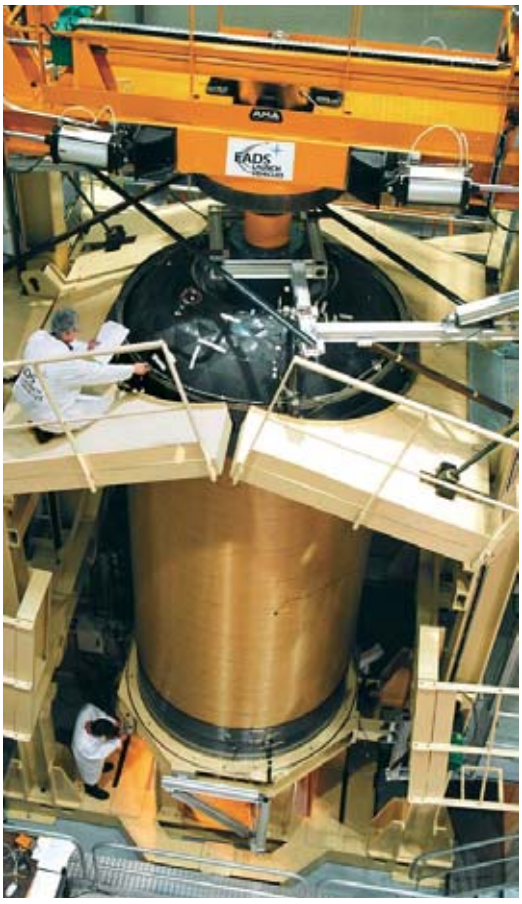
Energetic nanomaterials: towards technological breakthrough

Nanostructuring energetic materials opens up possibilities for improving both reactivity and energy performance levels in explosives, propellants and rocket propellants.



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Pressure test on a missile stage in wound carbon fibre. Solid propulsion for missiles or space launchers is one of the flagship applications of nanostructured composites.

A proven track record in nuclear weapons

The CEA's Military Applications Division (the DAM) has been designing, developing and manufacturing pyrotechnics subsystems (chemical explosives) for the warheads making up France's nuclear deterrent capability for over forty years. The principal objective of the DAM's explosives development activities has always been to combine the highest possible efficiency (performance), safety and security throughout a weapon's lifetime and in the most extreme environmental conditions. These criteria cannot be fully satisfied by the industrial sector of conventional arms development, which is why the DAM performs specific research in this field.

Over the last two years, in order to continue advances towards new, more powerful and safer energetic materials, the DAM has teamed up with the French Ministry of Defence procurement agency (the DGA) and the **SME** (SNPE Energetic Materials) on upstream research in nanostructured energetic composites.

Conventional solid explosives (TNT, Octogene, Hexogene(2), and others) have only limited performance (particularly detonation energy(3)) due to intrinsic features related to their **molecular** structure, which is made up of the juxtaposition of **oxidizer** groups (the *combustive* part of the molecule) and **reduction** groups (the *fuel* part). Recent decades have seen many research efforts attempting to gain access to more powerful molecules often run up against major barriers, either in the synthesis or in the extreme explosive sensitivity of the products obtained.

Other ways for obtaining energetic materials have been widely explored by formulation routes using "simple" base materials. Combining oxidizer powders (potassium or ammonium nitrate, perchlorates, etc.) with fuel powders (carbon, sulphur, hydro-

The development of molecular engineering and **nanostructuring** technologies has paved the way for the development of energetic composites (explosives, propellants(1)) with increased overall energy and reactivity, while maintaining or even improving safety. The applications targeted are essentially solid propellants for missiles or space launchers, enabling larger masses to be taken on board, or the same mass but in smaller vehicle. In other words, improving efficiency and service for a given mass of energetic material. The CEA has undertaken pioneering research initiatives to design and develop these materials and assess the enhancements achieved with a view to extending them to industry.

(1) Propellant: product containing one or more oxidizers (*combustives*, often oxygen, or *fuels* whose combustion, *i.e.* reaction with the combustive, produces the energy to be used) in order to form a composite or compound able to generate the propellant energy of a rocket motor.

(2) TNT, Hexogene, Octogene: powerful high explosives. The full chemical names are trinitrotoluene, cyclotrimethylene-trinitramine (or RDX) and cyclotetramethylene-tetranitramine (or HMX), respectively.

