OPTIMIZATION OF MODELING OF PROPELLANTS AGING INVESTIGATED ACCORDING TO NATO AOP-48 ED.2 TEST PROCEDURE

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Thermal degradation of high energetic materials

Nitrocellulose-based propellants
decompose slowly even at ambient temperatures.

↓

Decrease of the chemical stability.

↓

To prevent this undesired process
stabilizers are introduced to the propellants
to react with the degradation products.

Thermal degradation of high energetic materials

Experimental observation of propellant decomposition is difficult due to its **very low rate at room temperature.**

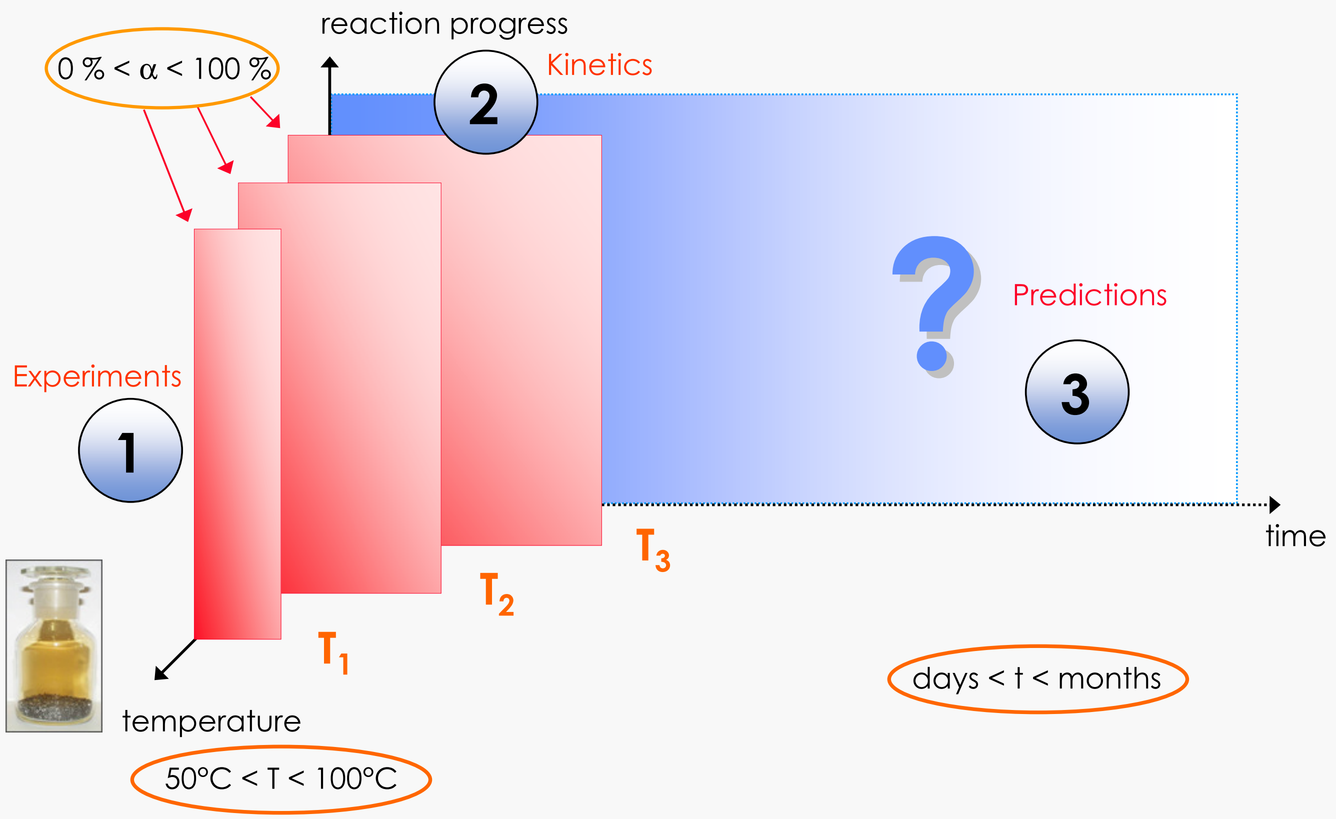
⇓

Immeasurable physicochemical changes.

