

PROPELLANT PROPERTIES

Propellants are intended to do work in a finite time. It is, therefore, with energy and burning speed that this topic is mainly concerned. The method of approach differs from that with high explosives, because the hydrodynamic theory, so useful in that case, is of little value with propellants. In view of the relative slowness of the process, the pressure of the propellant and the products can be considered equal, so that the transfer is effectively along a given line. Propellants, however, are always used in closed systems and the initial pressure (and final pressure) is no longer equal to atmospheric. Because deflagulation is defined only by the application of the propellant, the hydrodynamic theory gives no direct information. It does, however, tell us that the products of combustion stream backwards relative to the burning front and not forwards as in the case of a detonation wave.

The heat given out in the combustion of propellants is readily measured by exploding them in special calorimetric bombs built to withstand the high pressures produced. The result thus obtained, however, does not necessarily give exactly the heat available under practical circumstances, as in the calorimetric bomb the products are cooled and can undergo reactions which have different equilibrium at high and low temperatures. It is, therefore, usual for design purposes to obtain the calorimetric value of a propellant also by calculation.

The calculation of the heat liberated in the burning of the propellant can be carried out in a manner similar to that described for high explosives. The pressures encountered are, however much lower and correspondingly the gas densities also are lower. Simple equations of state are therefore adequate, and indeed for rocket propellants the combustion products are usually considered to behave as ideal gases. For gun propellants where the pressures are higher, the Abel equation of state is usually employed:

$$p(v-a) = RT$$

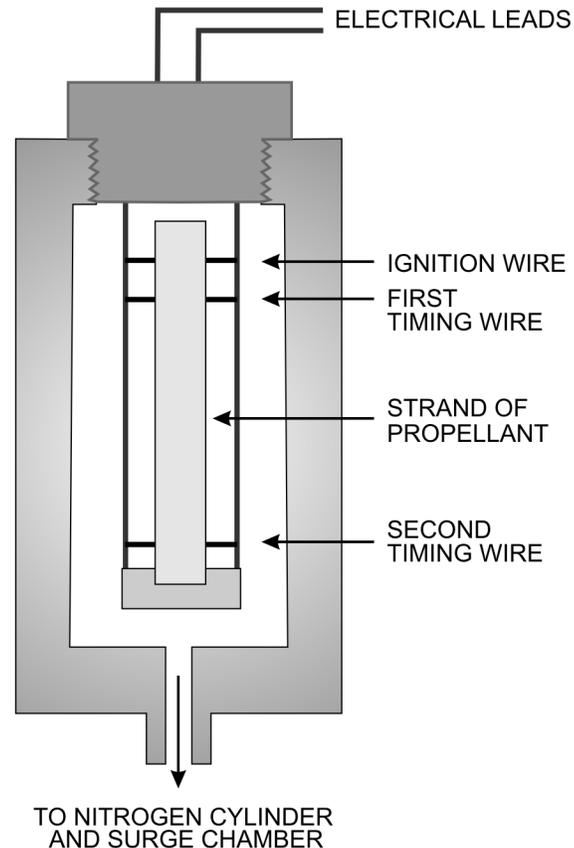
where a is a constant.

By constructing the Rankine-Hugoniot curve in the lower pressure region in this way, the volume, temperature and composition of the combustion gases can be calculated for various given operating pressures. In general the calculations must be carried out by successive approximation, but in the particular cases of single and double base compositions, simpler methods have been derived.

The other particularly important property of propellant explosives is their rate of burning. This cannot be calculated but must be measured. The measurements can be carried out in a number of ways, but the simplest is by the strand burner particularly used for rocket compositions. This is illustrated in diagram to the right. A strand of the propellant composition, commonly 1/8 " diameter and 6 to 7 in. long, is coated by a plastic so that

it can burn only from one end. This strand is held inside a bomb pressurized with nitrogen and allowed to burn. The rate of burning is measured by timing the interval between the melting of fuse wires resting on the strand. Tests are carried out at a number of pressures and the variation of burning rate with pressure is thus determined.

It is found that the rate of burning increases approximately linearly with the calorimetric value and lies in the range 0.15 to 0.5 in./sec at 1000 lb/in², although higher rates can be achieved.



This technique is much less suited to measuring the burning rates of propellants for use in rifles and guns. In these cases, it is not usually necessary to determine this rate accurately, but instead a measurement is made of the pressure developed in the actual use of the propellant. This is done by connecting a piezoelectric gauge to the chamber of a gun and recording the pressure change, during firing, by an oscilloscope.

The results of measurements made in these ways show that the rate of burning of a propellant depends markedly on the pressure. At the high pressures used in guns (perhaps 20 tons/in²) it is often sufficient to assume that the rate of burning, R , is directly proportional to the pressure, p . Rather more accurate results can be obtained by using a formula of the following type:

$$R = b + ap$$

where b and a are constants.

At lower pressures, such as are encountered in rockets and power cartridges, the relationship preferred is the exponential form:

$$R = ap^n$$

This is known as Vicille's Law. The exponent, n , is known as the pressure index of the propellant and is usually in the range 0.5 to 0.8.

Vicille's Law is obeyed well by the older types of single and double base propellants. Many of the more modern compositions do not obey this law. This is particularly true if the propellant contains a "platonising" agent, the purpose of which is to make the burning rate practically independent of pressure over a useful working region. Nevertheless, it is convenient to use the Vicille equation even if it can be regarded only as an approximation and used only over a limited range of pressure.