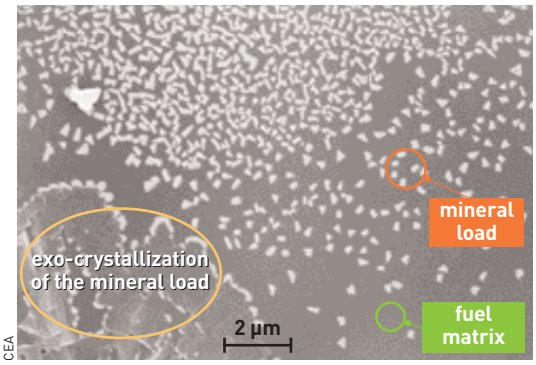
(3) detonation: the result of an extremely rapid chemical reaction accompanied by a shock-wave that spreads outwards, and a strong and extremely fast change in pressure. Not to be confused with *deflagration*, which is a rapid combustion in which oxygen is taken from the air and the "explosive material" only supplies carbon and hydrogen. *Detonics* is the science of how explosives work, and how detonated materials behave.

carbons, etc.) in a tightly-knit blend can thus lead to high-potential energetic composites. The simplest example is also the oldest: gunpowder, a mixture of potassium nitrate, sulphur and charcoal.
The potential interest in this type of material stems from the fact that it is relatively easy to prepare, and its performance can be "adjusted" as a function of its **stoichiometry** (the respective ratios of the various chemical ingredients). However, one major problem persists: the size of its elementary particles. Indeed, in this type of energetic compound, the combustion reaction between oxidizer and fuel particles is kinetically limited by the **granulometry** (on a micrometre scale at least) of its ingredients, even when the powders are perfectly blended. Thus, the species diffusion kinetics enabling the reaction are too slow for the propagation speed of the *deflagration* or *detonation* (from a few metres to several kilometres per second) within the material. The release of energy in the material is therefore either incomplete, or too slow (Box 1).

A multidisciplinary approach

Recent major research progress on nanostructuring composite materials has enabled researchers to deploy production processes for this kind of energetic material. The CEA itself is not directly involved in exploring the synthesis pathways of oxidizer, fuel or even explosive nanopowders, as this work is essentially carried out by SME. However, the DAM is involved in the final development of nanocomposites (oxidizer/fuel mixtures) in which each phase occurs at typically sub-micrometric scale, through a multidisciplinary approach harnessing the efforts of four major operations.
First, the molecular and reactive modelling phase, is to predict the behaviour of these materials on impact and as they break down, and to optimize them before the experimental stages. The second phase is to develop and set up processes for formulating nanocomposites. Phase three involves characterization by various methods (**electron** and **atomic force microscopy**, **X-ray diffraction**, differential scanning colorimetry[4], etc.). The fourth and final phase is to design and run micro-detonic tests. This involves determining the energetic performances of these new materials using only very small quantities of what is available. The main route for nanocomposite development being studied at the Explosives Department of the Le Ripault CEA centre in the Indre-et-Loire consists in the controlled and adjustable - in terms of oxidizer/fuel ratio and, as a result, overall perfor-

(4) DSC (Differential Scanning Calorimetry): method comparing sample response to reference response when both are subjected to the same heat flow rate. Typically used to study the thermal properties of a material (specific heat capacity, temperature and fusion energy, etc.) or the macroscopic structure of proteins.



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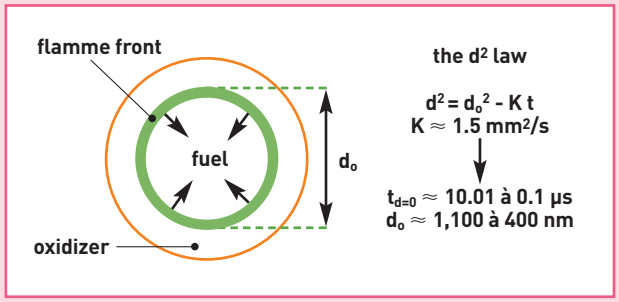
Scanning electron microscope showing the dispersion of a nanostructured mineral charge in a fuel matrix.

How to beat "slow combustion" 1

In order to take control of diffusion phenomena within an energetic material which limit or slow combustion and exert a negative influence on the initiation of the material, it is first necessary to measure the characteristic sizes of the particles involved. Simple, intuitive reasoning can estimate the scale of the particle size below which diffusion processes become negligible. To do this, we imagine that a spherical fuel particle enveloped in an oxidizer film burns like a hydrocarbon droplet, i.e. according to the so-called d^2 law. This law states that the diametre of the particle regresses linearly over time ($d^2 = do^2 - K\,t$ with $K \approx 1.5$ mm^2/s, the combustion constant). Hence, particles starting out with a diametre of 100 to 400 nm would be consumed very quickly, within 0.01 to 0.1 µs, i.e. in a sufficiently short time (given that a typical detonation time is of the order of a microsecond) to trigger the total release of the energy initially stored in the material. If this was not the case, there would still be non-reacted material after the combustion/detonation front, and therefore an overall energy deficit in the material. This is one of the reasons why current research is directed at designing **nanostructured** multicomponent materials. Another reason, though, is the potential influence this nanostructuring may have on the reactivity (initiation capacity, sensitivity) of the material. Imagine that mass diffusion processes are indeed negligible for materials made of particles typically around 100 nm in size and containing residual nanopores (due to defects in the material) that are ten times smaller. In this case, the initiation



The d^2 law.