⇓

Common investigation of the aging processes is based on the **experiments carried out at higher temperatures** when the reaction rates are significantly higher.

Stability test procedure



Common stability test procedure is described in

NATO Allied Ordnance Publication

AOP-48 Ed. 2

Kinetic analysis for determination of the thermal stability of solid materials

Three major steps:

1. Experimental collection of data
2. Computation of kinetic parameters
3. Prediction of the reaction progress for required temperature profiles applying determined kinetic parameters.

Following NATO AOP-48 Ed. 2 test procedure:

1. Monitoring stabilizer depletion can be carried out by **High Performance Liquid Chromatography (HPLC).** Stabilizer depletion requires the set of aging experiments performed at least **three temperatures, generally 60, 70 and 80°C.**

2. Computation of kinetic parameters assuming certain kinetic reaction model i.e. Reaction-Order (Fn) model:

$$f(\alpha) = (1-\alpha)^n$$

3. Prediction of the reaction progress for required temperature profiles applying determined kinetic parameters.

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \longrightarrow t_a = \int_0^t dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{k(1-\alpha)^n}$$

Following NATO AOP-48 Ed. 2 test procedure:

Thermal aging

$$t_\alpha = \int_0^{t_\alpha} dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A \cdot exp\left(-\frac{E}{R}\cdot\frac{1}{T}\right)\cdot(1-\alpha)^n}$$

Arrhenius

Model $f(\alpha)$

Common kinetic analysis

	Typical reaction model: *f(α)*
PT: Prout Tompkins	*(1-α)^n α^m*
Fn: nth order	*(1-α)^n*
F1: first order	*(1-α)*
F2: second order	*(1-α)^2*
F3: third order	*(1-α)^3*
P1: power law	*α^0*
P2: power law	*2 α^(1/2)*
P3: power law	*3 α^(2/3)*
P4: power law	*4 α^(3/4)*
Pn: power law	*n α^(1-1/n)*
An: Avrami-Erofeev	*n (1-α) [-ln(1-α)]^(1-1/n)*
A2: Avrami-Erofeev	*2 (1-α) [-ln(1-α)]^(1/2)*
A3: Avrami-Erofeev	*3 (1-α) [-ln(1-α)]^(2/3)*
Rn: n contracting	*n (1-α)^(1-1/n)*
R2: contracting cylinder	*2 (1-α)^(1/2)*
R3: contracting sphere	*3 (1-α)^(2/3)*
D2: 2-dimensional diffusion	*[-ln(1-α)]^-1*
D3: 3-dimensional diffusion	*1.5 [1-(1-α)^(1/3)]^-1 (1-α)^(2/3)*

Common kinetic analysis

	Typical reaction model: *f(α)*
PT: Prout Tompkins	*(1-α)^n α^m*
Fn: nth order	*(1-α)^n*
F1: first order	*(1-α)*
F2: second order	*(1-α)^2*
F3: third order	*(1-α)^3*
P1: power law	*α^0*
P2: power law	*2 α^(1/2)*
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	Typical reaction model: $f(\alpha)$
PT: Prout Tompkins	$(1-\alpha)^n \alpha^m$
Fn: nth order	$(1-\alpha)^n$
F1: first order	$(1-\alpha)$
F2: second order	$(1-\alpha)^2$
F3: third order	$(1-\alpha)^3$
P1: power law	α^0
P2: power law	$2\ \alpha^{(1/2)}$
P3: power law	$3\ \alpha^{(2/3)}$
P4: power law	$4\ \alpha^{(3/4)}$
Pn: power law	$n\ \alpha^{(1-1/n)}$
An: Avrami-Erofeev	$n\ (1-\alpha)\ [-\ln(1-\alpha)]^{(1-1/n)}$
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A3: Avrami-Erofeev	$3\ (1-\alpha)\ [-\ln(1-\alpha)]^{(2/3)}$
Rn: n contracting	$n\ (1-\alpha)^{(1-1/n)}$
R2: contracting cylinder	$2\ (1-\alpha)^{(1/2)}$
R3: contracting sphere	$3\ (1-\alpha)^{(2/3)}$
D2: 2-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$
D3: 3-dimensional diffusion	$1.5\ [1-(1-\alpha)^{(1/3)}]^{-1}\ (1-\alpha)^{(2/3)}$

