



9th International PVC & Chlor-Alkali Summit

PVC stabilisers for pipes – Quo vadis?

Sustainability frame work of "the natural step" which is a Swedish NGO working together the European PVC industry

Dr. Michael SCHILLER

15./16.04.2019, Mumbai/India



German Round

Robin Test

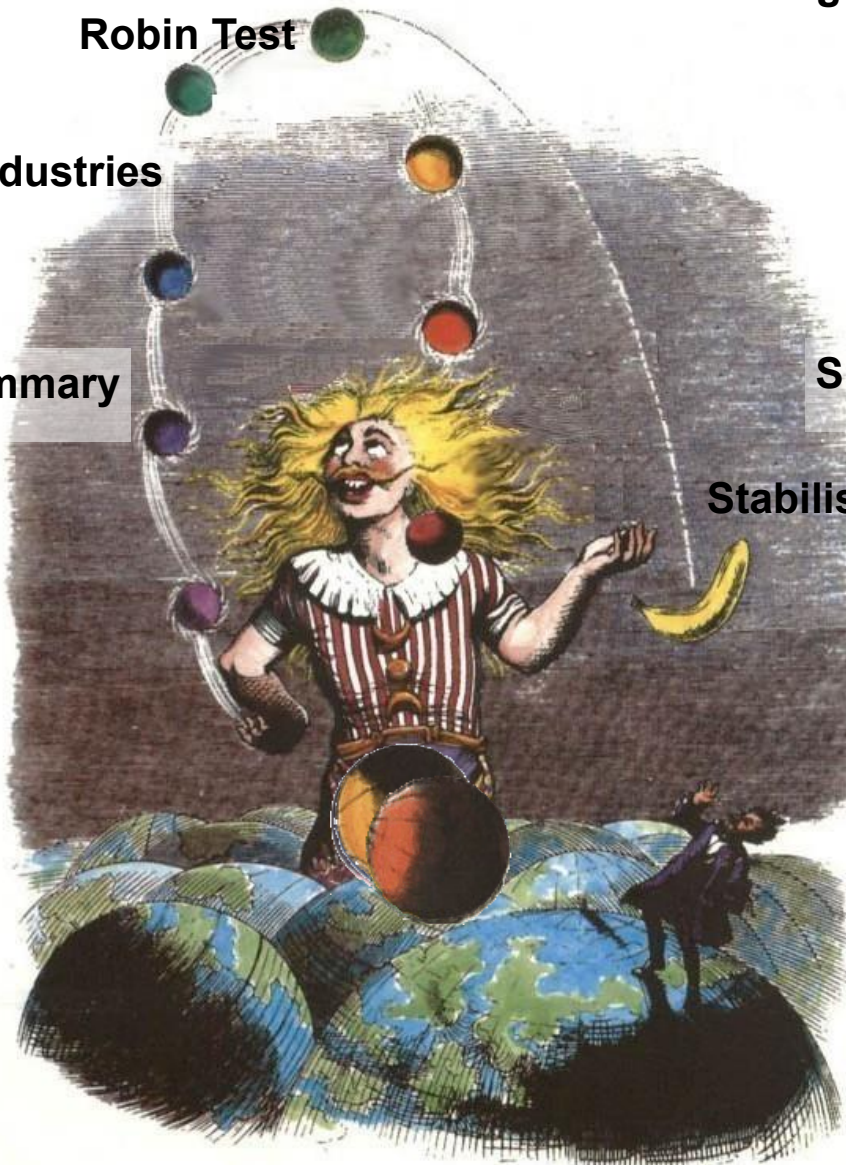
Migration

Platinum Industries

TNS[®] Framework

Summary

Sustainability definition



Stabiliser systems

Cover of QUEEN's Vinyl

"Innuendo" © EMI



Requirements on a stabiliser

- Substitution of unstable Chlorines
- Neutralisation of HCl
- Shortening of polyene sequences
- Avoiding of autoxidation
- Guaranteeing optimal processing and best performance of final product during its lifetime



Categories of stabiliser

- Lead based
- Tin based
- Rare earth metal based (no real market share)
- Organic systems
- Earth alkaline metals (Mg, Ca, Ba) in combination with Zn (or Cd)



Alternatives to Lead stabilisers

Alternatives to high Lead (1)	Benefits	Obstacles
Tin:	Excellent colour Wide processing window High stability	Weathering (more TiO ₂) Tin price Legal pressure in EU Cross-staining with Lead
Rare Earth Metals (REM):	No cross-staining	REM are heavy metals sometimes in combination with Lead If Lead free => narrowed processing window
Calcium-Organic:	Nontox Wide processing window Good colour High stability	

Source: M. Schiller; "These are the Days of our Lives – Stabilisation of PVC Window Profiles", i-PVC, Mumbai October 2012

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Alternatives to Lead stabilisers

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Alternatives to high Lead (2)	Benefits	Obstacles
Low Lead:	As good as high Lead Better price constancy Better sustainability potential	Still Lead-based
Calcium-Zinc:	Nontox No cross-staining Low plate out Better sustainability potential Long-term experience (in standard production for more than 21 years)	Narrow processing window Lower stability

Source: M. Schiller; "These are the Days of our Lives – Stabilisation of PVC Window Profiles", i-PVC, Mumbai October 2012

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Definitions of sustainability

Most known definition:

"Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

Brundtland Report (Our Common Future) – 1987





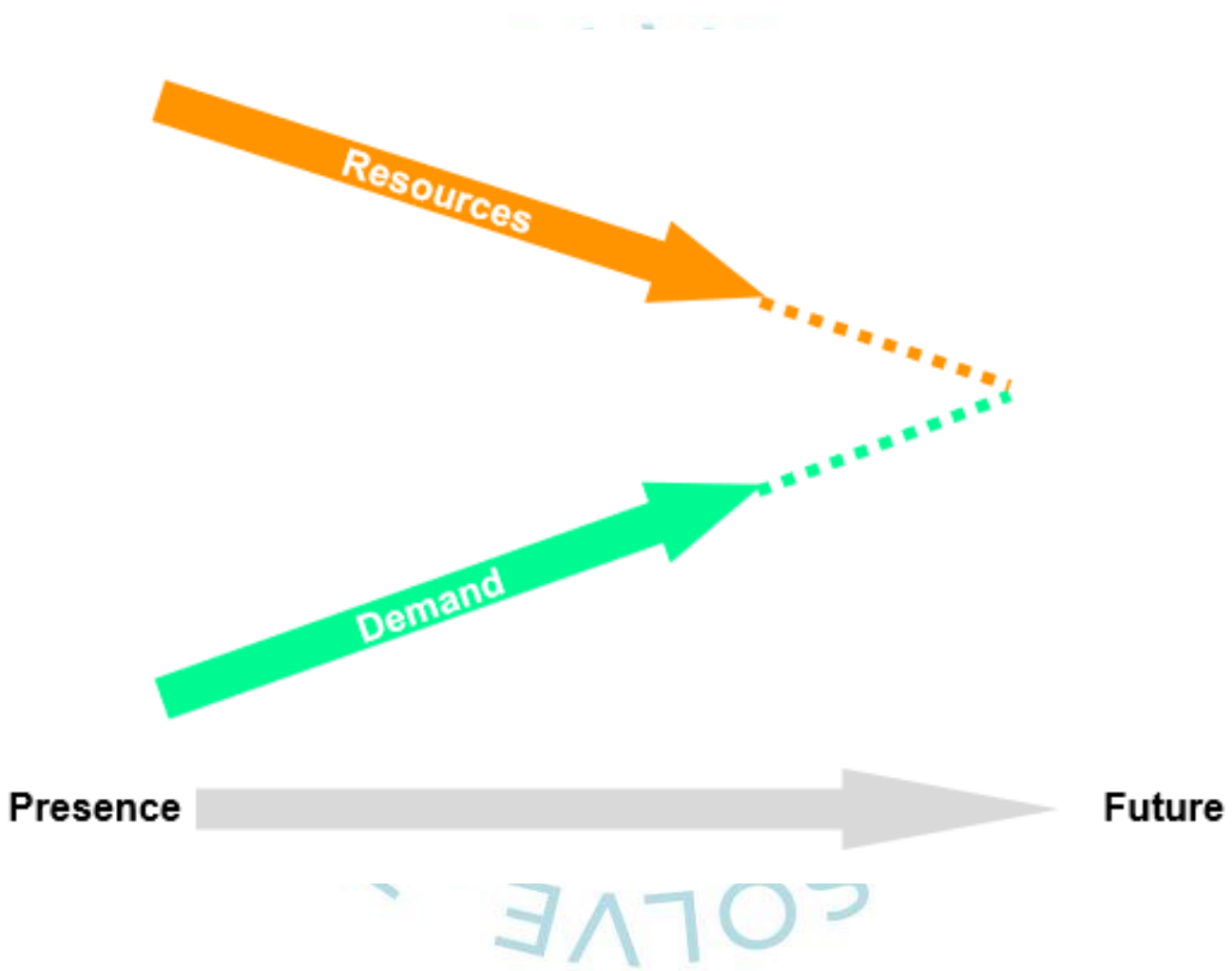
Definitions of sustainability – Three good questions

- Does your company have a generally endorsed definition of sustainability?
- What are, with reference to your definition of sustainability, the main challenges of your company today?
- What did you detect, as your main sustainability challenges regarding your supply of ingredients, i.e. your gap to comply with the system conditions?



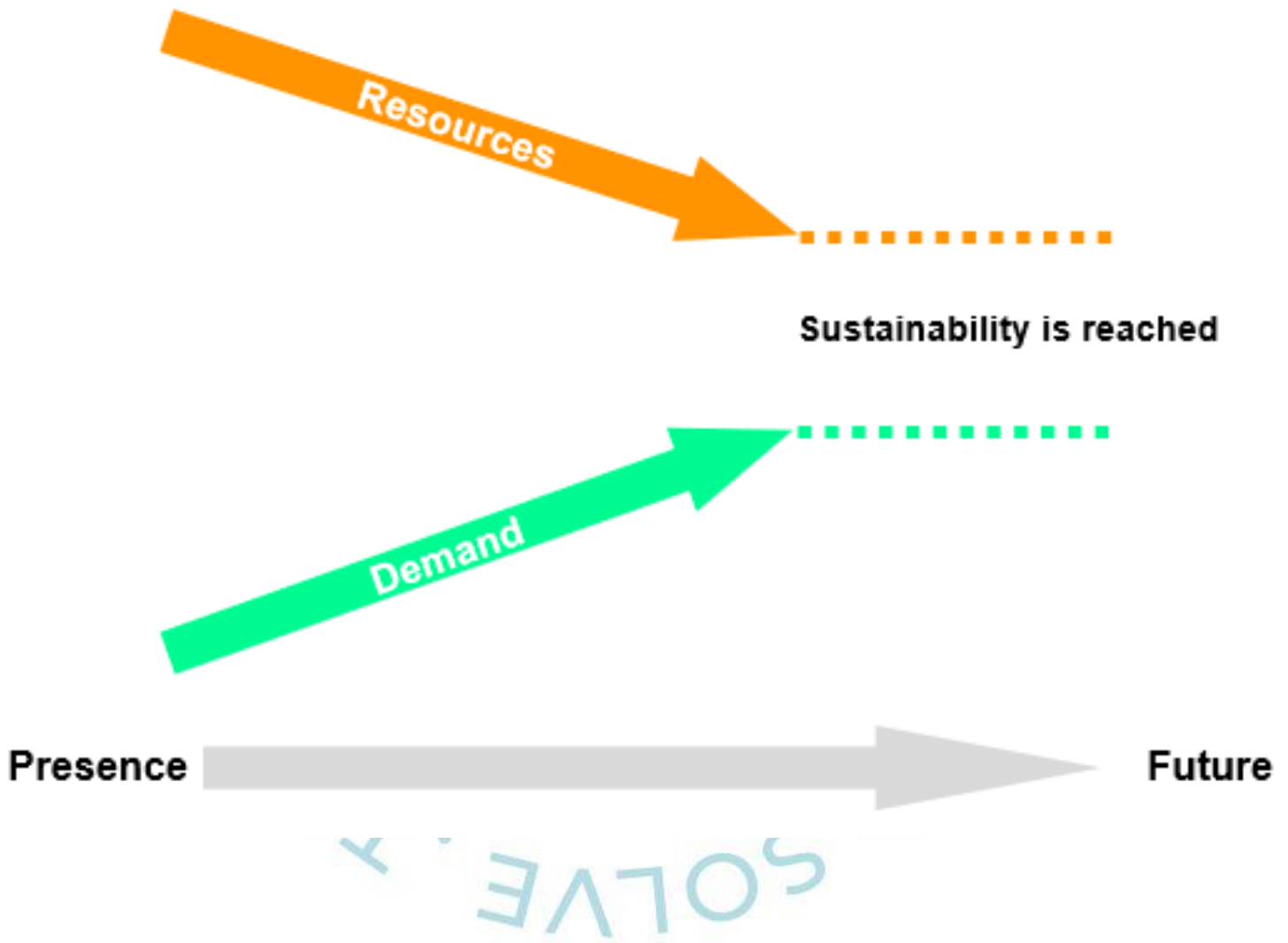


Why is sustainability necessary?



