

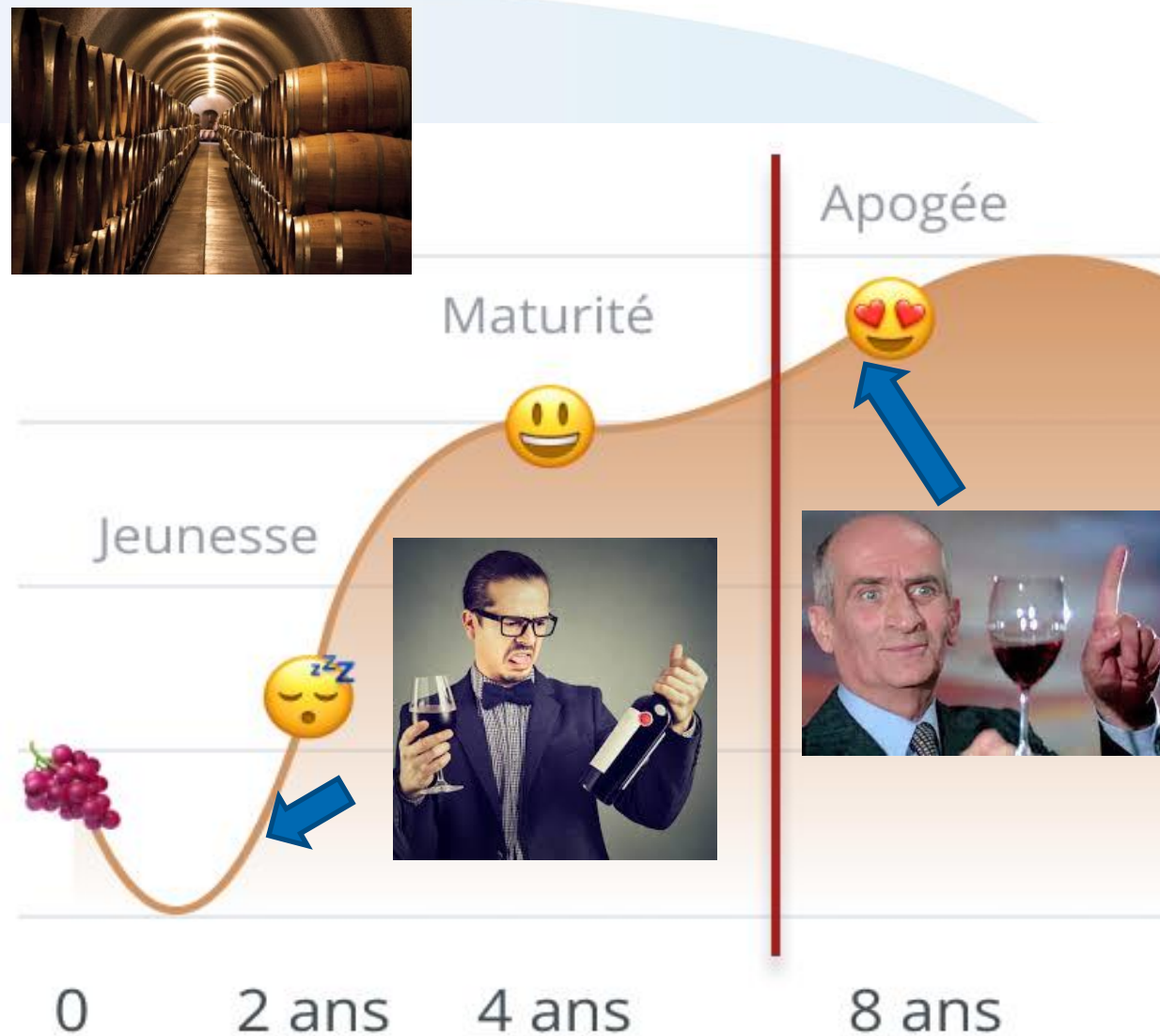
Ageing in pyrotechnic products : approach and methods

15th October 2025
Florian Foucoin, R&D Chemical Engineer



LACROIX

Introduction



Factors influencing the ageing of wine:

- 1) Raw materials: grape varieties, terroir...
- 2) Winemaking methods: oak barrels, stainless-steel tanks...
- 3) Storage conditions: temperature, humidity, light exposure...

« A pyrotechnic composition is like a good wine – it keeps well...
...unless you leave it open on the table»

« A pyrotechnic composition is like a good wine – it keeps well...
...unless you leave it open on the table»



Analyses d'une poudre noire VINTAGE de 1863 retrouvée en 1972 :

- Appearance: practically identical to a recent high-quality powder (same grain size, density, color)
- • Performance: comparable to current high-grade black powder
 - Ballistic tests: equivalent muzzle velocities;
- Only significant difference: vivacity ~35% slower

Factors influencing the ageing of pyrotechnic compositions:

- 1) Raw materials
- 2) Manufacturing process
- 3) Storage conditions: temperature, humidity, light exposure

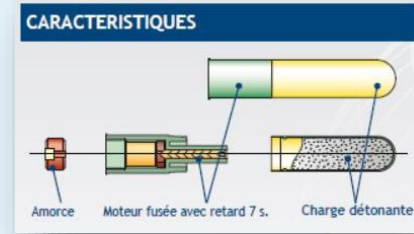
K. L. & B. J. Kosanke* and F. Ryan, "Performance Study of Civil War Vintage Black Powder", *Journal of Pyrotechnics*, No. 9, 1999.

Pyrotechnic Compositions - LACROIX

Lacroix develops and manufactures a wide range of pyrotechnic products, from ignition systems to terminal effects:



Pyrotechnic delays



Propulsion (motors...)



