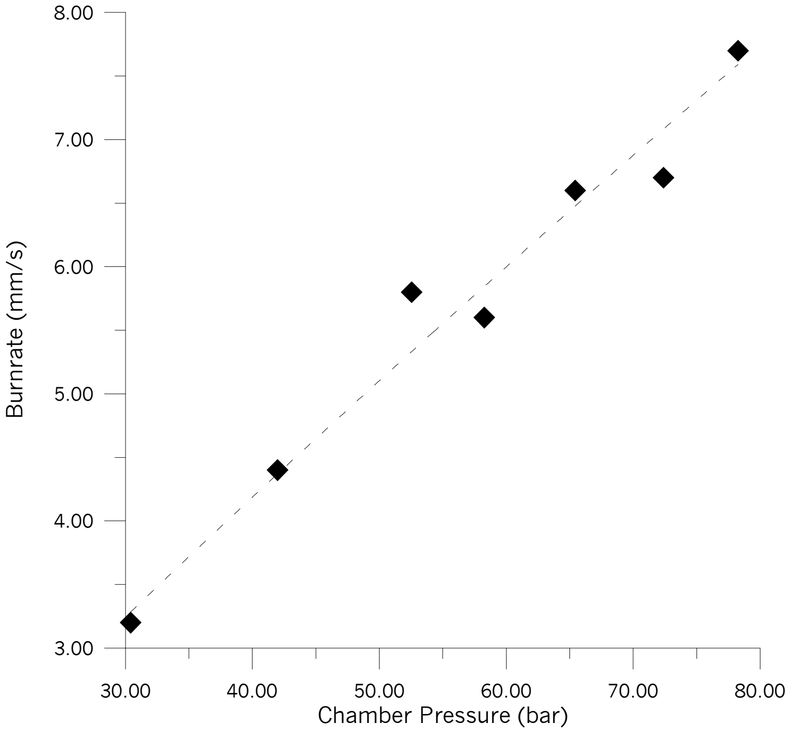
Propellant compositions containing aluminium combined with either Sulphur or Ammoniumdichromate shows improved burnrate when compared to compositions without aluminium. The resulting burnrate seems to improve dramatically by the prescense of even small quantities of aluminium.

Some of the tested propellant compositions tends to create a “crust” of residue. This has been observed only with the propellants containing aluminium. The crusted propellants does exhibit burnrate characteristics that are in general reproducible, and depends on both chamber pressure and the thickness of the crust layer. The crust layer seems to reduce the burnrate drastically. Also, the crust layer traps the solid combustion products within the motor, thus lowering the performance of the motor both in terms of mass ratio and c*, at the same time increasing the thermal exposure of the motor casing. The crust layer has been observed to separate in some cases, for reasons that are not fully understood. As such a separation will cause the burnrate to increase, it will result in either chuffing or plain CATO. This makes the crusted types of propellants unsuitable for rocket motor propellants.

The crusting may be avoided by keeping the aluminium content low. Successful tests has been achieved with aluminium contents of 2% for which the crust layer did not occur while the aluminium content was still sufficient to achieve a decent burnrate of more than 4mm/s at 68 bar (1000psi). This composition, which was used for TM0500 and TM0700 is considered to be an acceptable result of this investigation and seems to be promising in terms of amateur rocketry propulsion for its of low cost and easy manufacture and storage. There is still room for continued experimentation though, as the achieved c* does not live up to the expectations.

It should be noted, that in strand burner tests conducted by Richard Nakka, KNO_3/epoxy propellant samples with varying amounts of aluminium has been tested. Those propellant samples relied on iron oxide (Fe_2O_3) instead of sulfur to reduce ignition temperature and/or increase burnrate. Also in these tests crustation occured in some cases.

Measurements of burnrate versus pressure has been made for a composition of
67% KNO_3
8% Aluminum
1% Iron oxide (Fe_2O_3)
24% Epoxy
The resulting burnrates are somewhat higher than those found in the previous chapter for compositions with 2% aluminium - this is a further indication of the significance of aluminium as burnrate modifier for these types of propellant.



Burnrate measurements from strand burner tests by Richard Nakka.

The burnrate fits the St. Robert burnrate equation quite well with the parameters:

$$r = 0.159 \cdot P^{0.887}$$

This is however almost a straight line (as indicated on the graph) with an alarmingly high burnrate exponent of 0.887.