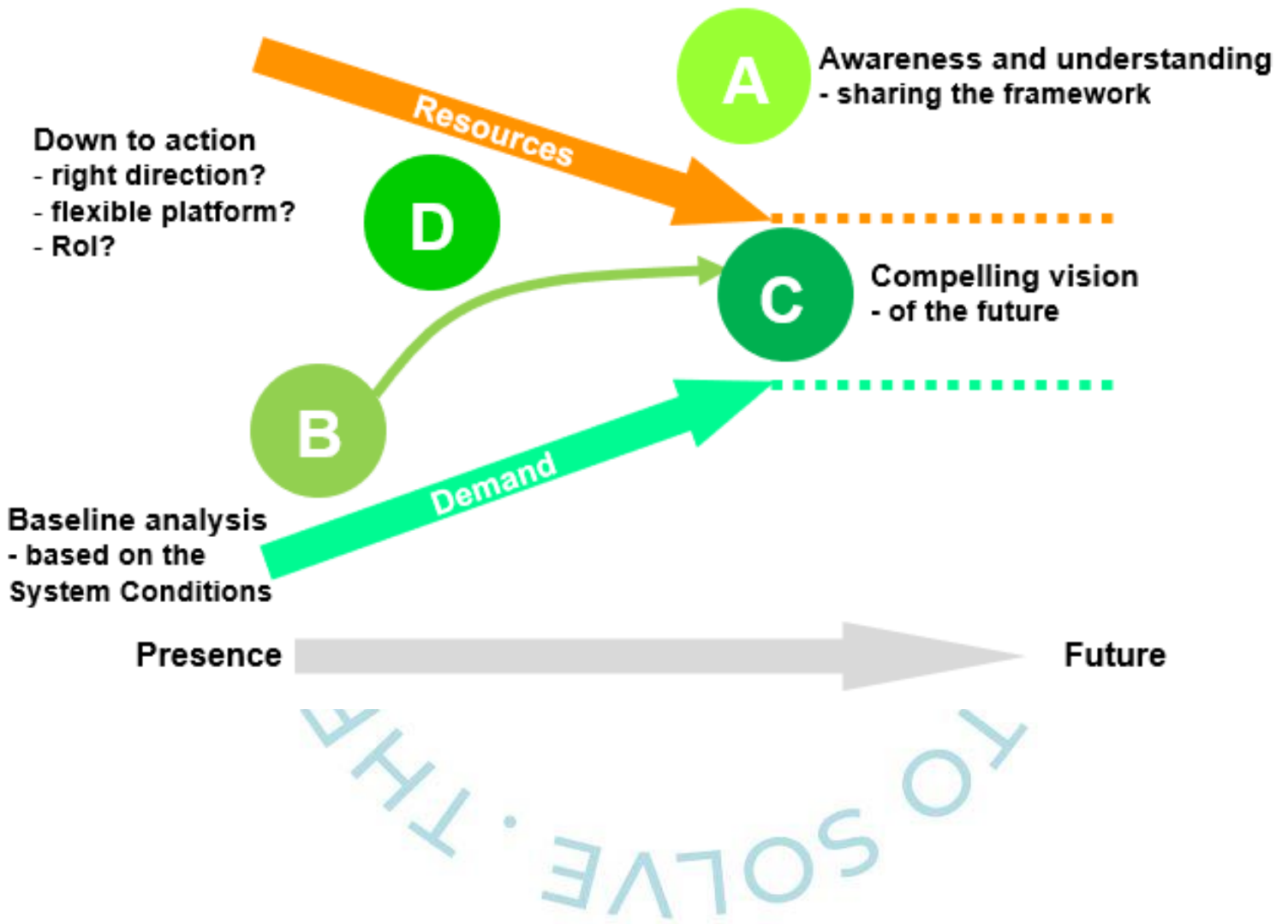


The funnel paradigm of TNS





The A B C D process by TNS





Definitions of sustainability – Four system conditions (SC) of TNS®

In the sustainable society, nature is not subject to systematically increasing...

- ...concentrations of substances extracted from the Earth's crust,
- ...concentrations of substances produced by society,
- ...degradation by physical means and,
- ... in the sustainable society people are not subject to conditions that systematically undermine their capacity to meet their needs.





The 5+1 Key PVC Sustainability Challenges

- VinylPlus: the new ten-year Voluntary Commitment of the European PVC industry
- Continues and expands the successful Vinyl 2010 program
- Derived from the framework set-up by TNS*
- It is built around 4 + 1 challenges
- 1 challenge: Avoiding direct and indirect influence on biodiversity



*TNS: The Natural Step





What was published in the past ?

K.E. Lunde, J. Leadbitter, M. Schiller; “Sustainability assessment of stabiliser systems for use in PVC pipes”, PVC ‘05, Brighton/U.K., April 2005:

“The results from the sustainability assessment show that both Calcium-Zinc and organic-based stabiliser have potential for development into fully sustainable stabiliser systems.

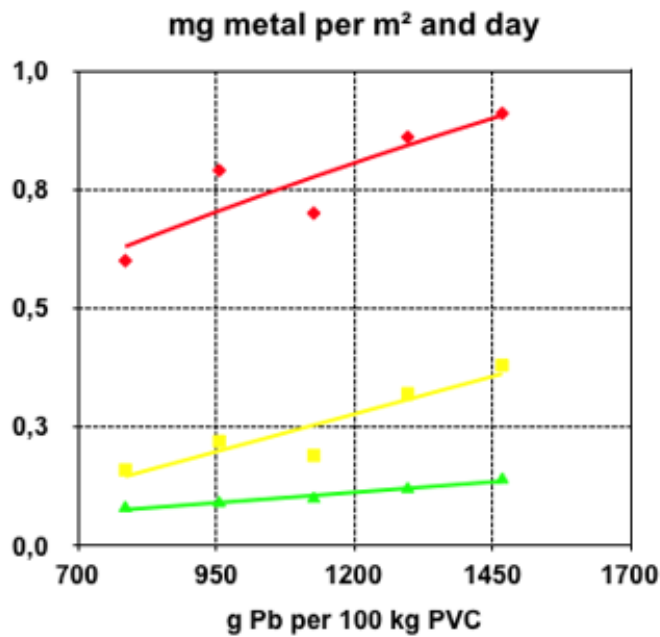
This work demonstrates the challenges required to achieve full sustainability of these systems.

We do not advocate that all these changes are made in the short term but recommend to raw material suppliers and others in the supplier chain to bear in mind these criteria especially when it comes to future investments.”





Migration



◆ 1st extraction ■ 2nd extraction
▲ 3rd extraction

Lead migration:

- depending on the total formulation
- depending on the Lead content in the pipe

Zinc migration:

- depending on the total formulation
- between 0.007 and 0.110 mg Zn per day and m²

Tin migration:

- less than 0.005 mg Sn per day and m²

Source: M. Schiller, W. Fischer; "Stabilisers for PVC pipe systems – Quo Vadis?", Plastics Pipes XII, Milan/Italy (04/2004)