Can Fn describe PT ?

'NO'

The aim of the present paper is to:

Propose another

<u>more universal</u>

kinetic model

Common kinetic analysis

	Typical reaction model: $f(\alpha)$
PT: Prout Tompkins	$(1-\alpha)$^n α^m
Fn: nth order	$(1-\alpha)$^n
F1: first order	$(1-\alpha)$
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F3: third order	$(1-\alpha)$^3
P1: power law	α^0
P2: power law	2 α^(1/2)
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P4: power law	4 α^(3/4)
Pn: power law	n α^(1-1/n)
An: Avrami-Erofeev	n $(1-\alpha)$ [-ln$(1-\alpha)$]^(1-1/n)
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D2: 2-dimensional diffusion	[-ln$(1-\alpha)$]^-1
D3: 3-dimensional diffusion	1.5 [1-$(1-\alpha)$^(1/3)]^-1 $(1-\alpha)$^(2/3)

Can Fn describe PT ?

'NO'

Common kinetic analysis

m=0

	Typical reaction model: $f(\alpha)$
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Fn: nth order	$(1-\alpha)$^n
F1: first order	$(1-\alpha)$
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D3: 3-dimensional diffusion	1.5 [1-$(1-\alpha)$^(1/3)]^-1 $(1-\alpha)$^(2/3)

Can PT describe Fn ?

'Yes'

Common kinetic analysis

	Typical reaction model: $f(\alpha)$
PT: Prout Tompkins	$(1-\alpha)^n \alpha^m$
Fn: nth order	$(1-\alpha)^n$
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Rn: n contracting	$n\ (1-\alpha)^{(1-1/n)}$
R2: contracting cylinder	$2\ (1-\alpha)^{(1/2)}$
R3: contracting sphere	$3\ (1-\alpha)^{(2/3)}$
D2: 2-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$
D3: 3-dimensional diffusion	$1.5\ [1-(1-\alpha)^{(1/3)}]^{-1}\ (1-\alpha)^{(2/3)}$

Common kinetic analysis

n m

	Typical reaction model: $f(\alpha)$
PT: Prout Tompkins	$(1-\alpha)^n \alpha^m$
Fn: nth order	$(1-\alpha)^n$
F1: first order	$(1-\alpha)$
F2: second order	$(1-\alpha)^2$
F3: third order	$(1-\alpha)^3$
P1: power law	α^0
P2: power law	$2\ \alpha^{(1/2)}$
P3: power law	$3\ \alpha^{(2/3)}$
P4: power law	$4\ \alpha^{(3/4)}$
Pn: power law	$n\ \alpha^{(1-1/n)}$
An: Avrami-Erofeev	$n\ (1-\alpha)\ [-\ln(1-\alpha)]^{(1-1/n)}$
A2: Avrami-Erofeev	$2\ (1-\alpha)\ [-\ln(1-\alpha)]^{(1/2)}$
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Rn: n contracting	$n\ (1-\alpha)^{(1-1/n)}$
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R3: contracting sphere	$3\ (1-\alpha)^{(2/3)}$
D2: 2-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$
D3: 3-dimensional diffusion	$1.5\ [1-(1-\alpha)^{(1/3)}]^{-1}\ (1-\alpha)^{(2/3)}$

Can PT describe Pn, An, Rn, D2, D3?