The c* of this composition is quite good with propep predicting 998 m/s, while the tests even showing a higher value of 1075m/s.

However promising these figures are, the results from full scale motor tests were dissapointing with very long burn durations (8 seconds, where 1 second was predicted) at low chamber pressures of less than 5bar. It is not clear why the motors fails to reach expected pressure, but one possible explanation is that this was due to the high burnrate exponent. Another possible explanation is that a crust layer (as was observed) did inhibit the burn. If this is the case, it is puzzling though, that crustation does not affect the burnrate when it is measured in the strand burner apparatus.

Performance

Even though the work with KNO_3/epoxy propellants mainly has been done to investigate ways to improve the burnrate so that it reaches a sufficient level for use in rocket motors (a rule of thumb says that it has to be at least 4mm/s), the overall performance can not be neglected.

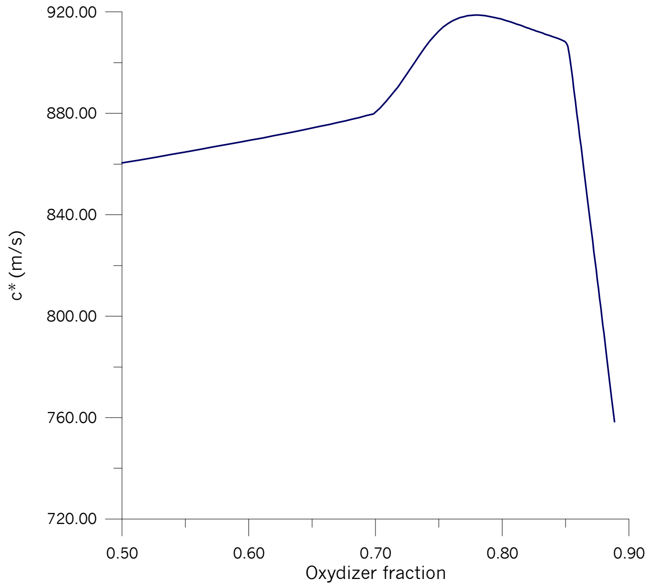
There may be many aspects of "performance" to be considered, but for the practical use for rocket propellant, four factors are considered of major importance:

- Costs
- Ease of manufacturing
- Exhaust velocity
- Density

The element of costs is basically embedded within the framework of this investigation - There is really no need to consider KNO_3 based propellants if costs are unimportant. The use of expensive additives like ammoniumdichromate may degrade this basic assumption, however some freedom has to remain to give the investigation a chance of leading somewhere.

Ease of manufacturing requires that extreme solids loading is avoided, and that the process should not require exotic equippment or complex workflow. This is reflected in the compositions that are covered by the experimental work that forms the base for this report.

The properties of density and exhaust velocity are basically independent of the experimental work, but these are worth some considerations. High propellant densities are considered important because of the increased amount of energy that can be stored in a certain volume of space - this is often reffered to as "volume specific impulse". The exhaust velocity governs the velocity increase that a given rocket can achieve - with "specific impulse" being the crucial figure. It should be noted however, that both types of specific impulse are properties rocket motors - the important figures for rocket propellants are the density and the characteristic velocity c*.



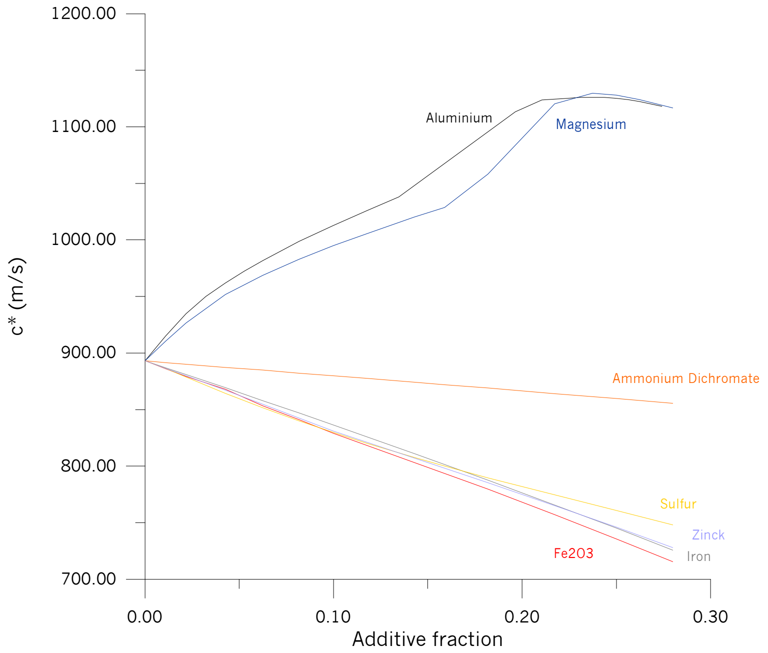
Predicted c* as function of oxydizer content for KNO_3/epoxy propellant

