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How Smokeless Powder Deteriorates

How nitrocellulose is made

Smokeless gunpowder (propellant) is made from nitrocellulose (NC). Nitrocellulose is made by nitrating[1] high quality cotton linters in nitric acid.

The cotton fibers are made up of glucose molecules;

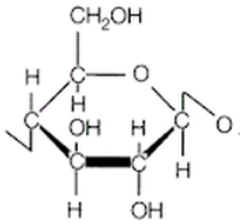

Figure 1- Glucose monomer

Glucose combines to form cellobiose molecules, which combine to form cellulose;

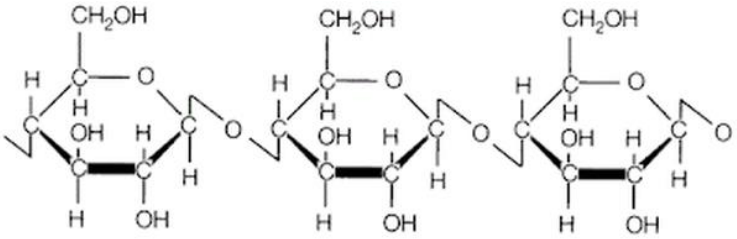

Figure 2- Glucose repeats forming cellulose

The cotton linters (cellulose) are soaked in a mixture of sulfuric and nitric acids[2], causing nitration (actually esterification)[1]

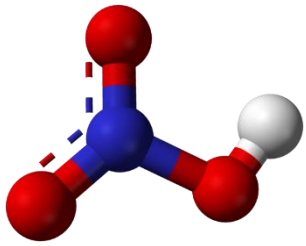

Figure 3 – Nitric acid

Red = Oxygen Blue = Nitrogen White = Hydrogen

The oxygen-hydrogen bond of the nitric acid molecule (the connected red and white balls) is important, as we shall see.

In the process of nitration some of the hydroxyl groups (-OH) of the cellulose are replaced with nitro groups (-NO2);

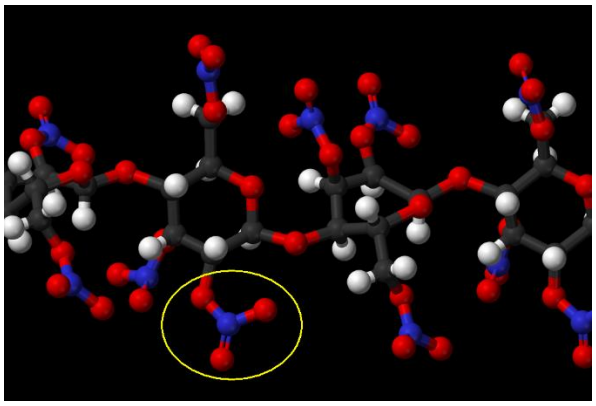

Figure 4-OH has been replaced by a -NO2 nitro group (multiple places)

The resulting nitrocellulose has one, two or three nitrate ester groups where the groups are attached to the carbon atom of the original glucose hydroxyl group (OH) molecule via an oxygen atom. (See Degree of Substitution below) This means that nitrocellulose (and nitroglycerin) are not true nitro compounds, but nitrogen esters. The more hydroxyl groups replaced, the higher the nitrogen content.

Only concentrations above 12% are used in energetics (propellants)

1 group replaced	Cellulose mononitrate	$C_{12}H_{19}(NO_2)O_{10}$	mononitrocellulose	6.76 %
2 groups replaced	Cellulose dinitrate	$C_{17}H_{18}(NO)_6O_{10}$	dinitrocellulose	11.11 %
3 groups replaced	Cellulose trinitrate	$C_{31}H_{17}(NO_3)SO_{10}$	trinitrocellulose	14.14 %

Figure 5 Nitrocellulose (cellulose trinitrate)

Why does this matter?

Nitrated cellulose has an oxygen atom between the carbon of the glucose and the substituted ester groups (C-O-NO2).