'Yes'

(*) *with A'=A·c or $f(\alpha)=c(1-\alpha)^n\alpha^m$*

(*) L.A. Perez-Maqueda, J.M. Criado, P.E. Sanchez-Jimenez, Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism, J. Phys. Chem. A 110 (2006) 12456–12462.

Common kinetic analysis

	Typical reaction model: $f(\alpha)$	More universal model: $f(\alpha)$		
		n	m	c in $(A'=A\cdot c)$
PT: Prout Tompkins	$(1-\alpha)$^n α^m	n	m	1
Fn: nth order	$(1-\alpha)$^n	n	0	1
F1: first order	$(1-\alpha)$	1	0	1
F2: second order	$(1-\alpha)$^2	2	0	1
F3: third order	$(1-\alpha)$^3	3	0	1
P1: power law	α^0	0	0	1
P2: power law	2 α^(1/2)	0	1/2	2
P3: power law	3 α^(2/3)	0	2/3	3
P4: power law	4 α^(3/4)	0	3/4	4
Pn: power law	n α^(1-1/n)	0	1-1/n	n
An: Avrami-Erofeev	n $(1-\alpha)$ [-ln$(1-\alpha)$]^(1-1/n)			
A2: Avrami-Erofeev	2 $(1-\alpha)$ [-ln$(1-\alpha)$]^(1/2)	0.806	0.515	2.079
A3: Avrami-Erofeev	3 $(1-\alpha)$ [-ln$(1-\alpha)$]^(2/3)	0.748	0.693	3.192
Rn: n contracting	n $(1-\alpha)$^(1-1/n)	1-1/n	0	n
R2: contracting cylinder	2 $(1-\alpha)$^(1/2)	1/2	0	2
R3: contracting sphere	3 $(1-\alpha)$^(2/3)	2/3	0	3
D2: 2-dimensional diffusion	[-ln$(1-\alpha)$]^-1	0.425	-1.008	0.973
D3: 3-dimensional diffusion	1.5 [1-$(1-\alpha)$^(1/3)]^-1 $(1-\alpha)$^(2/3)	0.951	-1.004	4.431

(*) L.A. Perez-Maqueda, J.M. Criado, P.E. Sanchez-Jimenez, Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism, J. Phys. Chem. A 110 (2006) 12456–12462.

NATO AOP-48 Ed-2 : Fn model

Following NATO AOP-48 Ed. 2 test procedure:

Thermal aging

$$t_\alpha = \int_0^{t_\alpha} dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A \cdot exp\left(-\frac{E}{R}\cdot\frac{1}{T}\right)\cdot(1-\alpha)^n}$$

Arrhenius

Model $f(\alpha)$

More universal kinetic model

Thermal aging

$$t_\alpha = \int_0^{t_\alpha} dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A \cdot exp\left(-\frac{E}{R}\cdot\frac{1}{T}\right)\cdot(1-\alpha)^n \cdot \alpha^m}$$

Arrhenius

Model $f(\alpha)$

More universal kinetic model

1. Set 27 points generated for three temperatures: 60, 70 and 80°C

$$t_\alpha = \int_0^{t_\alpha} dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A \cdot exp\left(-\frac{E}{R}\cdot\frac{1}{T}\right)\cdot(1-\alpha)^n \cdot \alpha^m}$$