To investigate what kind of c* is achieveable with KNO_3/epoxy propellants, simulations has been made, varying the oxydizer content between 50% and 90% for compositions containing only KNO_3 and epoxy. It is found that c* ranges roughly between 700 and 900m/s, and that the optimal composition is one of 77% KNO_3 and 23% epoxy, yielding a c* slightly short of 920m/s. This is not bad for a simple inexpensive propellant, but it does require however that such a propellant is able to maintain burnrates within the range of practical use - and this is not supported by any experiment from this report.

In order to increase the burnrate, several additives has been tried, either in full scale tests or in simple burn tests at ambient pressure. The following simulations shows the predicted consequences of adding different additives to a base composition of KNO_3 and epoxy in a 65/25 (by weight, meaning 72% oxydizer) ratio.

The simulations clearly predicts a significant improvement of c* when aluminium or magnesium is added to the base composition. In both cases, the optimal amount of metal powder is at around 25% of the total propellant weight. The peak value of c* is about the same in the two cases, but at lower quantities, aluminium gives the better performance. The other additives - even the metals - decreases the expected c*.

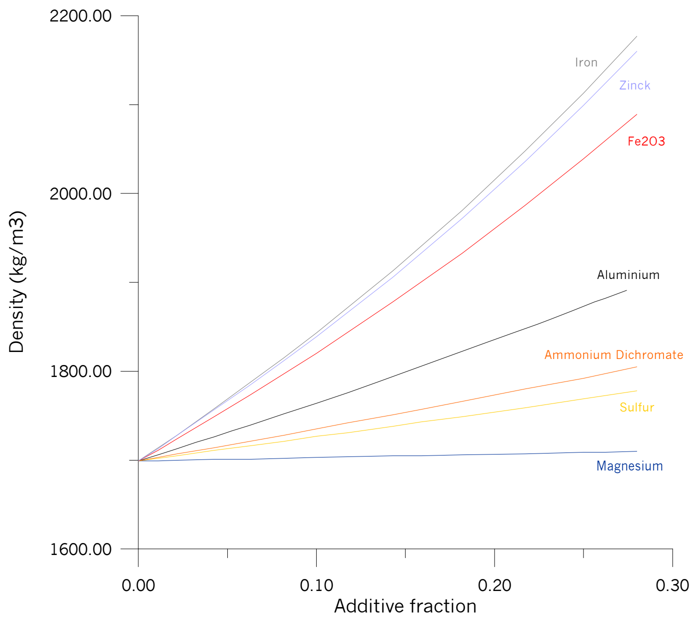
The figures may change slightly if the base composition is changed. It is believed however, that the results in general will not be affected if the 65/25 ratio is altered. Note that PROPEP is really not suited for calculations on compositions that has solid particles in the exhaust - still, it may give reasonable indications of the expected performance.



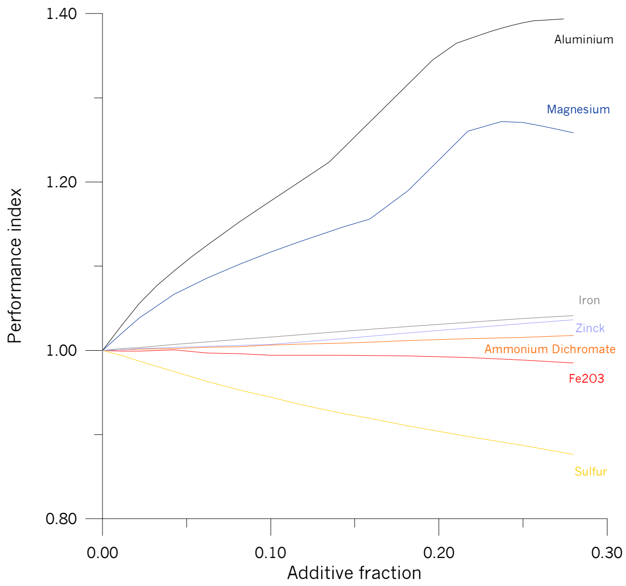
Predicted c* as function of amount of additive for KNO_3/epoxy propellants