Illuminants
(IR flares, signals...)



Smoke
(colored, obscurant...)



Sound effects
(CAPA...)



Thermites (séparateurs pyro...)

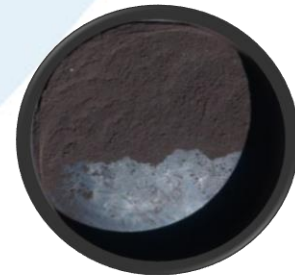
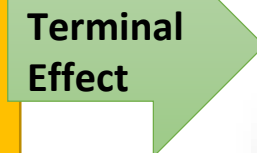
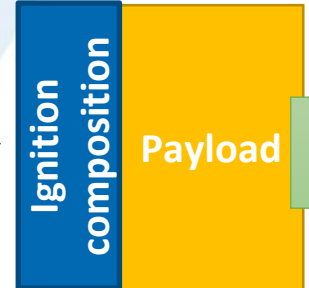
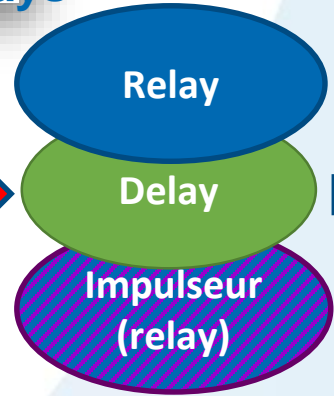


Gaz generation
(cable cutters...)

Initiator



Amorçage
(SQUIB...)



Ignition ($BKNO_3$...)



Ageing of Pyrotechnic Compositions

Pyrotechnic Compositions: heterogeneous oxidizer–fuel mixture whose decomposition is mainly combustion.



Oxidizer

- ▶ Nitrates : KNO_3 , NaNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$
- ▶ Perchlorates : KClO_4 , NH_4ClO_4 ...
- ▶ Chlorates : KClO_3 ...
- ▶ Chromates : BaCrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$...
- ▶ Carbonates : Na_2CO_3 , NaHCO_3 , BaCO_3 ...
- ▶ Oxalates : $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
- ▶ Oxides : Fe_3O_4 , SiO_2 , TiO_2 ...
- ▶ halogenated compounds: PTFE...

Binder

- ▶ Polyurethane resins, epoxies, polyesters...
- ▶ Linseed oil, gum arabic, nitrocellulose...
- ▶ Other polymers: Viton...

Reducer



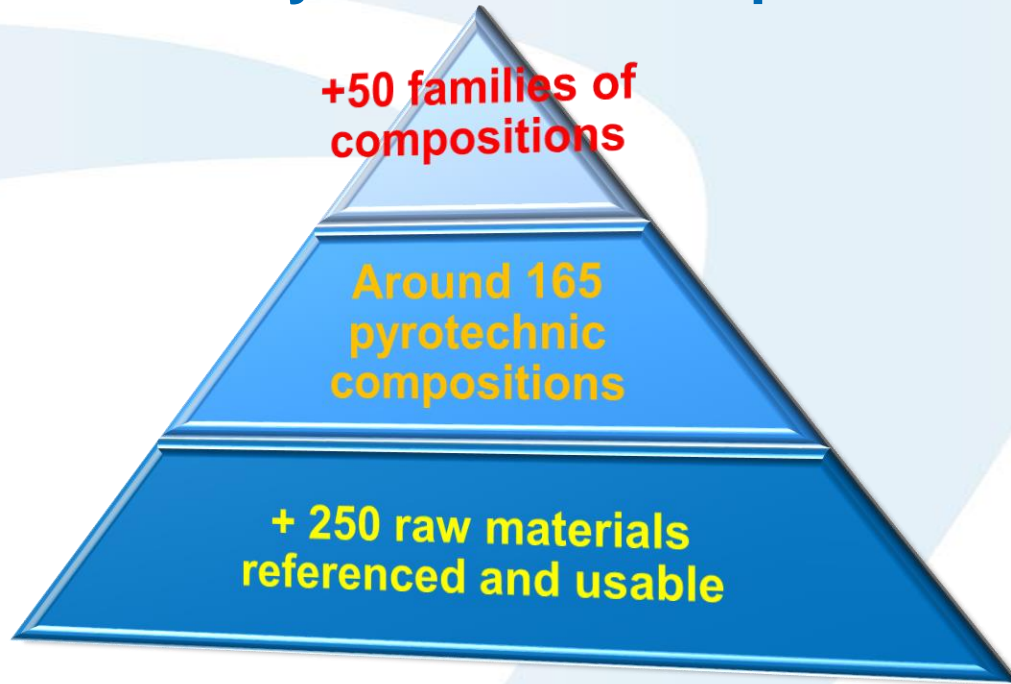
- ▶ Métaux: Mg, Al, Zr, W..
- ▶ Métalloïds : B, Si, P...
- ▶ Organics: lactose, fructose...
- ▶ Carbon : coal, graphite...

Additives

- ▶ Flame coloring agents: metallic salts...
- ▶ Smoke generators: dyes, ATP, carbon generators...
- ▶ Effect intensifiers: Cl, color enhancers, illuminators..
- ▶ Combustion accelerators: ferrocene...
- ▶ Retarders: SiO_2 , talc...
- ▶ Flame attenuators: sodium bicarbonate...
- ▶ Stabilizers: DPA, centralite, etc.

Effect

Lacroix Pyrotechnic Compositions in Numbers:



41 energetic materials are currently homologated 17500 with **12 new formulations in the last 15 years** :

- Formulations depending on application: mass %, raw materials...
- Various manufacturing processes: mechanical or manual, planetary or vacuum mixing, granulation, calibration...
- Different shaping methods: loose powder, pressing, casting...