E = 110 kJ/mol

A = 5E10 sec^{-1}

n = 1

m = 0.5

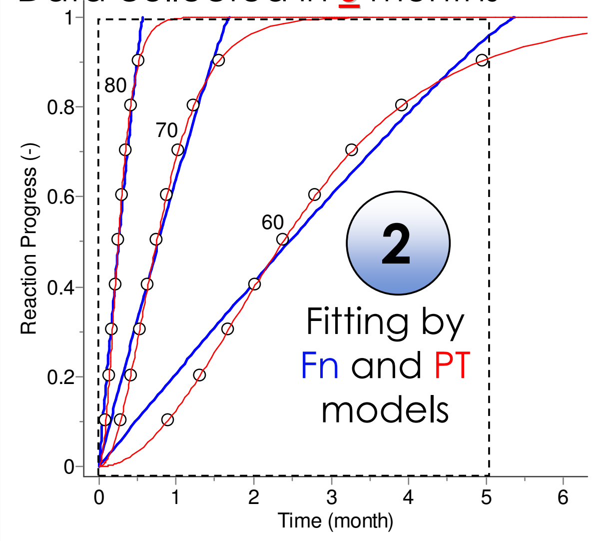
2. Fitting experimental or generated data by Fn and PT models

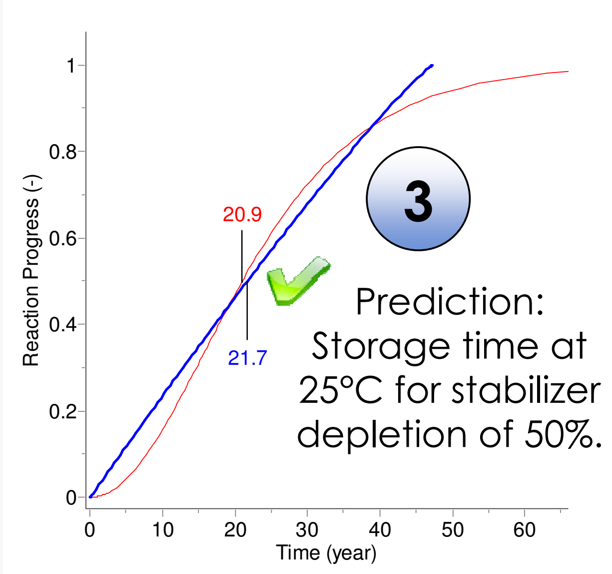
3. Prediction of reaction progress by Fn and PT models

Mathematical validation

1

Data collected in **5** months





Difference between **Fn** and **PT**-models results in relative error of prediction