Density is predicted to increase for all the shown additives. The additives having the highest individual densities, off course gives the highest contribution to the overall density. In order to rank the additives, a performance index is calculated as the product of c* and density, normalized with the values for the base composition.

Performance index is superior for aluminium compared to all other additives in question, with magnesium as a distinct second best. Sulfur is the poorest choice while the remaining additives gives a nearly neutral performance compared to the base composition - Fe2O3 slightly degrades performance while the other additives slightly increases performance.



Predicted density as function of amount of additive for KNO_3/epoxy propellants



Performance index as function of amount of additive for KNO_3/epoxy propellants

In reality however, the compositions containing aluminium, generally does not live up to the expected c* values. The composition with 2% aluminium achieves 89% of expected c* in two different tests while the compositions with 5% aluminium does not show any consequent behaviour. In one test however, it actually reaches almost 99% of the expected c*. The reason for these variations are not known, but it may be, that the combustion temperature is not sufficiently high to ensure the combustion of the aluminium additive. At 2%, the combustion process may be fairly well defined and repeatable, while at 5%, the combustion process may depend heavily on lots things like the temperature of the propellant, particle size of the aluminium and the condition of the aluminium powder, like oxide layer and moisture content.

It may be seen from the performance index graph that the gain from adding 2% aluminium is totally consumed by the loss of adding 5% sulfur. This may be acceptable if viewed as a means to improve burnrate only, but as the actually achieved performance is only 90% of the expected, it may be beneficial to consider other solutions.

Assuming that aluminium improves the burnrate due to some general properties of metals, any other metal powder should basically do the same trick (this was also indicated in the introduction, where it was noted that iron powder seemed to improve burnrate). It still has to be verified, but one can speculate that if aluminium is replaced by a metal with significantly lower boiling point (i.e. Zn or Mg), combustion will be smoother and higher metal fractions may be achieveable, even without the need for a sensitizer agent (sulfur).

Magnesium is known to improve performance (both c* and burnrate) for ammonium nitrate propellants and it is likely to do the same for the KNO_3/epoxy compositions covered by this report. Magnesium powder is quite expensive however. Zinck powder in small quantities may be a cost effective solution to boost the burnrate of the base composition to a practical value, at only a slight reduction of characteristic velocity.

One possible reason that aluminum powder improves the burnrate could be that it simply absorbs IR radiation. If this is the case, than a small amount of carbon black would yield significant improvements in the burnrate. It is known that carbon black in some cases may act as a catalyst, so replacing the aluminium or the sulfur could also be an experiment worth trying.

Appendix

Effects of trapped air in composite propellants

Trapped air in composite propellants is normally considered unfavourable although it could be beneficial as burnrate modifier if the amount of trapped air could be controlled.

The main disadvantages of trapped air are decreased propellant density and safety concerns. Decrease of density means that the motorcasing has to be larger (heavier) to hold a specific amount of propellant, causing the total performance of the rocket as a system to drop. For amateur rocketry, this is usually of secondary importance. The primary concern is that trapped air influences on the burning surface of the grain, thus increasing the risc of a CATO. To reduce the amount of trapped air, it is common practice to degas the propellant during mixing. Using this technique, the resulting propellant density is usually very close to the theoretical, often better than 98%. Mixing without degassing may result in densities between 90 and 95% of the theoretical. In most cases however, the propellant may still turn out to work reliably. The natural question to ask is then: What is the critical propellant density? – The answer to this question depends on various things, including the burnrate exponent of the propellant in question, and it is possible only to get an overview of the effects.

Trapped air may be in three different forms: isolated air bubbles, air channels - “wormholes” and cracks.

Cracks are the results of bad propellant compositions, a poor manufacturing process, wrong storage conditions or plain handling errors. Cracks should not uccur under normal circumstances and will not be discussed further.