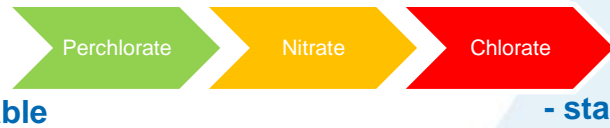
All combinations of materials, formulations and processes require vigilance regarding ageing and stability of us pyrotechnic compositions from the early design phase to ensure safety and reliability throughout the product lifetime

Ageing of Pyrotechnic Compositions

Main Ageing Mechanisms

Oxidizer

3) Reduction or degradation of oxidizers due to humidity, impurities, acidity, temperature BUT relatively stable => Non-limiting ageing factor



Binder

2) Decomposition of organic binders and polymer matrix

- Thermal oxidation: chain scission...
- Hydrolysis : deformation / dilatation...
- Thermal shocks: cracking due to expansion...
- ...

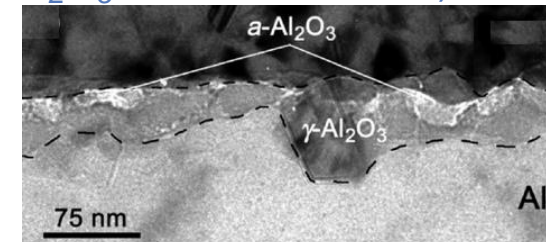
Reducer

1) Oxidation of reducers:

- Hydrolysis



- Air oxidation (ex : Al_2O_3 barrier formation)



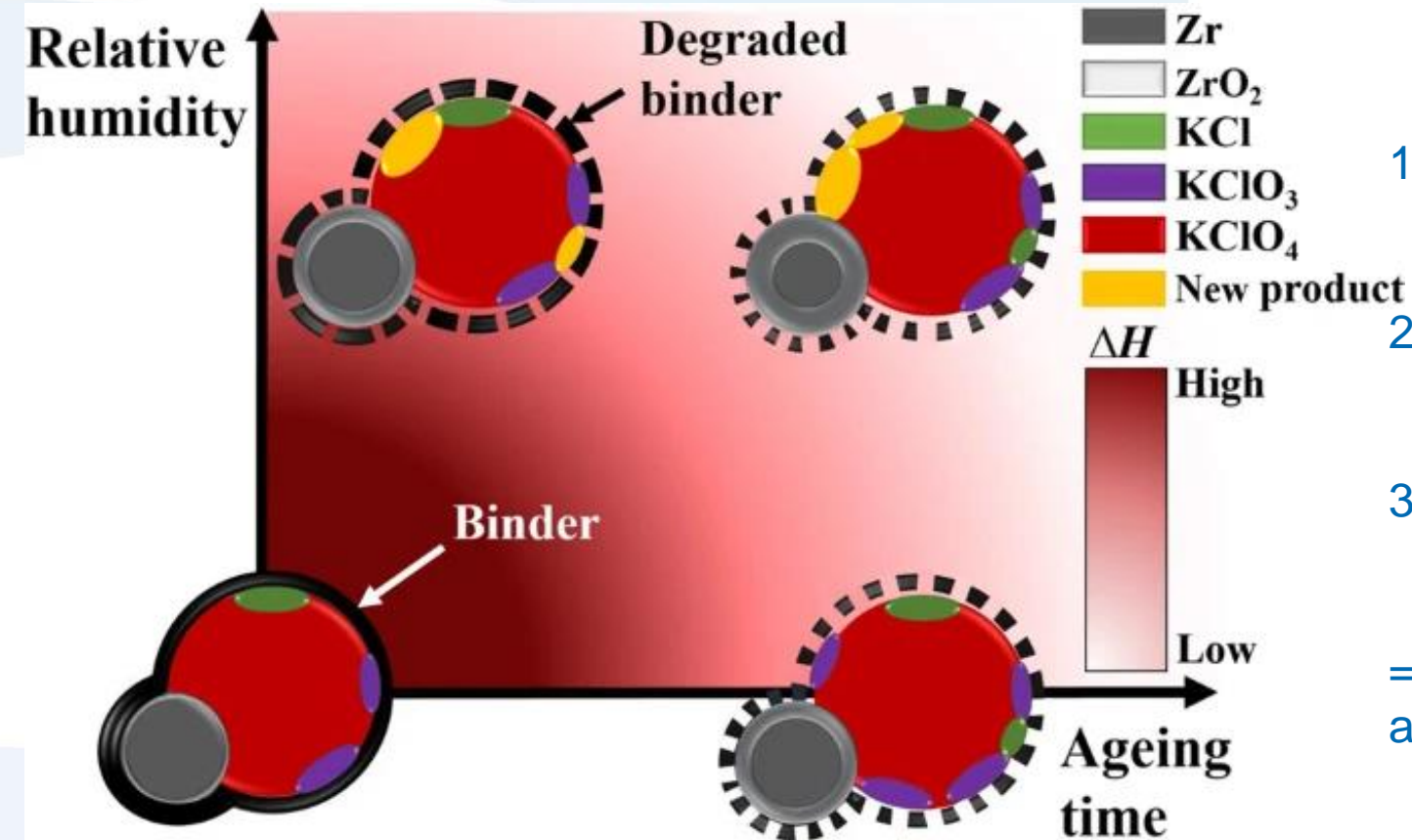
- Galvanic effects
 - Chemical incompatibilities
- } processed upstream during design

Additives

4) Oxidation, degradation, or migration depending on additive nature

Ageing of Pyrotechnic Compositions

Illustration of Ageing of a ZPP Composition under Humidity



- 1) Binder degradation over time and humidity → protective layer becomes porous
 - 2) ⊕ binder degrades, ⊕ Zr and KClO₄ are exposed to humidity
 - 3) Leads to Zr oxidation into ZrO₂ and KClO₄ decomposition
- => Performance ZPP degradation increases when ageing and humidity are combined

Ageing of Pyrotechnic Compositions

Consequences of Ageing

Oxidizer

3) Reduction or degradation of oxidizers due to humidity, impurities, acidity, temperature BUT relatively stable => Non-limiting ageing factor



Binder

2) Decomposition of organic binders and polymers matrix

- Thermal oxidation: chain scission...
- Hydrolysis : deformation / dilatation...
- Thermal cracking due to expansion
- ...