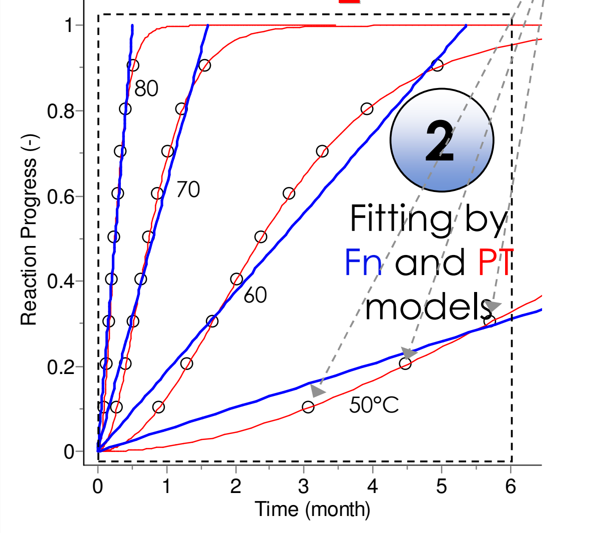
(21.7-20.9)/20.9 = **3.8%**

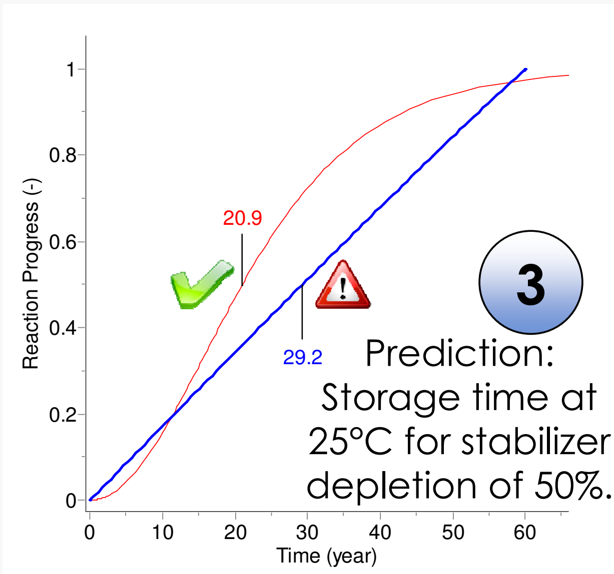
Mathematical validation

1

„3 points collected at 50°C are taken into considerations"

Data collected in **6** months



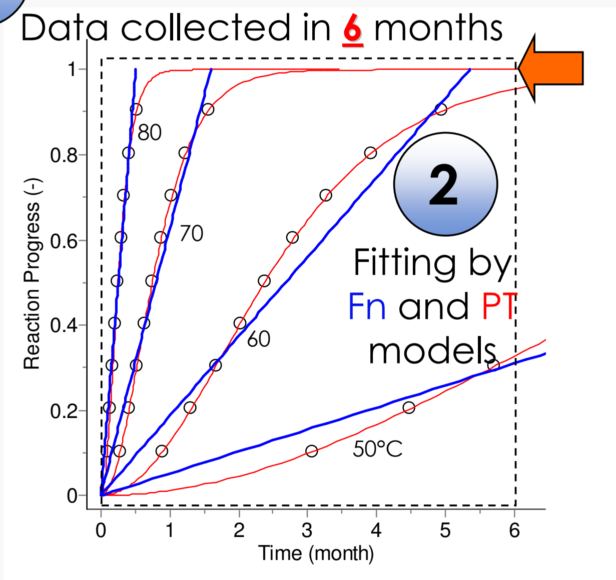


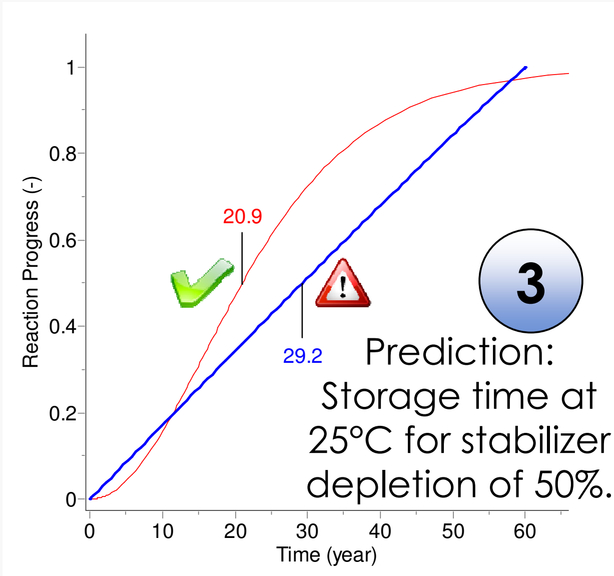
Difference between **Fn** and **PT**-models results in relative error of prediction

(29.2-20.9)/20.9 = **39.7%**

1

„3 points collected at 50°C are taken into considerations"