Isolated air bubbles is the most common type of trapped air and may be the result of poor degassing, viscosity problems or of “foaming” of certain types of binders. The effect of isolated air bubbles may be anything from neglegtable to catastrophic.

Wormholes are the result of either insufficient binder of foaming. Wormholes are usually microscopic, and may not be discovered by visual inspection. They do however form a network of channels throughout the grain, and when the grain is ignited an pressurised, the hot gases will penetrate the grain resulting in certain CATO.

Larger air bubbles or cracks may be discovered by inspection, visually or X-ray. Microscopic bubbles or wormholes may require inspection under microscope or dye-bathing. Still, the trapped air takes up volume, and estimation of actual propellant density is the most obvious way of non destructive determination of the amount of trapped air.

The theoretical density of a propellant consisting of N ingredients may be written as:

$$\rho_{thery} = \frac{\sum_N m_i}{\sum_N \frac{m_i}{\rho_i}}$$

Where m_i is the mass of the i’th ingredient and ρ_i is the density of the i’th ingredient. The values of m_i is determined by weighing the ingredients during the process of manufacturing the propellant, while ρ_i may be determined from materials proporties tables or from experiments.

The actual density may be written as

$$\rho_{actual} = \frac{m}{V}$$

Where m and V is the mass and volume of the casted propellant, which may be determined by simply weighing and measuring the geometry of the propellant grain. Ideally, m should equal the sum of ingredient masses and V should equal the sum of ingredient volumes.

As an illustration on what the actual density means, consider a propellant segment for a coreburner, 100mm long, 54mm outer diameter and 24mm bore diameter. If the actual density is 95% of the theoretical, this means that the length of the grain increases by 5.26mm. Cutting such a grain into two parts and inspecting the surfaces roughly corresponds to counting the bubbles in a 2mm thick slice, which turns out to be: 5.5 bubbles of 4mm diameter or 44 bubbles of 2mm diameter or 351 bubbles of 1mm diameter.

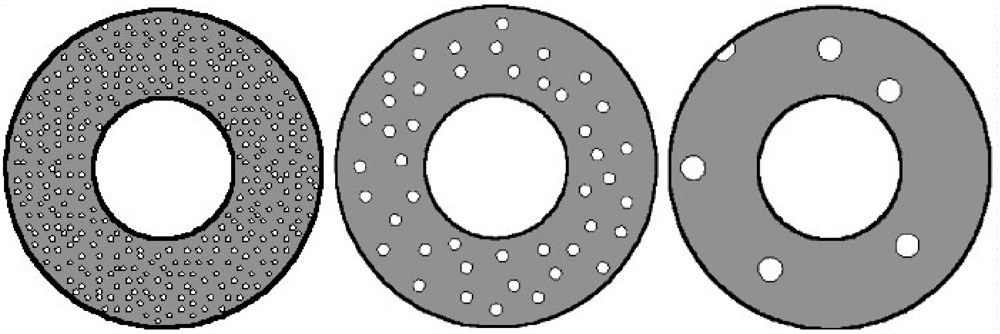


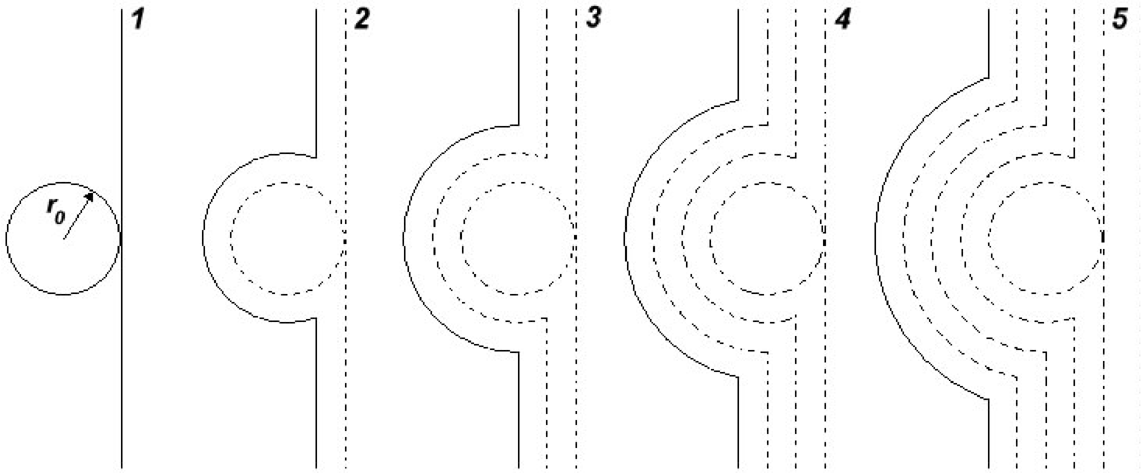
Illustration of 95% of theoretical density