TO SOLVE THE PROBLEM



KRV Round Robin test in 2005

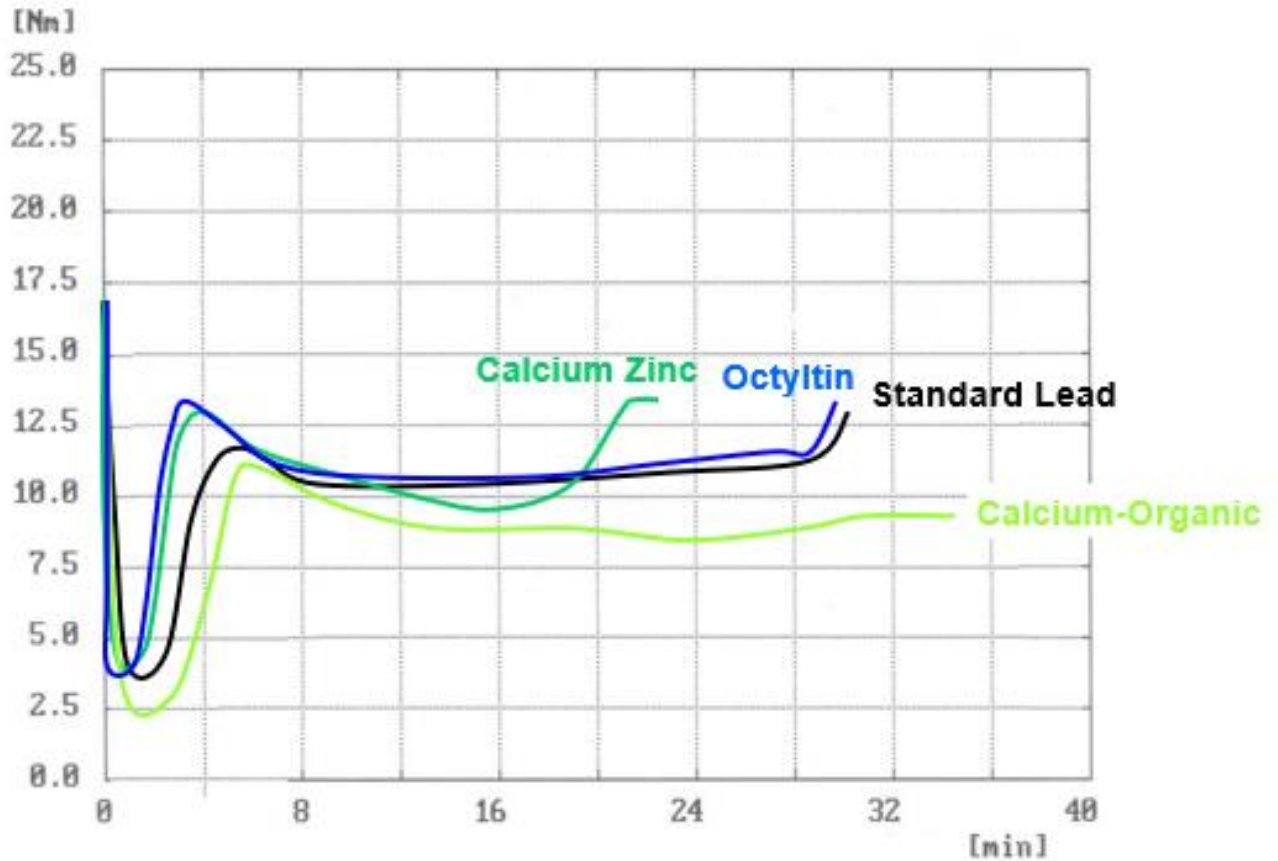
Main trial

- 4 pipes Calcium-Zinc stabilised (Ca/Zn)
- 1 pipe Lead stabilised (Ca/Pb)
- 2 pipes Tin stabilised (Ca/Sn)
- 1 pipe Calcium organic stabilised





Dynamic stability

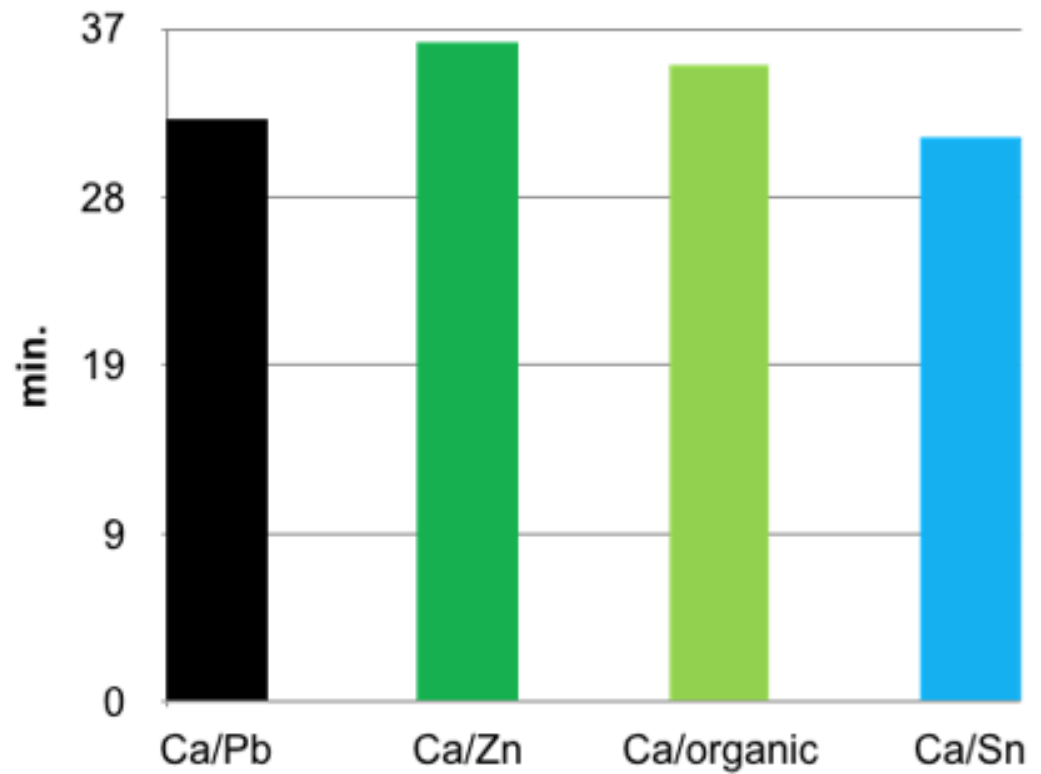


Source: M. Schiller, W. Fischer, "Stabilisers for PVC pipe systems – Quo Vadis?", Plastics Pipes XII, Milan/Italy (04/2004)

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DHC stability (average)