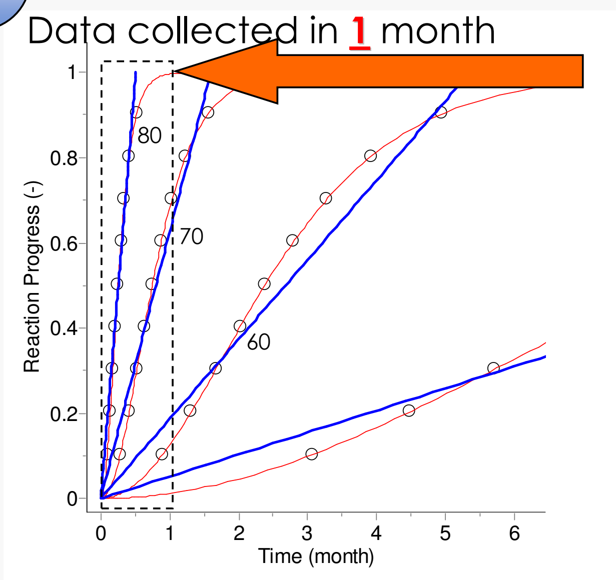


Difference between **Fn** and **PT**-models results in relative error of prediction

(29.2-20.9)/20.9 = **39.7%**

1

„ Data collected in one month only ! "

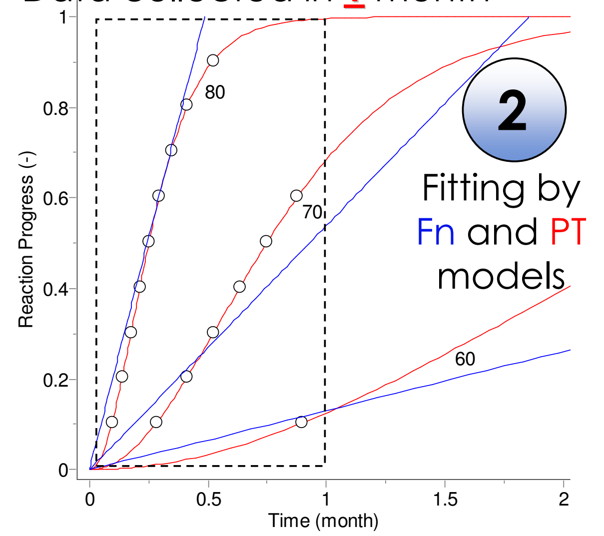


Mathematical validation

1

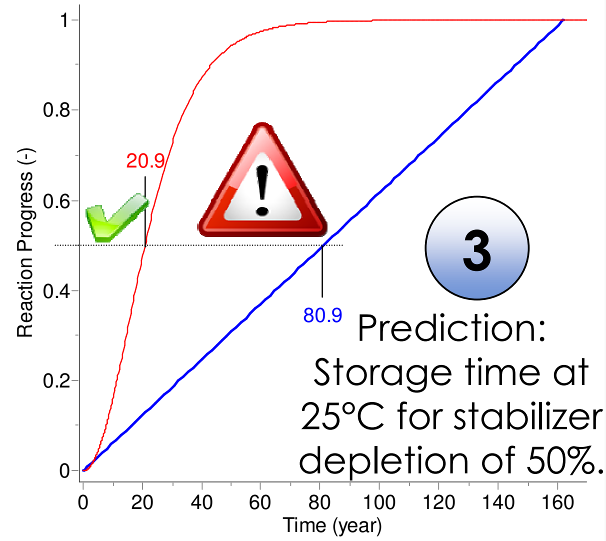
„ Data collected in one month only ! ”

Data collected in 1 month



2

Fitting by Fn and PT models



3

Prediction: Storage time at 25°C for stabilizer depletion of 50%.

Difference between **Fn** and **PT**-models results in relative error of prediction

(80.9-20.9)/20.9 = **287% !**

Mathematical validation

Application of more universal PT model

1. Significant <u>decrease of points</u> required for kinetic analysis
i.e. Significant <u>reduction of experimental time</u> for the data collection.