Reducer

1) Oxidation of reducers:

- Hydrolysis

Performance and/or safety impacted



Ageing of Pyrotechnic Compositions

Consequences of Ageing

Oxidizer

3) Oxidizer reduction or degradation:

- Performance decrease due to high hygroscopicity

Binder

2) Decomposition of organic binders:

- Mechanical resistance: cracks, dilatation, loss of cohesion
- Density variation with a modification of burning rate

Reducer

1) Oxidation of reducers:

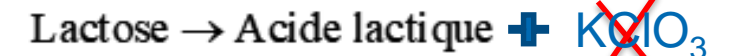
- Gas release => Overpressure risk



- Reduced performance: delayed ignition, lower energy, slower burning rate...

○ Safety :

- Increased sensitivity
- Formation incompatible impurities



Additives

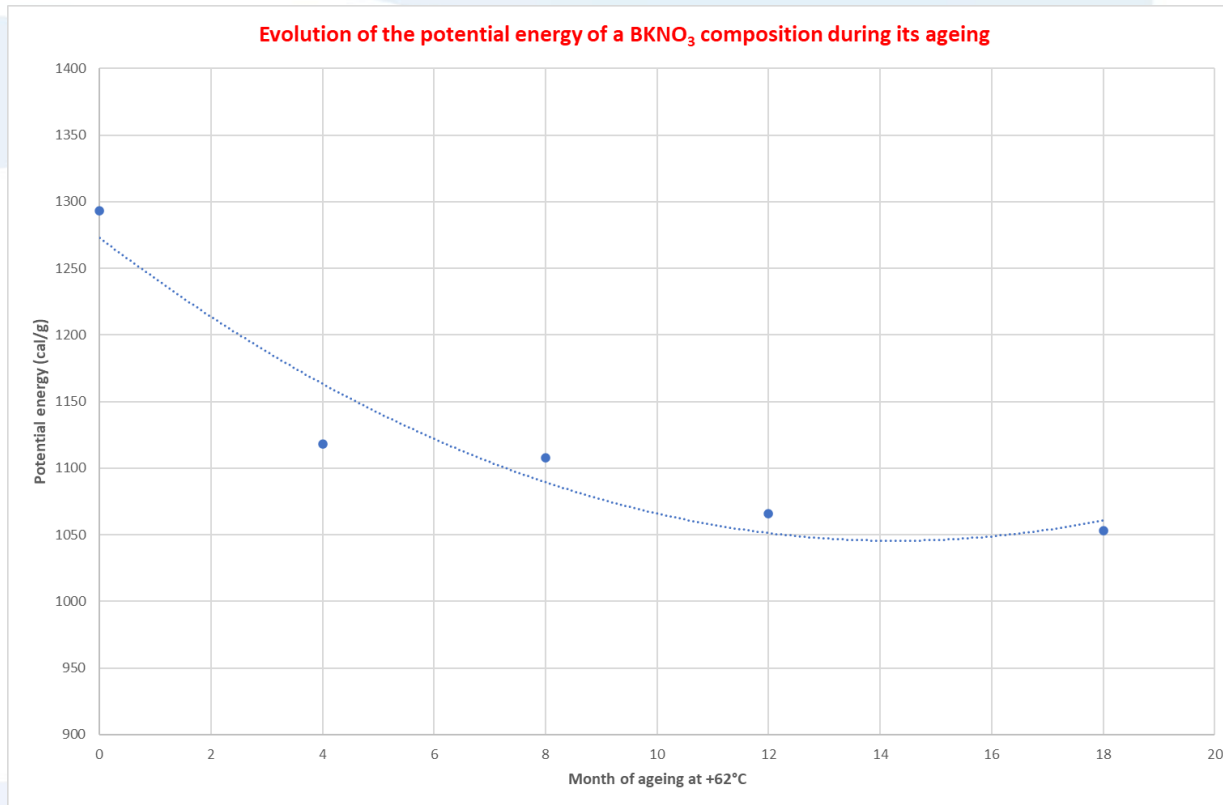
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Consequences depending on additive nature

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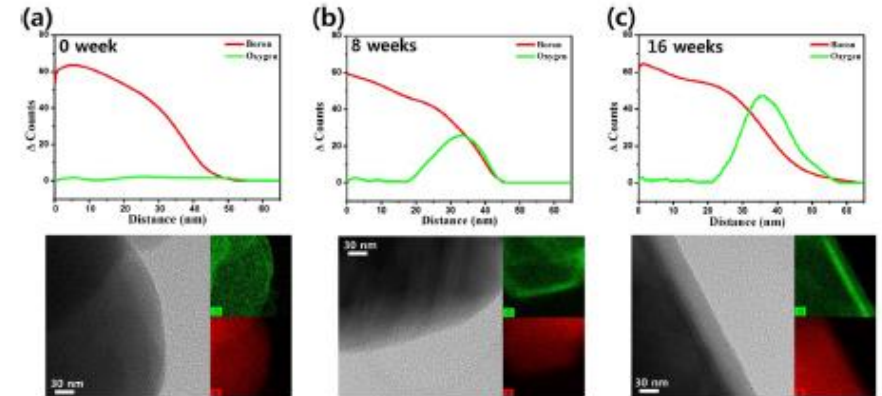
Ageing of Pyrotechnic Compositions