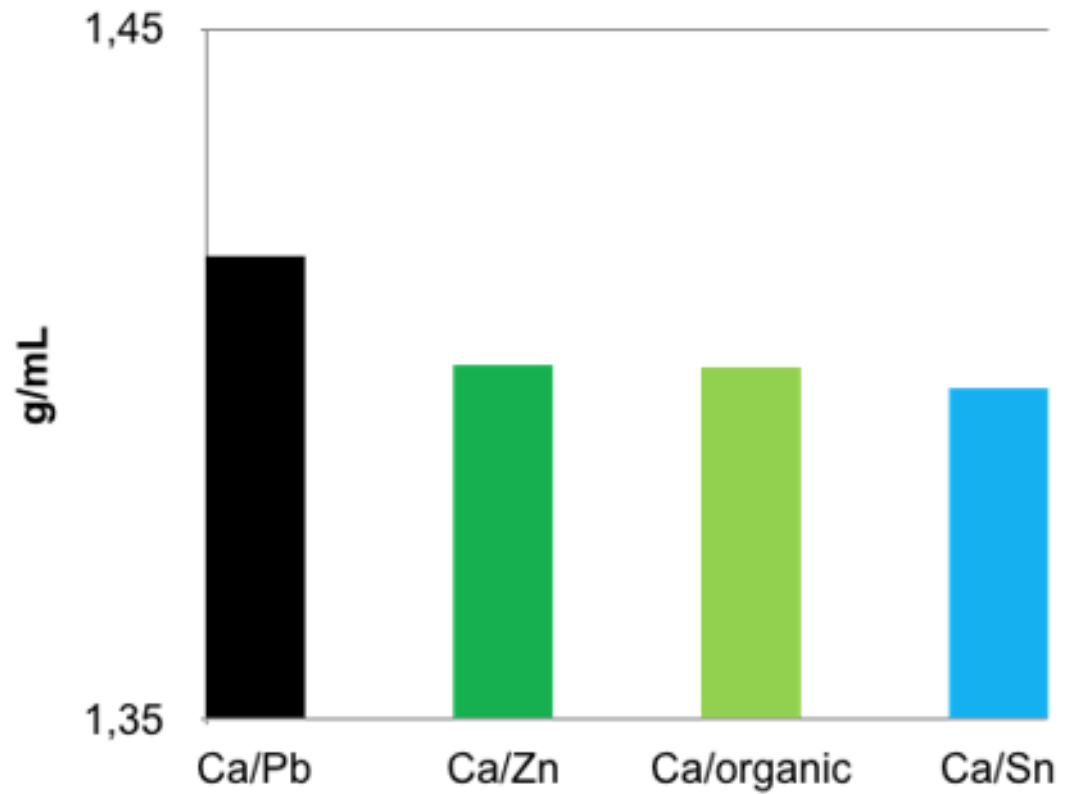


Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)

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Density of pipe (average)

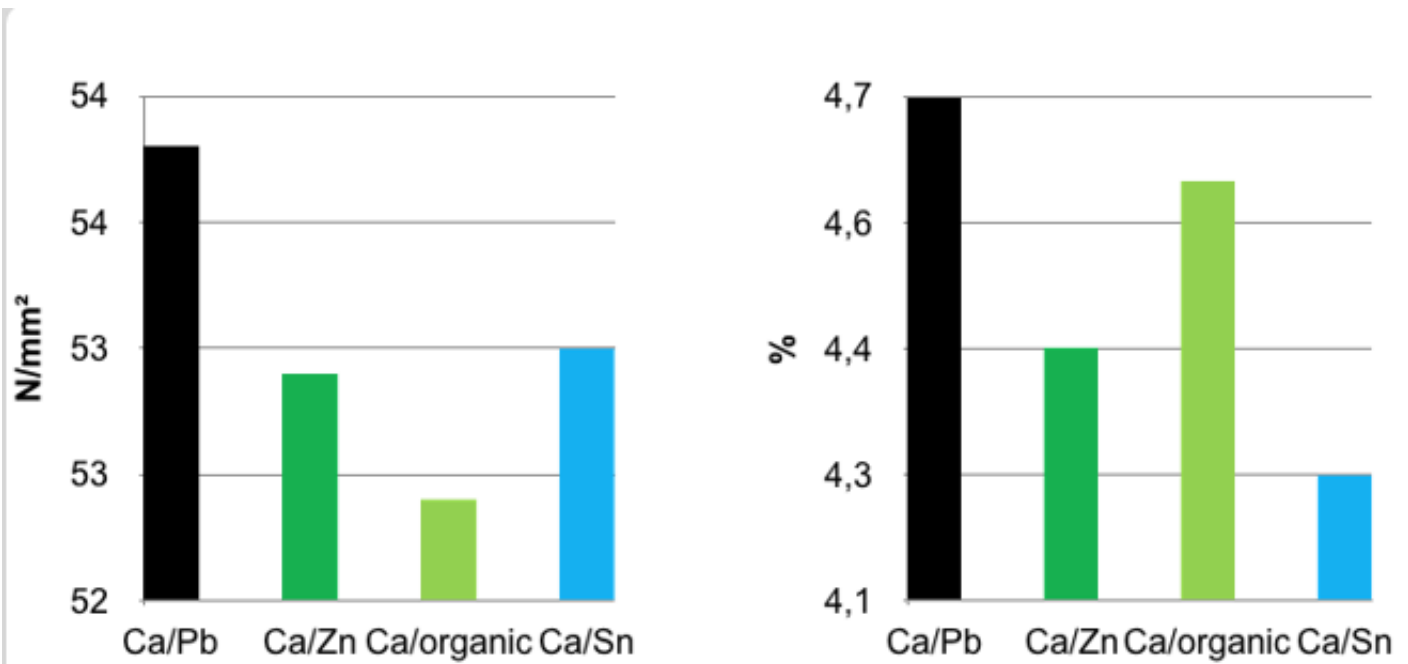


Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)

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Yield stress & Elongation at yield (averages)

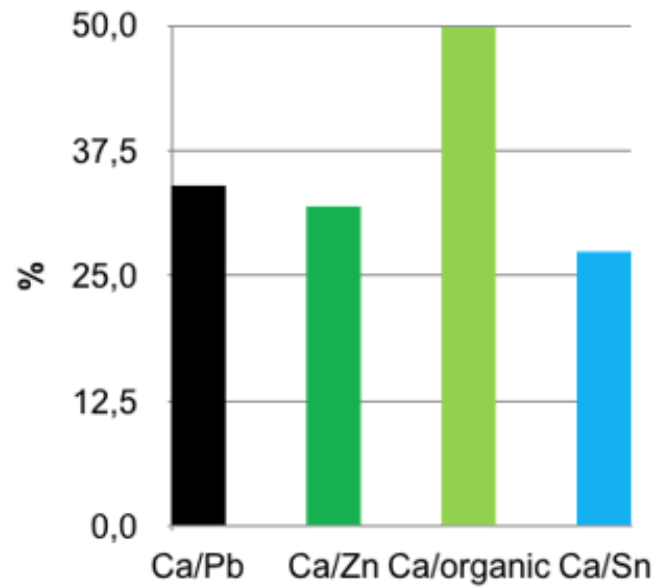
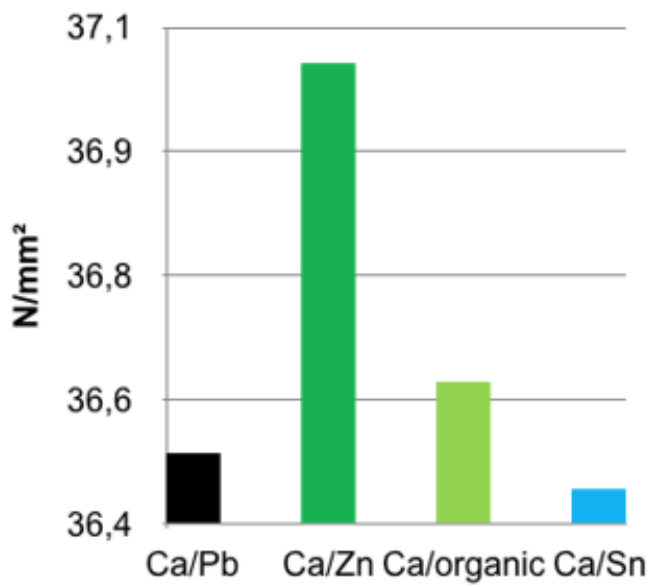


Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)

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Tensile strength & Elongation (averages)