2. <u>Correct stability prediction</u>

Summary of the kinetic analysis of all propellants:

kinetic parameters derived during fitting experimental data by Fn and PT models, t_{25}- i.e. the storage time at 25°C after which a stabilizer depletion of 50 % is reached

sample	Mo-del	α_0	A sec^{-1}	E kJ/mol	n	[illegible]	t_{25}- 50%
SB-1	Fn	0	1,7E+11	117,1	0,43	0	[illegible]
	PT	2,5E-11	7,7E+10	111,2	[illegible]	0,43	[illegible]
SB-2	Fn	0	8,2E+11	122,8	[illegible]	0	[illegible]
	PT	2,3E-09	8,2E+11	122,8	[illegible]	7,1E-06	[illegible]
SB-3	Fn	0	7,6E+15	147,7	[illegible]	[illegible]	[illegible]
	PT	6,3E-11	7,4E+11	118,8	[illegible]	[illegible]	[illegible]
SB -4	Fn	0	2,4E+09	109,7	0,40	[illegible]	[illegible]
	PT	3,6E-11	2,4E+09	109,7	[illegible]	[illegible]	[illegible]
SB-5	Fn	0	6,0E+09	110,7	[illegible]	0	78,5
	PT	2,3E-10	4,3E+09	[illegible]	[illegible]	3,8E-07	76
DB-1	Fn	0	7,9E+11	[illegible]	0,66	0	27,87
	PT	1,0E-10	1,2E+12	[illegible]	0,78	0,14	28,42
DB-2	Fn	0	1,6E+10	[illegible]	0,92	0	4,85
	PT	7,2E-11	1,6E+10	105,9	0,92	1,0E-4	4,84
DB-3	Fn	0	8,6E+10	112,5	0,78	0	12,35
	PT	1,1E-10	2,2E+11	113,9	0,96	0,25	12,8
DB-4	Fn	0	2,2E+10	114,9	0,40	0	114,5
	PT	4,4E-09	2,2E+10	114,9	0,41	1,8E-05	114,5
DB-5	Fn	0	4,0E+13	130,1	0,57	0	30,2
	PT	2,8E-10	4,0E+13	130,1	0,57	1.7E-03	30,4
DB-6	Fn	0	6,7E+10	118,5	0,35	0	156,8
	PT	1,5E-08	6,7E+10	118,5	0,35	6,7E-06	156,9
DB-7	Fn	0	3,1E+14	132,7	0,91	0	12,5
	PT	2,6E-09	3,1E+14	132,7	0,91	1,8E-03	12,4

sample	Mo-del	n	m	t_{25}- 50%	t_{25}- 80%
SB-2	Fn	1,71	0	113,1	375
	PT	1,71	7,1E-06	113,1	375
SB-3	Fn	1,45	0	262	761
	PT	1,97	0.45	58,9	156
SB -4	Fn	0,40	0	127,05	232
	PT	0,40	1,1E-11	127,05	232
SB-5	Fn	0,57	0	78,5	152

Application of more universal PT model

1 Significant decrease of points required for kinetic analysis i.e. Significant reduction of experimental time for the data collection.

2 Correct stability prediction

3 Mathematical considerations confirmed by the evaluation of the stability of single- and double based propellants (= experimental verification).

Following NATO AOP-48 Ed. 2 test procedure:

Thermal aging

$$t_\alpha = \int_0^{t_\alpha} dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A \cdot exp\left(-\frac{E}{R}\cdot\frac{1}{T}\right)\cdot(1-\alpha)^n}$$

Arrhenius

Model $f(\alpha)$

More universal model : PT model

More universal kinetic model

Thermal aging

$$t_\alpha = \int_0^{t_\alpha} dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A \cdot exp\left(-\frac{E}{R}\cdot\frac{1}{T}\right)\cdot(1-\alpha)^n \cdot \alpha^m}$$

Arrhenius

Model

$$f(\alpha)$$

Conclusion

The correct kinetic analysis applying **more universal PT-model**

can be successfully carried out

even if the number of experimental data is significantly smaller

than those required by NATO-AOP 48 Ed.2 test procedure.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MDC Tec systems
Institute of Safety and Security
PalMetrics
ACL Instruments
understanding oxidation
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