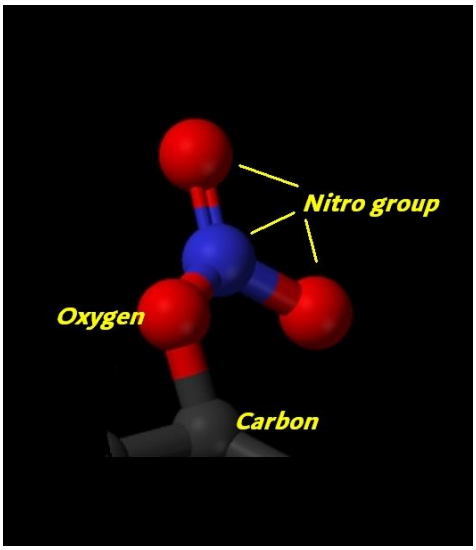

Figure 6 - Nitrocellulose is a nitrogen ester

Nitro compounds, on the other hand, have nitro groups (-NO2) directly bonded to carbon atoms.

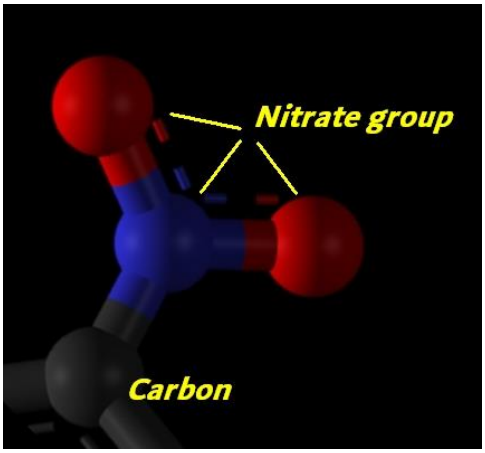

Figure 7 - Detail of TNT, a true nitro compound

Energetics with an activation energy of decomposition higher than 170 kJ/mol are stable for thousands of years at room
temperature, whereas for values below 155 kJ/mol, chemical stability is limited.

Nitrocellulose is inherently unstable because the C-O-NO2 bond (figure 5) has a low activation energy – 72 to 157 kJ/mol.
Conversely, the C–O-NO2 bond of nitro compounds such as TNT and nitroethane is stable around 238 kJ / mol

Activation energy of nitrocellulose

The activation energy of nitrocellulose by itself is in the range of 72 to 157 kJ/mol depending on the Degree of Substitution (DS). DS is determined by how many of the 3 glucose repeats are fully substituted or esterified. The cellulose backbone has 3 hydroxyl groups that can be replaced with nitrate esters, so the maximum DS is 3.0. When all three positions are replaced, the substance contains 14.1% nitrogen. This is the maximum possible. In practice, cellulose is nitrated to a maximum degree of substitution (DS) of about 2.6 – 2.9 so all glucose repeats are not fully esterified. This is a function of the process used, and the quality of the raw materials used. Cotton linters, being a natural product, has variations in quality, even among the highest grades. There is active research in developing synthetic cellulose fibers to increase the quality of NC closer to the ideal 3.0 DS.

The higher the degree of substitution, the higher the nitrogen content, the higher the activation energy, and thus the higher the stability of the propellant.

High quality raw materials, exacting processes, and careful attention to details and quality make a big difference in the performance and longevity of nitrocellulose propellants.

Nitrocellulose degradation

Nitrocellulose, and the propellants made from it, are inherently unstable because of the weak O-NO2 bond discussed above. The cleavage of this bond is a homolytic process (occurs by itself) and a basic law of nature. It can't be prevented. This homolytic reaction creates nitrogen radicals that then attack the remaining bonds. This occurs via 2 pathways – a thermolytic process that accelerates with increased temperature, and a hydrolytic process that is dependent on the presence of moisture.