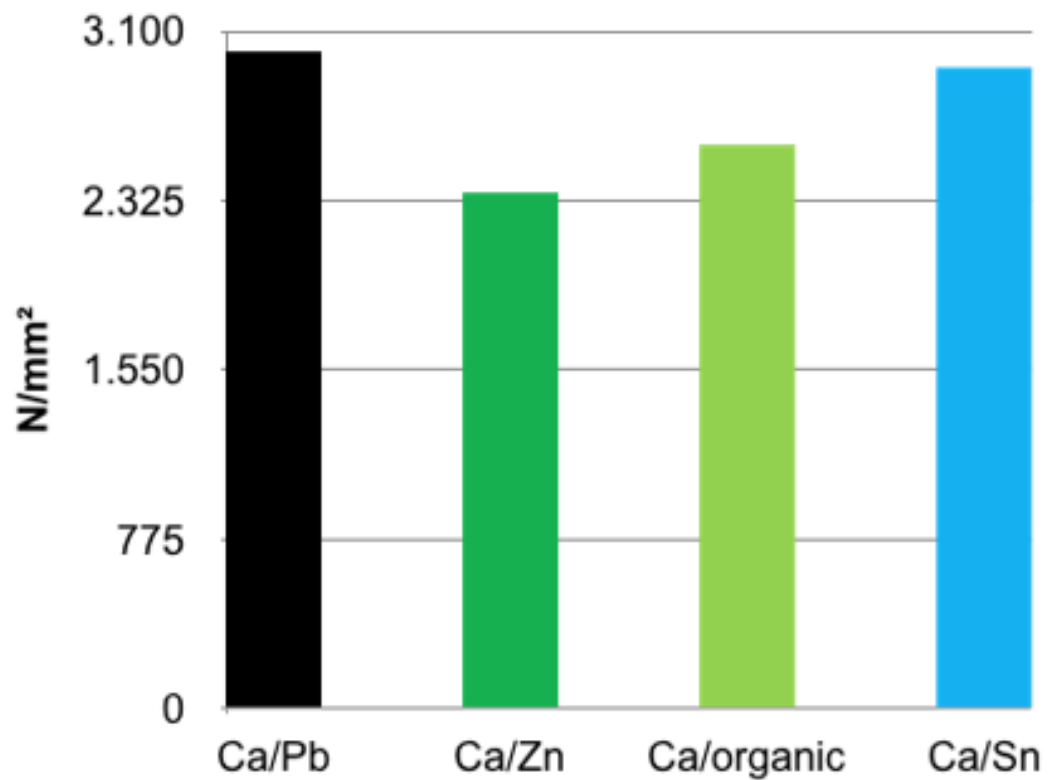


Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)





E modulus (average)

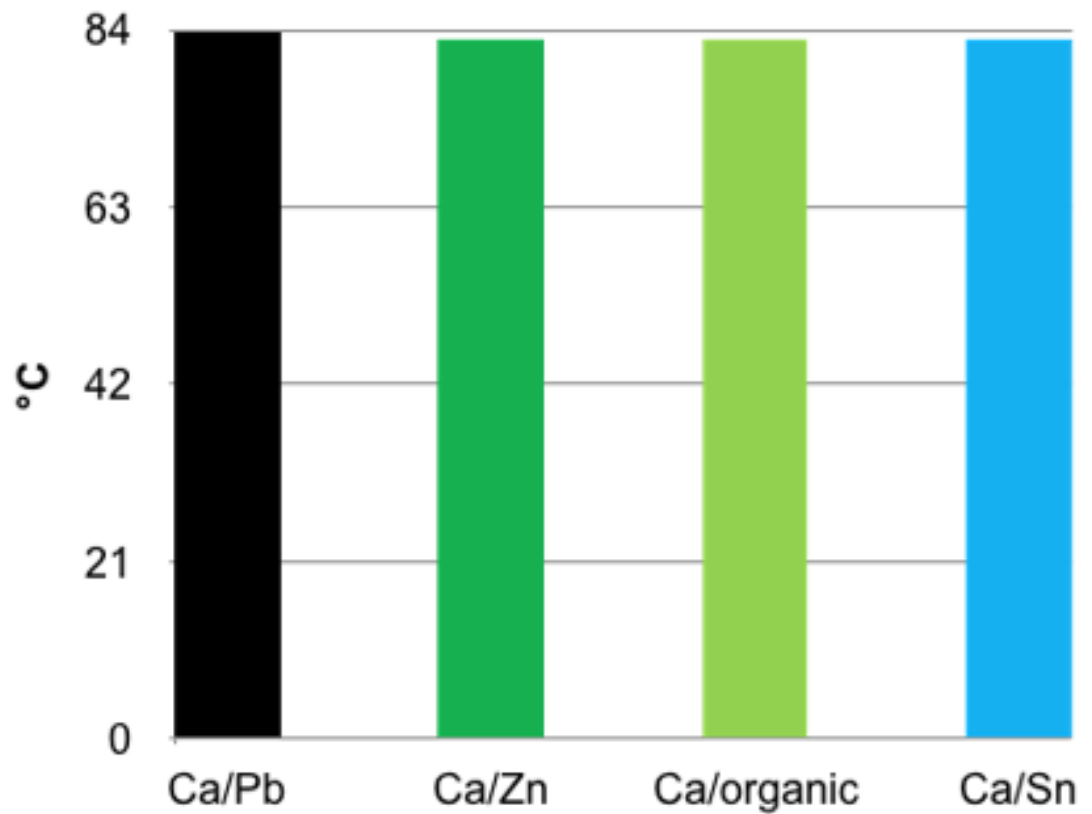


Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)

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VICAT softening point (average)



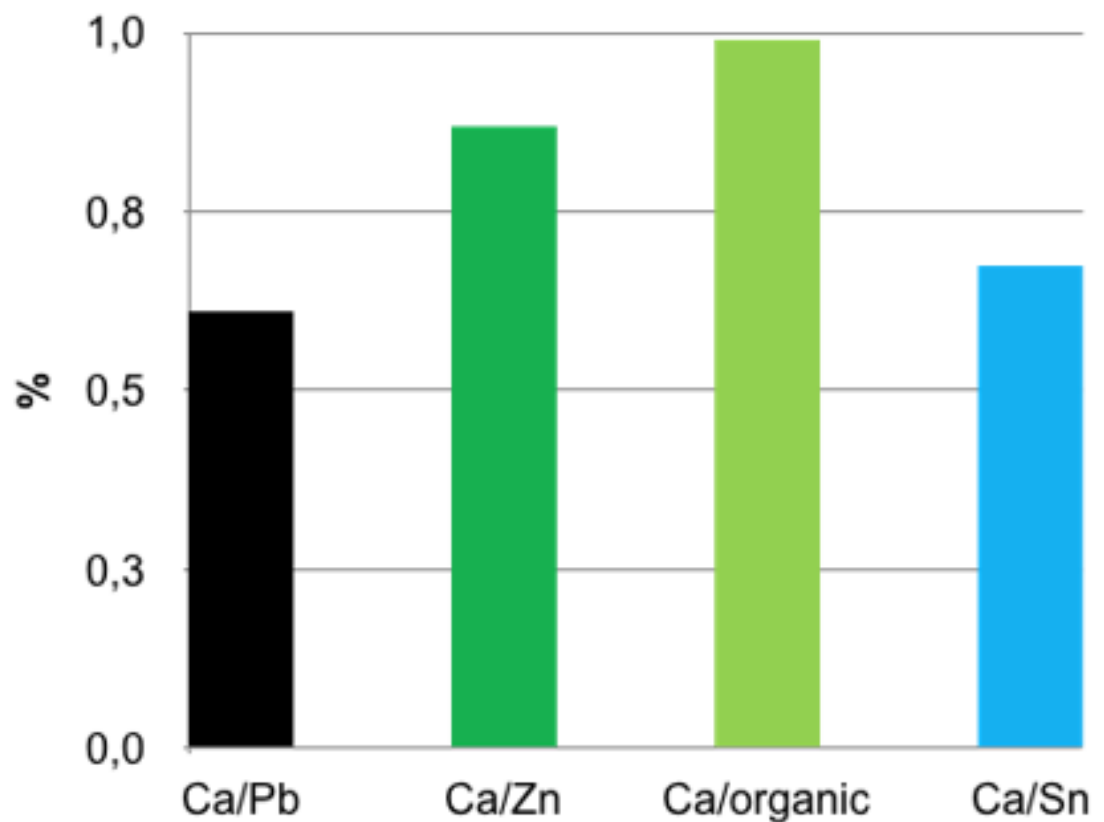
Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)