(by heat) of this kind of composite according to a mechanism forming hot points in the pores (the most commonly accepted principle) would appear highly unlikely. Indeed, preliminary calculations factoring in a viscoplastic collapse of the pores indicate that the initiation pressures involved in this scenario are very high, at around several hundred kilobars! At this kind of pressure level, the temperature of the solid material would be enough to induce a volume breakdown. This supposed initiation phenomenology approach will need to be supported by experimental data.

Micro-detonic testing 2

The first nanostructured energetic materials are available in very low quantities (around 1 gram). To demonstrate their enhanced energetic properties, a great deal of thought needs to be applied to the temporally and spatially-resolved diagnostics to be developed, and the initiation triggers to be deployed. It is also necessary to obtain a maximum of quantitative data per trial, preferring to target the multidiagnostic aspect of metrology. Finally, scale-induced effects due to the reduced geometries (transient effects, critical diametre[1]) also have to be taken into account. *Micro-detonic testing* was designed to meet these new needs. An optical multipoint chronometry probe developed at CEA Le Ripault is used to measure the passage of the detonation wave through an explosive cylinder a few millimetres wide (Figure 1). This micro-diagnostic approach has the advantage of simplifying the data acquisition chain while maintaining measurement accuracy at levels comparable to conventional multiprobe diagnostics, which require a large sample mass (Figure 2).

(1) Dimensions above which a reactive effect no longer propagates through the material.

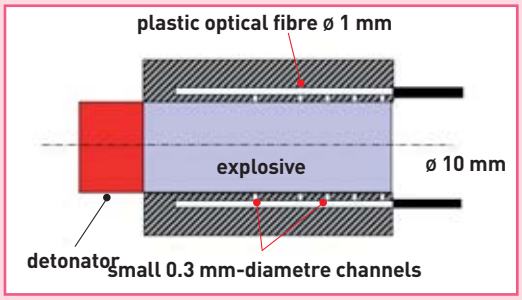


Figure 1.
Multipoint fiberoptic micro-device for measuring detonation speed.

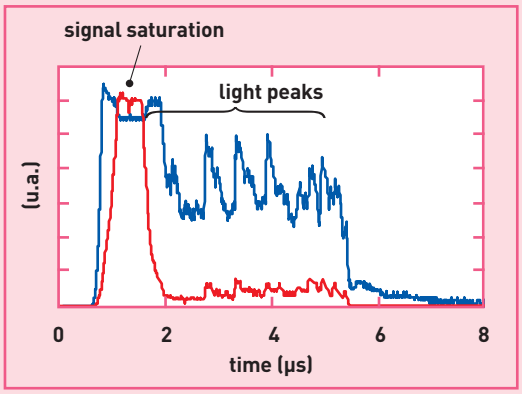


Figure 2.
Opto-electric conversion signal obtained during a detonation followed by a multipoint optical fiber in a micro-device.
(A.U = arbitrary units)

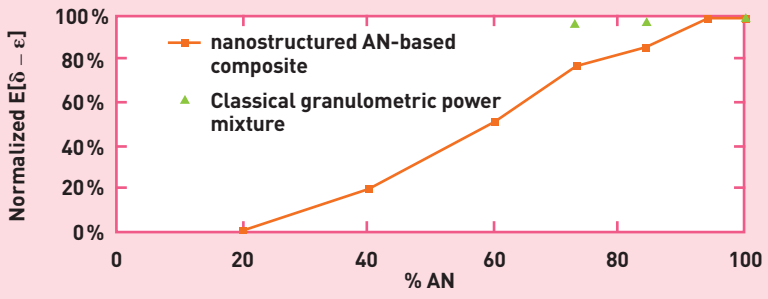
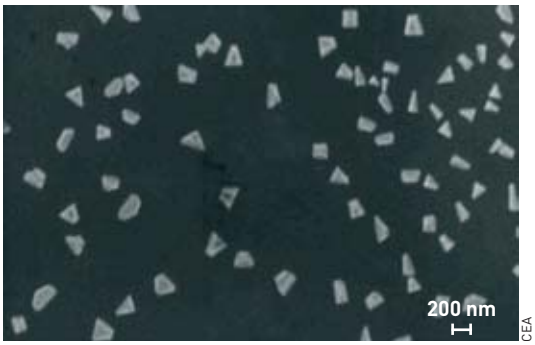


Figure.
Normalized energy difference for the delta-epsilon ($\delta \rightarrow \varepsilon$) transition of ammonium nitrate (AN) as a function of AN content: comparison between a nanostructured composite and a powder mixture by conventional granulometry.
In a nanometre-scale particle, the proportion of atoms, molecules and ions present on the crystal surface is significantly higher than for a micrometre-scale particle. The cohesive forces of the solid are therefore weaker overall, which leads to a significant fall in melting temperature or changes in allotropic form.