Consequences of Ageing of $BKNO_3$ Composition



1) Ageing mechanism:

- Surface oxidation of boron



2) Consequences:

- Increase of auto-ignition temperature (observed by DSC)
- Decrease in combustion energy (calorimeter)
- Slower burning rate

3) Evolution over time:

- Rapid degradation in the first years, then stabilization
- Formation of a protective boron oxide layer limits further oxidation

¹ J. Lee, T. Kim, S. U. Ryu, K. Choi, G. H. Ahn, J. G. Paik, B. Ryu, T. Park, Y. S. Won ; *Study on the Aging Mechanism of Boron Potassium Nitrate ($BKNO_3$) for Sustainable Efficiency in Pyrotechnic Mechanical Devices* ; Scientific Report ; 2018.

² K. M. Kim, S. I. Choi, K. H. Eom, G. H. Ahn, J. G. Paik, B. T. Ryu, Y. H. Kim, Y. S. Won ; *Thermodynamic Analysis on the Aging of THPP, ZPP and $BKNO_3$ Explosive Charges in PMDs* ; Energies ; 2019.

³ K. S. Lai ; *Boron potassium nitrate ($BKNO_3$) aging study* ; AIAA, ASME, SAE, and ASEE Joint Propulsion Conference and Exhibition ; 1998.

Integration of Ageing Studies in the Development of Pyrotechnic Products



1) Moses tests: risk reduction phase

¹ Moses, S.A., « Accelerated Life Test for Aerospace Explosive Components » *Seventh Symposium on Explosives and Pyrotechnics*, Philadelphia, Pennsylvania, 1971.

Hypotheses of this method :

- Ageing follows an Arrhenius-type law (cf. Arrhenius Law),
- High-temperature/short-time exposure \approx long-term storage at lower temperature
- Reaction rate constant doubles or triples for every 10°C increase

Moses considered reaction time multiplied by a factor between 2.7 and 2.9 when temperature increases by 10°C (more realist than a factor 2)

$$H_L = H_T \times 2,7^{\left(\frac{T_1 - T_2}{10}\right)}$$

$$H_U = H_T \times 2,9^{\left(\frac{T_1 - T_2}{10}\right)}$$

- H_T test duration (28 days)
 - T_1 = température du test (+70°C) T_2 = storage temperature (+20°C)
- $\Rightarrow H_L$ = estimated lifetime of **11 years (90% certitude level)**
 $\Rightarrow H_U$ = estimated lifetime of **15.7 years (80% certitude level)**

Integration of Ageing Studies in the Development of Pyrotechnic Products



1) Application of Moses tests:

For new pyrotechnic composition:

- Testing in bulk form with physico-chemical analyses => good predictive indicator of ammunition ageing because it evolves more quickly in “bulk”
- Testing within the product environment with performance controls and physico-chemical analyses

For well-known compositions:

- Testing within the product environment only, with performance controls and physico-chemical analyses

Advantages of this test :

- **Fast test** giving an **overview of ageing behavior**;
- Complements compatibility analysis

Limitations of this test :

- Does not allow fine analysis of degradation phenomena
- **All or nothing** behavior.

Ageing of Pyrotechnic Products

Integration of Ageing Studies in the Development of Pyrotechnic Products

Preliminary Design

Detailed Design

Qualification

Moses Tests

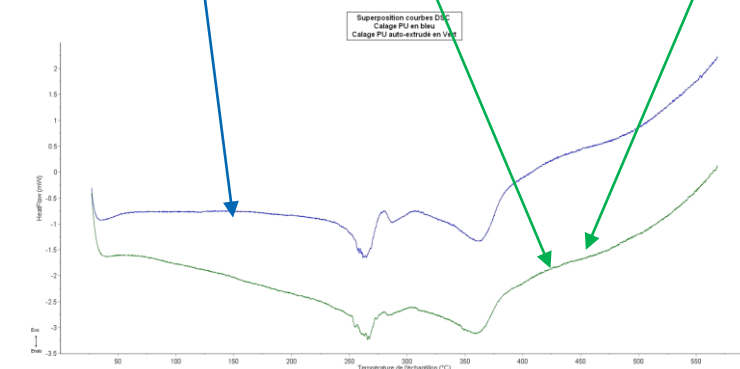
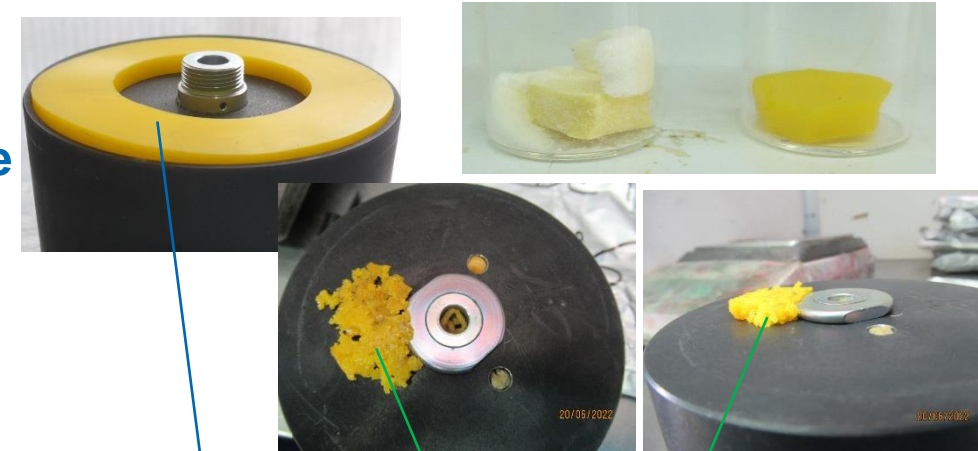
Example of a Moses test used to identify a design issue before detailed design phase:

Product: smoke pots with PU buffer

Observation: swelling and structural degradation of the buffer under stress

Cause: absorption and partial dissolution of the buffer by vapors of slightly volatile smoke agents

Note : no chemical incompatibility detected (identical DSC between raw spacer and aged extract)



Integration of Ageing Studies in the Development of Pyrotechnic Products



2) Accelerated ageing according to Arrhenius's law

$$\text{Loi d'Arrhenius : } k = A \cdot e^{\frac{-E_a}{RT}}$$

Arrhenius law defines the dependence of a chemical reaction rate on temperature.

This study helps to better identify ageing-related mechanisms and evolutions:

- Duration: 6 to 18 mois (longer than Moses tests)
- Temperature: 50-60°C (lower than Moses).

Acceleration Factor: $F = k_1/k_2$



$$t_2 = t_1 * e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$



Integration of Ageing Studies in the Development of Pyrotechnic Products



2) Accelerated ageing according to Arrhenius's law

$$t_2 = t_1 * e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Determination of test duration t_2 from the following input data:

- T_2 : test température
 - Neither too high to avoid causing parasitic reactions due to other physical phenomena and not due to ageing
 - Nor too low to avoid having a test duration t_2 that is too long..

$T_2 = 60^\circ\text{C}$: temperature usually used in accelerated ageing but it is possible to go up to $70\text{-}75^\circ\text{C}$ for certain pyrotechnic compositions (like thermites...)

Ageing of Pyrotechnic Products

Integration of Ageing Studies in the Development of Pyrotechnic Products

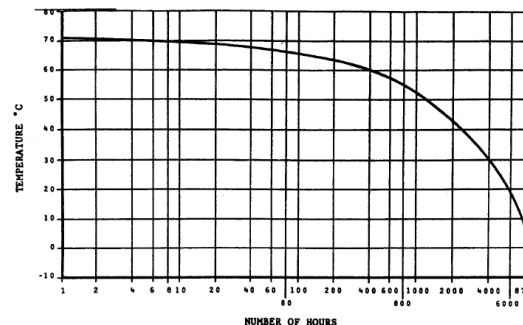


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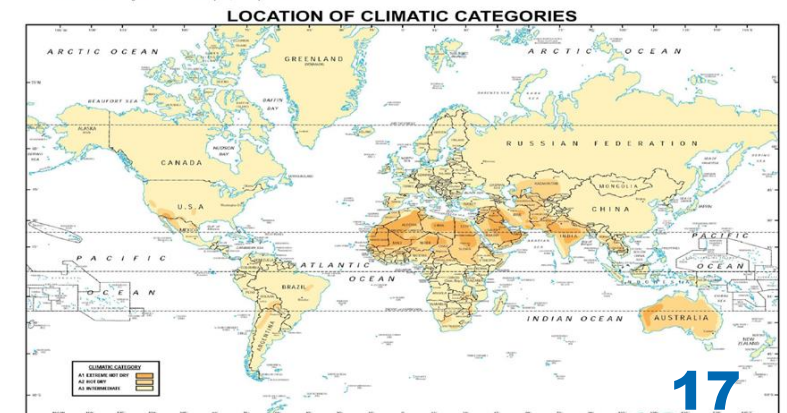
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Determination of test duration t_2 from the following input data:

- t_1 : storage duration at temperature T_1 = corresponds to the product's life profile.
- STANAG 2895 Ed. 1 : Extreme Climatic Conditions and Derived Conditions Use in Defining Design/Test Criteria for NATO Forces Materiel
- AECTP-230 Ed. 1 : Climatic Conditions



2.1 MAP 1 Climatic Categories: Extreme Hot Dry A1, Hot Dry A2 & Intermediate A3. AECTP-230 (Edition 1) LEAFLET 2311/1



Ageing of Pyrotechnic Products

Integration of Ageing Studies in the Development of Pyrotechnic Products

Preliminary Design

Detailed Design

Qualification

Moses Tests

Accelerated ageing

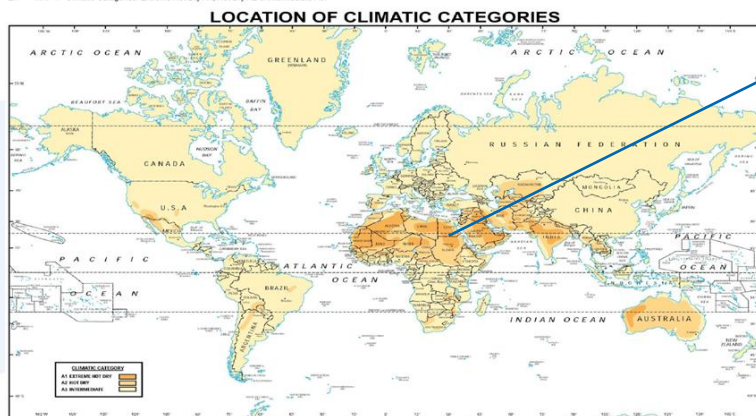
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Determination of test duration t_2 from the following input data:

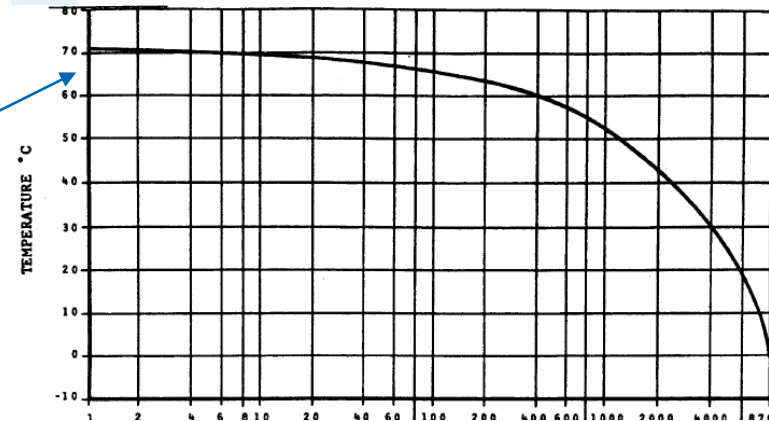
- t_1 : storage duration at temperature T_1 = corresponds to the product's life profile.

$$t_2 = t_1 * e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

2.1 MAP 1 Climatic Categories: Extreme Hot Dry A1, Hot Dry A2 & Intermediate A3



AECTP-230
(Edition 1)
LEAFLET 2311/1



Well-defined life profile optimizes test duration

Ex : For 8 years of lifetime, 5 years in France (20°C) + 3 years OPEX (Zone A1)

Zone A1 induces the most severe thermal profile

Integration of Ageing Studies in the Development of Pyrotechnic Products



2) Accelerated ageing according to Arrhenius's law

Determination of test duration t_2 from the following input data:

- E_a : activation energy of the main degradation reaction
- Hypothèse : E_a independent of temperature but ⚠ exceptions exist ⚠
Example : Nitrocellulose with 1 E_a for $T \leq 60^\circ\text{C}$, another E_a for $T > 60^\circ\text{C}$
- Take the most conservative case: the lowest E_a or the one affecting safety/performance -
May concern other materials than pyrotechnic compositions
Example : degradation of seals or other plastic materials

$$t_2 = t_1 * e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$



MTV ageing hardened tests without seal

Ageing of Pyrotechnic Products

Integration of Ageing Studies in the Development of Pyrotechnic Products

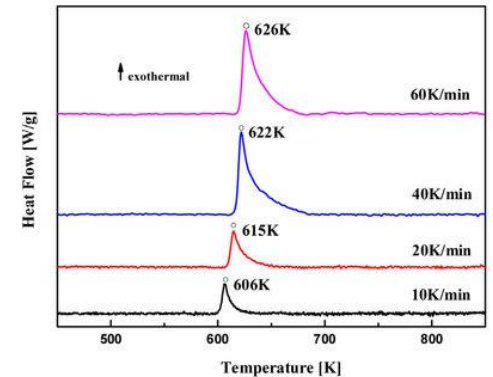


2) Accelerated ageing according to Arrhenius's law

$$t_2 = t_1 * e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Determination of test duration t_2 from the following input data:

- E_a : activation energy of the main degradation reaction
- Bibliographic research on E_a or when not available in literature, E_a is measured experimentally by DSC
 In pyrotechnics, $40 \text{ kJ/mol} < E_a < 200 \text{ kJ/mol}$
- Lacroix database includes E_a values for degradation of pyrotechnic compositions and polymer materials (seals, plastics...).



Produit	Formule brute	Ea littérature						Ref Ea min	Ea min (kJ/mol)	E ^d	DSC LAPC	PV
PA 66		257	114	91	##	##	Characterization of Thermal Degradation of Polyamide 66 composition : Relationship between lifetime prediction and activation energy, Jung & Weon, Polymer(Korea), 2012, 36,6:712-20	91	257			
Magnésium	Mg						Oxide formation on Mg single crystals - Kinetics of Growth - 1963 - R.L. Schwobel.					
Bore - B	B						Kinetics of oxidation of boron powder Avril 2011.	101				

Ageing of Pyrotechnic Products

Integration of Ageing Studies in the Development of Pyrotechnic Products

Preliminary Design

Detailed Design

Qualification

Moses Tests

Accelerated ageing

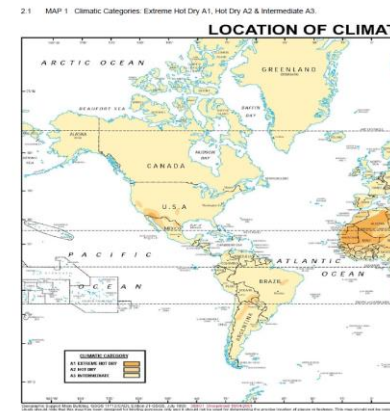
$$t_2 = t_1 * e^{\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