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Water absorption (average)

DIN 8061 - 4.5



Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)



Impact test

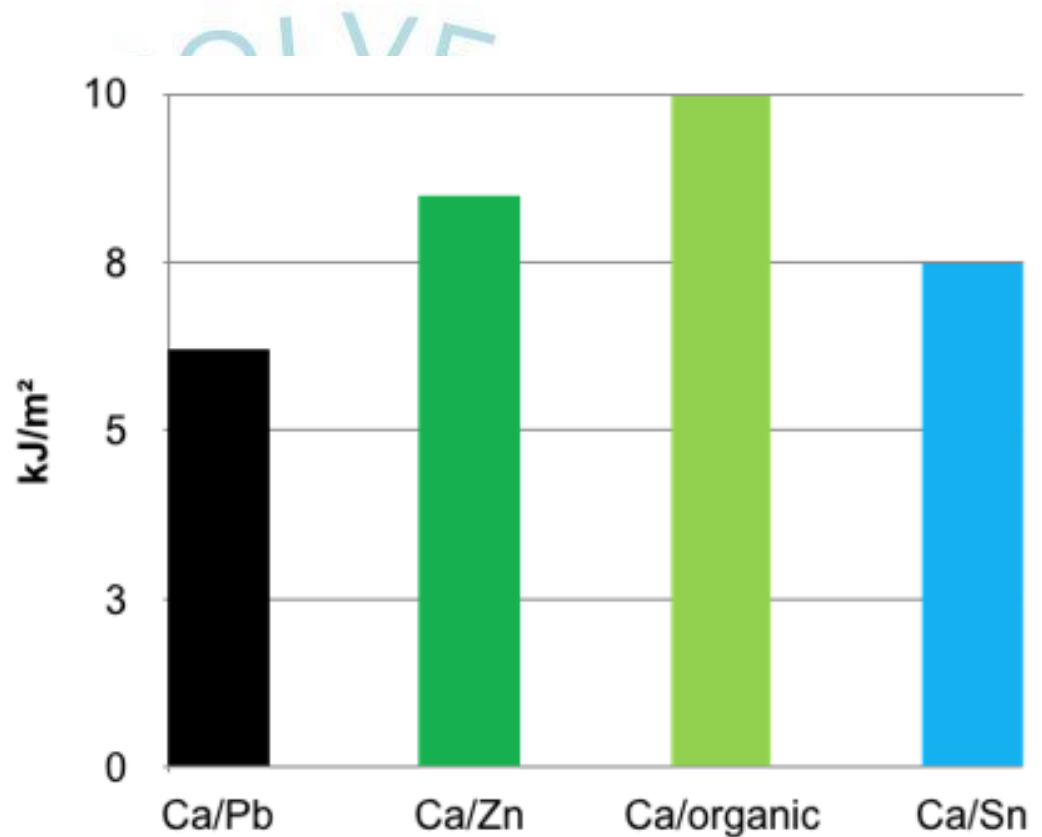
- @ 23°C all pipes passed (each 10 repetitions, no pipe broken)
- @ 0°C all pipes passed (each 10 repetitions, no pipe broken)
- @ -20°C all pipes passed (each 10 repetitions, 4 (of 20) Ca/Sn & 3 (of 40) Ca/Zn were broken)
- @ -40°C:
 - Ca/Pb – 9/10 passed
 - Ca/Zn – 28/40 passed
 - Ca/organic – 9/10 passed
 - Ca/Sn – 8/20 passed

Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)





**Impact test – Charpy (average)
double V notch, r = 0.1 mm, 23°C
DIN EN ISO 306**

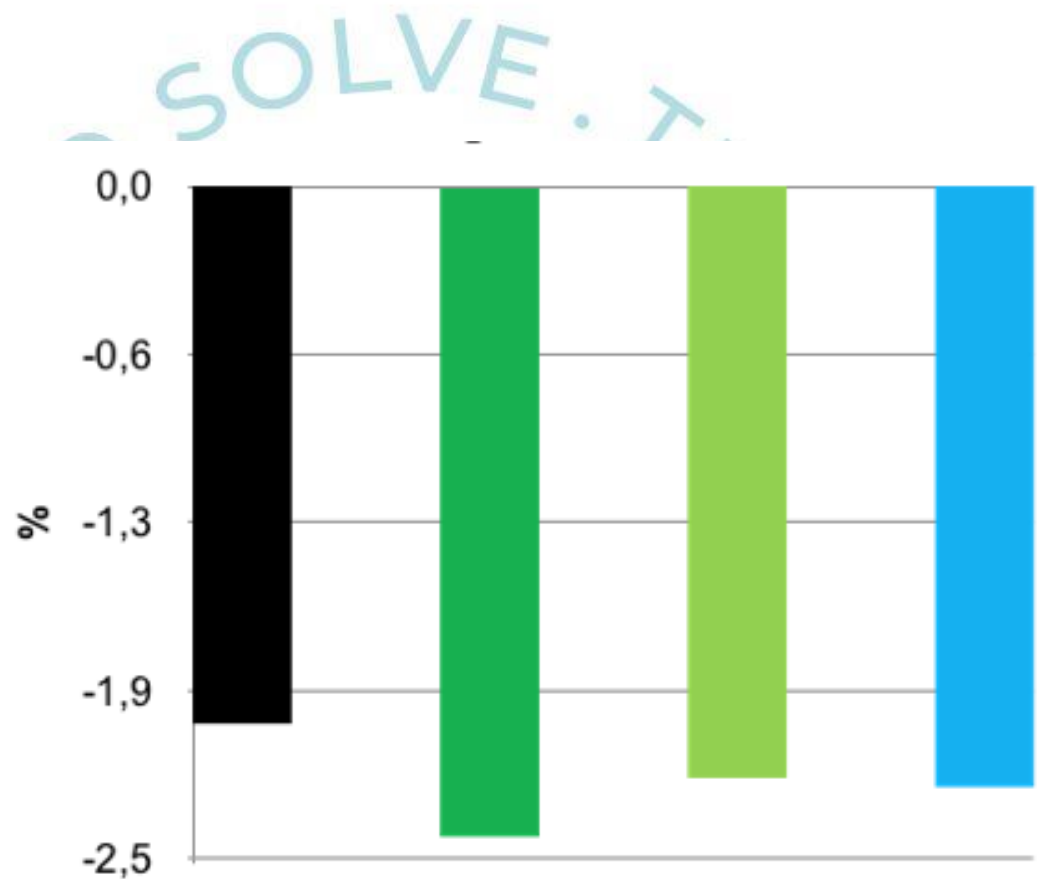


Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)