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Scanning electron microscope micrograph of a nanostructured mineral load.

mance - incorporation of an oxidizer load in a fuel matrix, or *vice versa*. The processes deployed, which are either under patent application or in publication, will not be described here. Generically speaking, the principle is to develop powders or solid-state materials in which the oxidizer and fuel phases are separated, have homogeneous typical dimensions, and are isotropic to the order of a few tens to hundreds of nanometres[5]. This type of nanocomposite has already given some promising results, such as dispersion in a fuel matrix of mineral loads characteristically lower than or equal to 200 nm, or a decrease – typical of nanoparticles – in the energy, as measured by differential scanning calorimetry, of the allotropic transition[6] $\delta \rightarrow \varepsilon$ of ammonium nitrate nanostructured into a fuel matrix polymer (Figure).

Models with explanatory power

Studies are in progress to characterize the sensitivity and performance of the nanostructured materials thus obtained. These experimental data will go on to be used as a database for developing and validating the behavioural models engineered at Le Ripault for these new molecular systems. Then, as with the DAM developments in the field of conventional solid explosives, these same models will be able to gain explanatory power and therefore direct synthesis and formula research efforts towards better materials for each particular application and its specifications.

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(5), One way of obtaining this, partially described in the scientific literature and which the CEA is working on by developing a novel concept, consists in using the sol-gel pathway to engineer mesoporous fuel materials in which the volume of nanopores is filled with crystallized oxidizer. This gives a perfectly homogeneous material organized at sub-micron scale.

(6) Allotropic transition: change in the crystalline structure of a material (which keeps its chemical properties) at a given temperature.

F How do we see or "feel" the nanoworld?

To find something out about an object we have to approach it in some way and obtain information from it. The methods we can use may be grouped into three families: (i) methods that study a signal that is naturally or artificially emitted by an object, (ii) methods that send a signal to it and study the signal it re-emits, and (iii) methods that use direct contact with the object to measure a force of interaction between it and a probe.

Detecting signals emitted by the object

We can see the stars without having to interact with them. Large structures can naturally emit signals that are strong enough to be detected far away. The emissions from nano-objects are generally so weak they are smothered by the signals of neighbouring objects. There are two ways to get round this: we can (i) isolate the nano-object to make sure the emitted signal really originates there and nowhere else (e.g., isolation of atoms with a laser beam or of certain nanostructures on etched nanodots to study their luminescence), or (ii) position the detector close to the object. However, most nano-objects are not radioactive or naturally phosphorescent, and so they have to be stimulated in some way to emit a signal. *The Tomographic Atom Probe* is a powerful technique that analyses a particular signal (for more details see http://www.cameca.fr/html/tap_technique.html). A short, intense electric pulse is used to strip **atoms**, layer by layer, from an object that has been shaped to a fine point. The atomic mass of the stripped atoms can be determined by mass spectrometry, and the three-dimensional atomic structure can be reconstructed layer by layer. Unfortunately, this method requires a conducting object and a perfect radius of curvature, and not all nano-objects can be given this shape. In **scanning tunnelling microscopy (STM)**, a very fine point is brought near the surface of the object and strips **electrons** locally.

Using a probe signal

This is the "classical" approach used by all **conventional microscopy**. A probe is brought to the object and the re-emission (reflection or transmission) of the incident signal is used to characterize the object. Depending on the type of probe used (visible light, X-rays, electrons, ions, ultrasound), we have **optical, Raman, X-ray, electron, ion or acoustic microscopy**. Here, the **resolution** attained by the method is determined by the wavelength associated with the probe signal. A strong interaction between the probe and the object is necessary to obtain an image of a small lone object.

Pseudocontact or interaction force

This is the "groping in the dark" method. A probe is brought near the object until a force of interaction, or "pseudocontact" is established. The information is obtained by scanning the surface of the object and observing how the force acting on the probe varies. To obtain highly local spatial information the contact probe must be very small. This method generally yields information only about the surface, but it is a fascinating technique and one of the few that can manipulate atoms *individually*! *Atomic force* microscopy (**AFM**) and *magnetic force* microscopy (**MFM**) belong to this family.