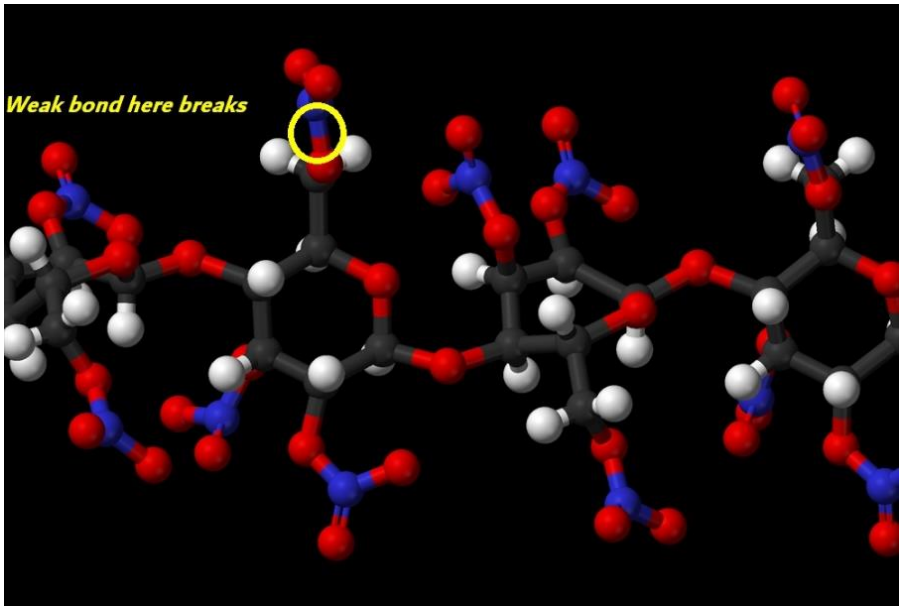

Figure 8 Weak CO-NO2 bond

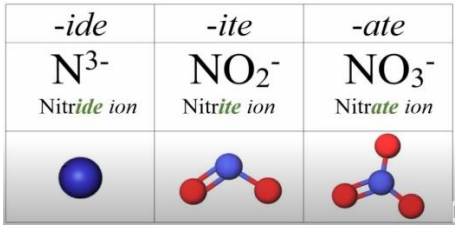

Figure 9 The degradation of cellulose nitrate creates nitrogen radicals, primarily NO2, but also others including nitric oxide

Propellant stabilizers

Smokeless propellant manufacturers add stabilizers to absorb the free radicals, a common one being Diphenylamine (DPA), an ammonia derivative in which two of the hydrogens have been replaced by phenyl groups. DPA can undergo nitration by absorbing the NO2 radicals, transforming into a series of compounds;

N-nitrosodiphenylamine
2-nitrodiphenylamine
4-nitrodiphenylamine
N-nitroso-2-nitrodiphenylamine
N-nitroso-4-nitrodiphenylamine
4,4', 2,4', 2,2', and 2,4-dinitrodiphenylamines
N-nitroso-4, 4'-dinitrodiphenylamine
N-nitroso-2, 4'-dinitrodiphenylamine
2, 4, 4' and 2, 2', 4-trinitrodiphenylamines
2,2', 4,4'-tetranitrodiphenylamine
0 2,2', 4,4', 6-pentanitrodiphenylamine
Hexanitrodiphenylamine

Once all the DPA is converted to the hexamine there is nothing to trap nitrogen oxides, and the propellant undergoes rapid degradation. Other stabilizers are commonly used as well. All have similar decay chains, albeit with different intermediate decay products. For a list of additives and their properties, see our Propellent Additives entry

This is why we see anecdotal cases of powder lasting many years, then seemingly goes bad overnight

The role of nitroglycerin

Single base powders are made of nitrocellulose and various additives. Double base powders also contain nitroglycerin (NG). The presence of nitroglycerin, while improving the performance of the propellant, greatly decreases the longevity because nitroglycerin has a very low activation energy of 71 kJ / mol - even lower than lower grades of nitrocellulose and far below the level that is subject to homolytic degradation. Studies done by Nitrochemie have shown that single base powders have a safe lifespan 4 to 8 times longer than double base.

What to do about it?

For information about what to do to get the best performance and longevity from nitrocellulose propellants see our article

How Long Do Propellants Last?

[1] Neither nitrocellulose nor nitroglycerin are true nitro compounds, they are nitrate esters. The manufacture of both compounds is accomplished via nitrooxylation rather than nitration. However, the use of 'nitrate' and 'nitration' is commonly used and accepted in the scientific literature and commercial trade.

[2] Sulfuric acid acts as a catalyst in the nitration of cellulose by capturing the hydrogen atom and forming water. It is not consumed, unlike the nitric acid, and can be dewatered and reused.

> In 1845 Christian Friedrich Schönbein first synthesized cellulose nitrate and believing it to be a nitro compound instead of an ester of nitric acid, mistakenly called it nitrocellulose. The name stuck.

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