Shrinkage (average)

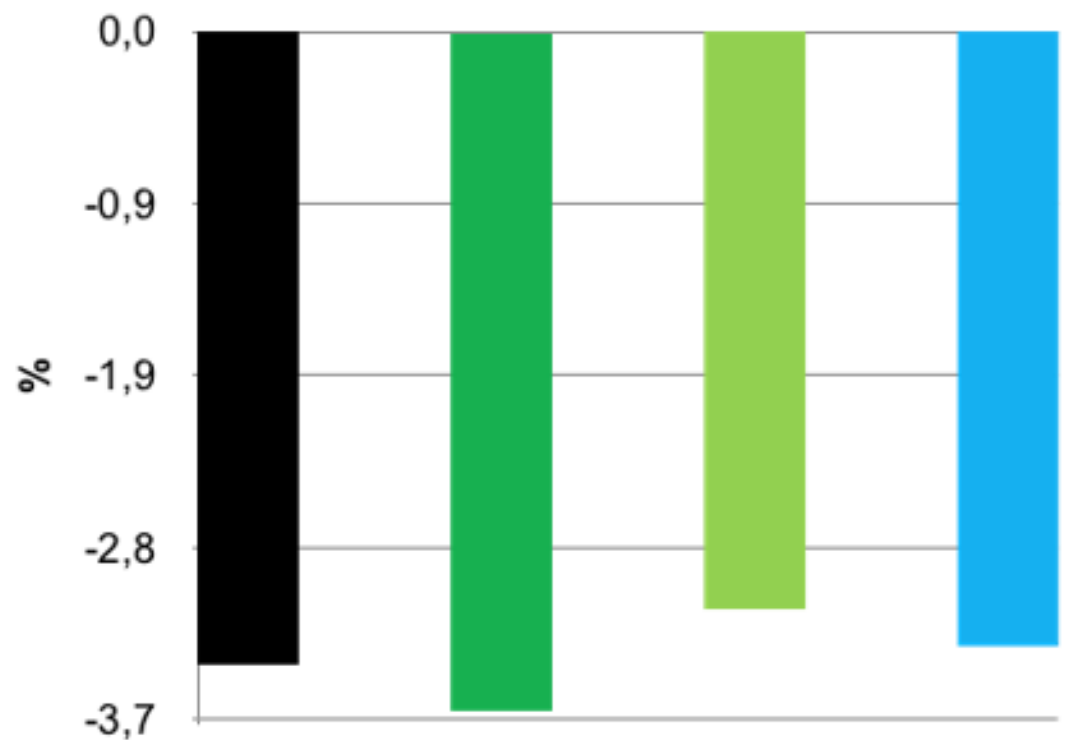
30 min @ 140°C



Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)



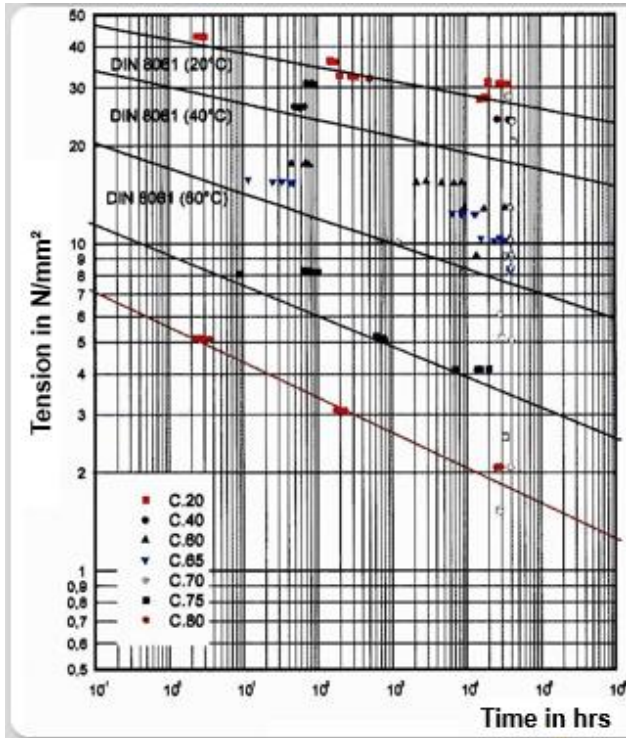
Shrinkage (average) 60 min @ 150°C



Source: E. Barth; "Das Langzeitverhalten von PVC-U-Rohren mit unterschiedlicher Stabilisierung" KRV (2005)



Pressure resistance



Pipes during main test in pressure resistance test
At 20°C in water/in air

Source: E. Barth, *KRV-Nachrichten* 1 (2003) 17-27

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Pressure resistance

- If an operating temperature for potable water pipe of 20°C is assumed an extrapolated lifetime of 2'500'000 hrs is obtained. (~ 285 years)
- If the Arrhenius plot is used the extrapolated lifetimes of the investigated pipes will be:
 - at 40°C operating temperature 10⁸ hrs (~ 11'000 years)
 - at 20°C operating temperature 10¹² hrs (~114'000'000 years)

Source: E. Barth, *KRV-Nachrichten* 1 (2003) 17-27



Platinum's activities in stabilisers

- Stabilisers for pipes: Ca/Pb, Ca/Zn and Ca/organic; approved at several big producers
- Stabilisers for fittings: Ca/Zn and Ca/organic, approved at several big producers
- Stabiliser for cables: Ca/Zn, approved at several producers
- Stabilisers for profiles and sheets: Ca/Zn, available
- Lead based booster: approved at several producers
- Ca/Zn based booster: approved at several producers
- Booster for Tin stabilised PVC
- Stabiliser blend Ca/Zn based for C-PVC

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Tin booster





Summary about stabilisers

	Pb	CaZn	Ca/organic
Thermal stability	+++	++	+++
Sustainability	—	++(+)	+++
Health & Safety	—	++(+)	+++
Initial colour	+++	++	++
Colour retention	++	++	++
Processing window	+++	++	+++
Mechanical properties	+++	+++	+++
Light stability	++	++	+
Cost efficiency	+++	++	++

Let's go together more sustainable either based on Calcium-Zinc or Calcium-Organic!

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Cover of QUEEN's Vinyl "Innuendo" © EMI