2) Accelerated ageing according to Arrhenius's law

Calculation tools to determine the test temperature

Température	Conditions de stockage zone A1 induit (20% de la durée de vie)		Conditions de stockage isotherme à 20°C (80% de la durée de vie)		Durée épreuve vieillissement accéléré à +60°C			
	Nbre jours	% jours	Nbre jours	% jours	T° (°C)	Kelvin	F : t1/t2	t2:t1/F
-15	0	0,000%	0	0,000%	-15	258	2665,77	0,00
-10	0	0,000%	0	0,000%	-10	263	1369,77	0,00
-5	0	0,000%	0	0,000%	-5	268	721,54	0,00
0	0	0,000%	0	0,000%	0	273	389,11	0,00
5	111	9,470%	0	0,000%	5	278	214,55	0,52
10	124	10,586%	0	0,000%	10	283	120,82	1,02
15	88	7,570%	0	0,000%	15	288	69,40	1,27
20	135	11,564%	4675	100,000%	20	293	40,63	118,39
25	99	8,430%	0	0,000%	25	298	24,22	4,07
30	98	8,370%	0	0,000%	30	303	14,68	6,66
35	113	9,691%	0	0,000%	35	308	9,05	12,52
40	96	8,214%	0	0,000%	40	313	5,66	16,95
45	84	7,212%	0	0,000%	45	318	3,60	23,44
50	80	6,818%	0	0,000%	50	323	2,32	34,40
55	55	4,732%	0	0,000%	55	328	1,51	36,57
60	31	2,650%	0	0,000%	60	333	1,00	30,97
65	36	3,042%	0	0,000%	65	338	0,67	53,11
70	17	1,436%	0	0,000%	70	343	0,45	37,03
71	3	0,257%	0	0,000%	71	344	0,42	5,98

Jours	1168,8	4675,2	Jours	382,9	NRJ d'activation (J/mol)	75000
Années	3,2	12,8	Années	1,0	Température d'épreuve (°C)	60
			Mois	12,6	Nbre d'années de vie	3,2



Oven ageing



Paramètres à faire varier

Integration of Ageing Studies in the Development of Pyrotechnic Products



3) Application of S-CAT 17500 for the new energetic materials (Edition n°6)

- Launch of the 17500 qualification process when formulation and process are “frozen”
- Ensures long-term stability and safety of energetic materials
- For pyrotechnic compositions: physico-chemical analyses before and after 6 months at +60°C (ESV, DSC, TG)

Ageing of Pyrotechnic Products

Integration of Ageing Studies in the Development of Pyrotechnic Products



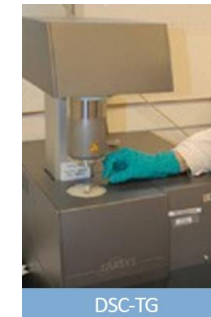
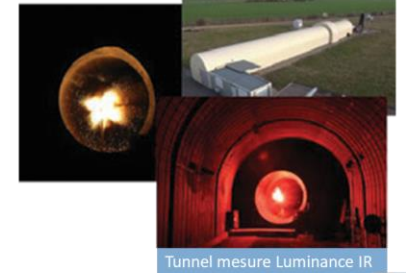
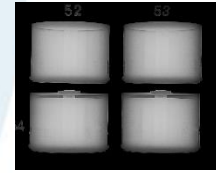
4) Intermediate and final evaluations:

- Accelerated ageing is long and critical for development (6–18 months)
- ⇒ Intermediate evaluations prevent surprises at the end of the test and allow re-estimation of service life.
- ⇒ Monitoring methods include:
 - visual inspection,
 - performance tests,
 - physico-chemical analyses,
 - and safety tests...

Ageing Monitoring Methods

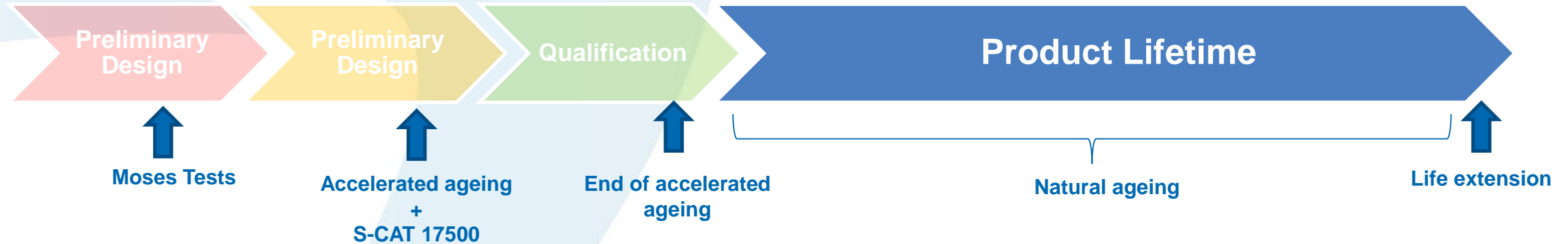
4) Comparison with initial (t_0) results

- Visual inspection:
 - X-ray
 - Mass and dimensional analyses: density, expansion
 - Inspection: visual or microscopy
- Firing tests to verify operation, performance evolutions and performance vs. specifications
- Physico-chemical analyses of compositions:
 - Thermal: DSC, TG...
 - Chemical : IR, SEM, HPLC...
 - Physical : granulometry...
 - Energétique : calorimetry...
- Safety tests: impact, friction, ESD et burning rate



Ageing of Pyrotechnic Products

Integration of ageing studies in the development of pyrotechnic products



5) Natural ageing and life extension

- Natural ageing: reference samples stored to gather long-term data or support investigations on fielded products.
- Life extension study: performed when products remain safe and effective at end-of-life to extend service duration.

Synthesis of Ageing Approach in Pyrotechnic Product Development

Ageing studies of pyrotechnic compositions and products are integrated from early development to end-of-life:

- 1) **Moses test:** fast evaluation to estimate lifetime confidence level
- 2) **Accelerated ageing (Arrhenius):**
 - Long-term study (6–18 months)
 - Clearly define the input data and more specifically the life profile of the ammunition to have a study that is best optimized in terms of duration and reliability of the results.
- 3) **17500 qualification** to ensure long-term stability and safety of new energetic materials
- 4) **Naturel ageing** to provide reference data for investigations
- 5) **Life extension** for pyrotechnic products still reliable and efficient at the end of their life

« **Although numerous degradation reactions may occur, the majority of pyrotechnic compositions remain largely unaffected by ageing...
...provided they are stored under good conditions.**»



Thank you for your attention