For comparison: a cut through a real propellant segment (approximately natural size).

Cut through propellant segment

Isolated air bubbles

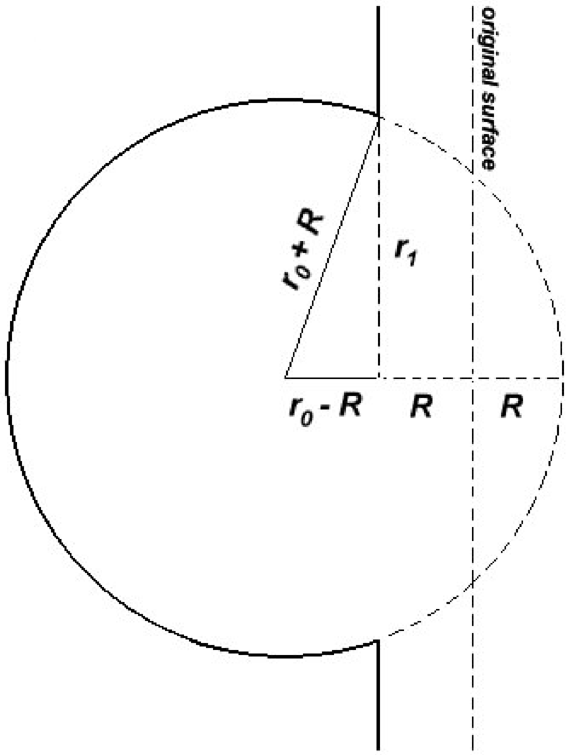
As an example, consider the case of a single spherical air bubble of radius r_0, just beneath the burning surface of solid propellant. A soon as the flame front reaches the bubble, the inside surface of the bubble ignites, and the bubble becomes part of the burning surface. The evolvement of the flame front may be illustrated as follows:



Propagation of flame front when an isolated air bubble is encountered

The evolving surface of the bubble will of course contribute to the total burning surface area. This additional (unwanted) surface area may be calculated from simple geometrical considerations as a function of the Regression length R.

For R < r_0 the geometrical quantities are as follows:



The surface contribution may be calculated as the surface of a sphere with radius $R+r_0$ minus the surface of the spherical cap lying to the right of the burning surface. Also the bubble "eats away" a circular area with radius r_1 of the original planar surface. In total, the surface may be determined from:

$A = A_{sphere} - A_{cap} - A_{plan}$

$A_{sphere} = 4\pi(R+r_0)^2$

$A_{cap} = 4\pi R(R+r_0)$

$A_{plan} = \pi r_1^2$

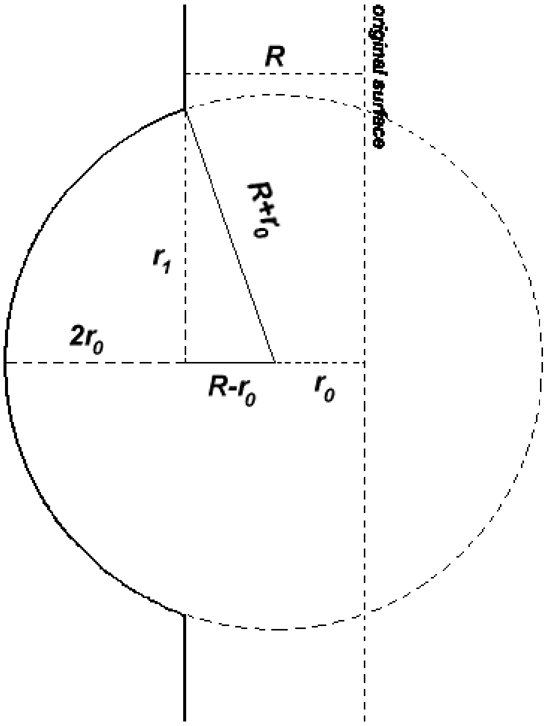
$r_1^2 = (R+r_0)^2 - (r_0-R)^2 = 4Rr_0$

Combining everything yields:

$\underline{A = 4\pi r_0^2}$

Geometrical considerations, air bubble just encountered

For $R > r_0$, the additional surface area may be determined in a similar fashion:



This time it is easier to calculate the area as the surface of the spherical cap to the left of the flame front minus the circular area in the planar surface:

$A = A_{cap} - A_{plan}$

$A_{cap} = 4\pi r_0(R+r_0)$

$A_{plan} = \pi r_1^2$

$r_1^2 = (R+r_0)^2 - (R-r_0)^2 = 4Rr_0$

Again, we end up with:

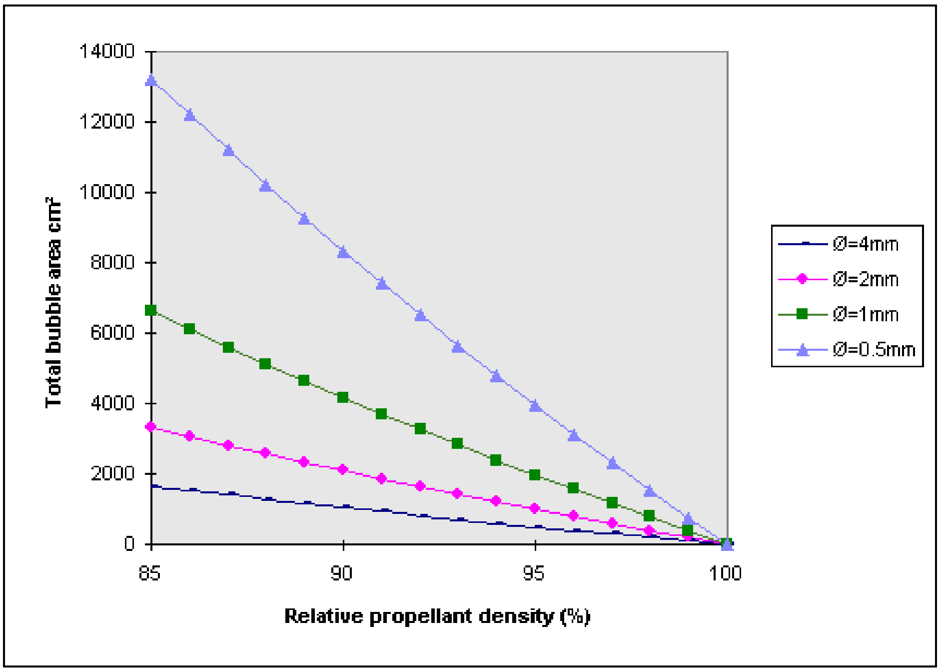
$\underline{A = 4\pi r_0^2}$

Geometrical considerations, air bubble almost consumed

This result is somewhat surpricing, as $4\pi r_0^2$ is exactly the surface area of the original bubble. The evolvement of the flame front looks dramatic, but the net contribution to the burning surface area of a small bubble of air remains constant, regardless of the regression length.

In the case of isolated air bubbles, the total surface contribution is the sum of the surface of all bubbles in the grain. There is also the effect of bubble size: It is easily shown, that dividing the air from one large bubble into N smaller makes the total bubble surface area increase by a factor of $N^{1/3}$. Also the surface area is inversely proportional to the bubble radius, so at a fixed density, even while the total surface does not increase as fast as the number of bubbles, it is still prefereable with a few large bubbles instead of many small.