The rate of burning of a propellant is also influenced by the initial temperature of the charge. The effect is much less than the normal effect on chemical reactions, but can still be important when the material is to be used over a wide range of temperatures from arctic to tropical and those encountered in supersonic flight.

A characteristic of propellant burning is that it proceeds by layers with the burning front always parallel to the surface. This is known as Piobert's Law, and it is on this law that the design of propellant grains depends. If, for example, we consider a long solid cylinder of propellant, then as burning proceeds the cylinder remains of the same shape but with gradually reducing radius. It is clear that the surface area of the propellant gradually decreases so that the mass rate of burning of the propellant also decreases. This is obviously undesirable and many means of avoiding it have been designed.

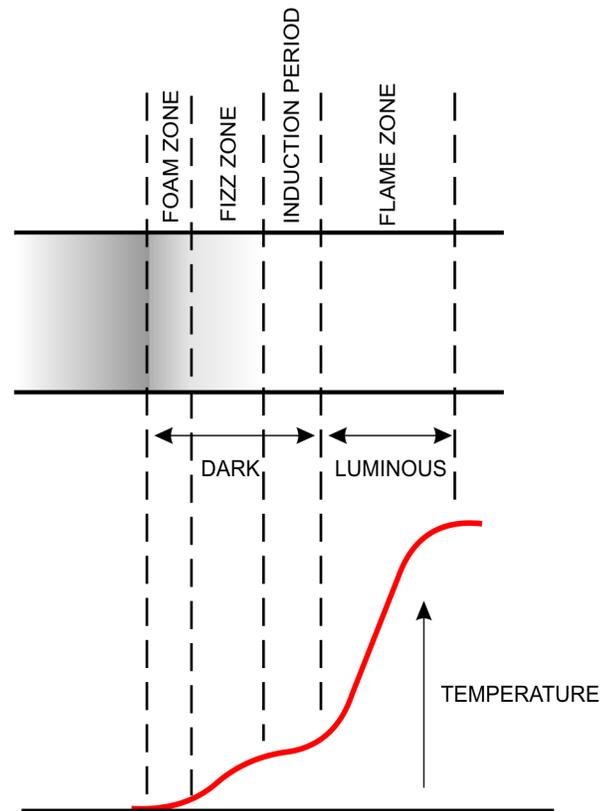
One common method of designing propellant grains is to use a long annulus. This can burn on both the interior and exterior surfaces, so that as burning proceeds the outer surface decreases, but the inner surface increases in such a way that the total surface and therefore mass burning speed remains constant.

For some purposes, it is indeed desirable that the rate of burning should increase during the process rather than remain constant. This is true in certain guns. For such purposes grains can be produced perforated by a number of holes so that the burning surface increases as combustion proceeds.

While the shape of a propellant grain determines the constancy or otherwise of the burning process, the actual time occupied depends on the grain dimensions. The shortest distance in a grain through which burning can go to completion is known as the web thickness. In a solid cylinder this is for example the radius, or in the case of a plate half the thickness (the plate can, of course, burn from both sides). For a rifle propellant, which must burn very rapidly, the web thickness is small and may even be as little as one-hundredth of an inch. On the other hand, for the largest rockets with long periods of burning, the web thickness may be several feet.

The actual process of burning of single and double base propellants has been studied in some detail and shown to consist of a number of stages, as shown to the right. The succession of stages is as follows.

Solid propellant is first caused by radiation and convection to melt and evolve sufficient gas to give a foamy structure. This is known as the foam zone. The gaseous products from this zone pass through the fizz zone where an initial reaction occurs. These intermediate products enter the flame zone where after a brief induction period they undergo the final reaction to the combustion products. It is only in this final reaction that there is any luminosity, so that the fizz zone and the initial stages of the flame zone are in fact dark. The actual thickness of this dark zone depends on the pressure under which the propellant is burning. Below 200 lb/in² the flame zone does not exist. When the pressure increases the dark zone decreases in thickness until at 1000 lb/in² it can no longer be observed. These changes explain well the marked dependence of burning rate on pressure.



The burning mechanism of composite propellants differs from that described above. There is no exothermic reaction which can lead to a self-sustaining fizz zone. Instead, the first process appears to be the softening and breakdown of the organic binder/fuel which surrounds the ammonium perchlorate particles. Particles of propellant become detached and enter the flame. The binder is pyrolysed and the ammonium perchlorate broken down, initially to ammonia and perchloric acid. The main chemical reaction is thus in the gas phase, between the initial dissociation products.

The stability of propellants from both the chemical and physical points of view is of considerable importance, because they frequently have to be stored for many years under adverse conditions of temperature. Minor changes, such as could well be tolerated with high explosives, cannot be allowed with propellants because they would seriously affect the performance of the gun or other weapon. Accelerated storage tests, usually involving cycling between the extremes of temperatures likely to be encountered, are used to determine the long term stability of products. In the case of

large grains, such as those used in rockets, physical strength and stability can be of great importance. Thus it is usual to determine tensile strength and elongation under both static and dynamic conditions. Even more important is the examination of the grain for tendency to crack under conditions of varied temperature.

Many methods have been proposed and are used to study the thermal stability of propellants and to ensure the absence of possible autocatalysed decompositions during storage. None are sufficiently reliable to merit individual description. In practice, stabilizers are added, the usual being diphenylamine for nitrocellulose powders and symmetrical diethyl diphenyl urea (carbamate or centralite) for double base propellants. Provided a reasonable proportion of stabilizer remains, the propellant can be assumed to be free from the possibility of autocatalytic decomposition. The best test of stability is therefore a chemical determination of the stabilizer present.