As an example of the surface area that isolated air bubbles may create, the bubble area is calculated for bubbles of various diameters in a propellant segment of 1kg of propellant with a nominal density of $1.6 g/cm^3$ and with an actual density of 85-100% of the nominal density. As it can be seen, the diameter of the air bubbles is crucial for the total additional surface area, generated by the bubbles:



Total surface area of isolated air bubbles of different sizes

If the bubbles of trapped air can be considered as isolated, the total surface contribution from the trapped air is the sum of the surfaces of every bubble within the propellant. Is the bubble diameter small, the total surface may be alarmingly large, even at densities near the theoretical. In practice however, the bubbles are not really isolated. As the burning surface evolves, bubbles will collide tending to “eat” each other. Another effect is the final web thickness of the grain. When a bubble has grown to a sufficiently large diameter, it will hit the outer restriction of the grain. From that point it will evolve rather in a cylindrical fashion. Consider, for simplicity, that the air bubble is a cylinder of radius r_0 and length L. Such a cylinder will add $2\pi r_0 L$ to the total surface, while at the same time it will reduce the original surface with its cross section area πr_0^2. The resulting net surface contribution is then: $\pi r_0(2L- r_0)$. When $r_0 > 2L$, the net area contribution is negative. As the combustion process actually increases r_0 and decreases L it can be seen, that any bubble will start its “life” expanding spherically at a constant net surface contribution of $4\pi r_0^2$ until it at some point reaches the outer restriction of the grain and its net surface decreases – even getting negative.

All in all, this means that the bubbles lying near the initial burning surface will contribute to the burning surface with their nominal $4\pi r_0^2$, while bubbles lying deeper, to some extent will be “eaten up” by the expanding bubbles already “in play”. Furthermore, the bubbles near the outer restrictions of the grain, will have very little impact on the total burning surface.

Overview of the tests

Theoretical performance as calculated by means of *propep*, using "epoxy201" to represent the epoxy binder.

Designation	**Composition (by weight)**	**Calculated density (kg/m^3)**	**Calculated c* (m/s)**
KM0199	64% KNO3 26% Epoxy 5% Sulphur 5% Aluminium	1732.5	952.9
TM0299	64% KNO3 26% epoxy 5% Sulphur 5% Ammoniummolybdate		
TM0399	64% KNO3 26% epoxy 5% Sulphur 5% Ammoniumdichromate	1718.2	846.9
TM0499	64% KNO3 26% epoxy 5% Aluminium 5% Ammoniumdichromate	1736.9	961.7
TM0599	64% KNO3 26% epoxy 5% Aluminium 5% Ammoniumdichromate	1736.9	961.7
TM0699	65% KNO3 25% epoxy 5% Aluminium 5% Ammoniumdichromate	1749.8	968.1
TM0799	65% KNO3 25% epoxy 5% Aluminium 5% Ammoniumdichromate	1749.8	968.1
TM0899	65% KNO3 25% epoxy 5% Aluminium 5% Ammoniumdichromate	1749.8	968.1
TM0100	65% KNO3 25% epoxy 5% Aluminium 5% Sulfur	1745.3	958.7
TM0200	65% KNO3 25% epoxy 5% Aluminium 5% Sulfur	1745.3	958.7
FM0100	65% KNO3 25% epoxy 5% Aluminium 5% Sulfur	1745.3	958.7
FM0200	65% KNO3 25% epoxy 5% Aluminium 5% Sulfur	1745.3	958.7
TM0500	66% KNO3 27% epoxy	1711.0	889.5

	2% Aluminium 5% Sulfur		
TM0600	68% KNO3 27% epoxy 5% Sulfur	1706.7	854.7
TM0700	66% KNO3 27% epoxy 2% Aluminium 5% Sulfur	1711.0	889.5

Measured performance:

Designation	**Propellant weight (kg)**	**Estimated density (kg/m^3) & (% of predicted)**		**Estimated c* (m/s) & (% of predicted)**	
KM0199	0.58	1744	100.7	619.2	65.0
TM0299	0.60	1603	NA	745.0	NA
TM0399	0.60	1595	92.8	787.4	93.0
TM0499	0.59	1546	89.0	835.2	98.6
TM0599	0.59	1600	92.1	852.6	88.7
TM0699	0.59	1774	101.4	750.2	77.5
TM0799	0.59	1562	89.3	771.2	79.7
TM0899	0.59	1588	90.8	811.8	83.9
TM0100	0.80	1766	101.2	853.0	89.0
TM0200	0.94	1710	98.0	NA	NA
FM0100	3.77	1679	96.2	814.0	84.9
FM0200	3.80	1692	96.9	NA	NA
TM0500	0.76	1708	99.8	798	89.7
TM0600	0.54	1419	83.2	975	114.1
TM0700	0.82	1808	105.7	799	89.5