

# Lead-free stabilization for PVC pipes

## The new alternative



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# European pipe market

- Increasing use of plastics pipes over other materials: 54%
- PVC remains the material of choice: approximately 2/3 of the EU pipe market

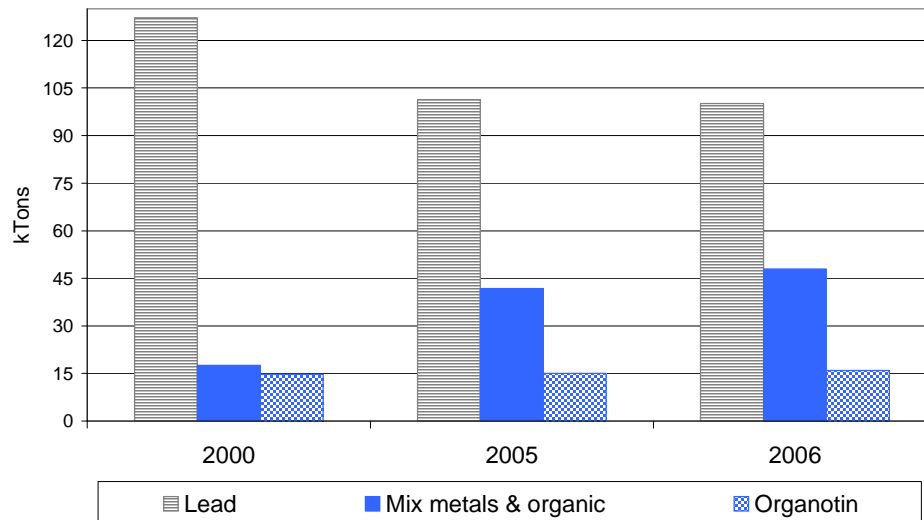
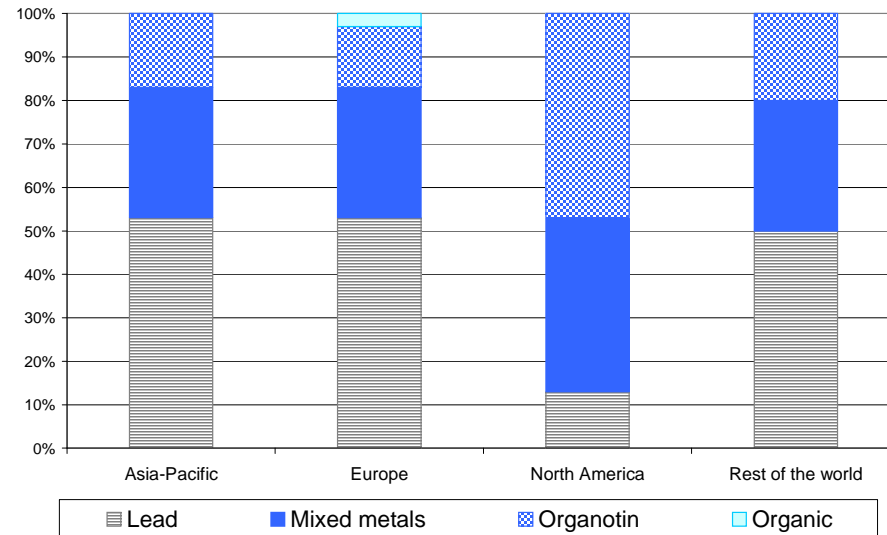
	PVC market (kt)	PVC Pipe production (kt)	Plastics pipe production (kt)
Western Europe	5625	1365	
Eastern Europe	1120	225	
Total	6745	1590	2500

## ER PVC pipe market

Source: PVC4pipes, 06/05

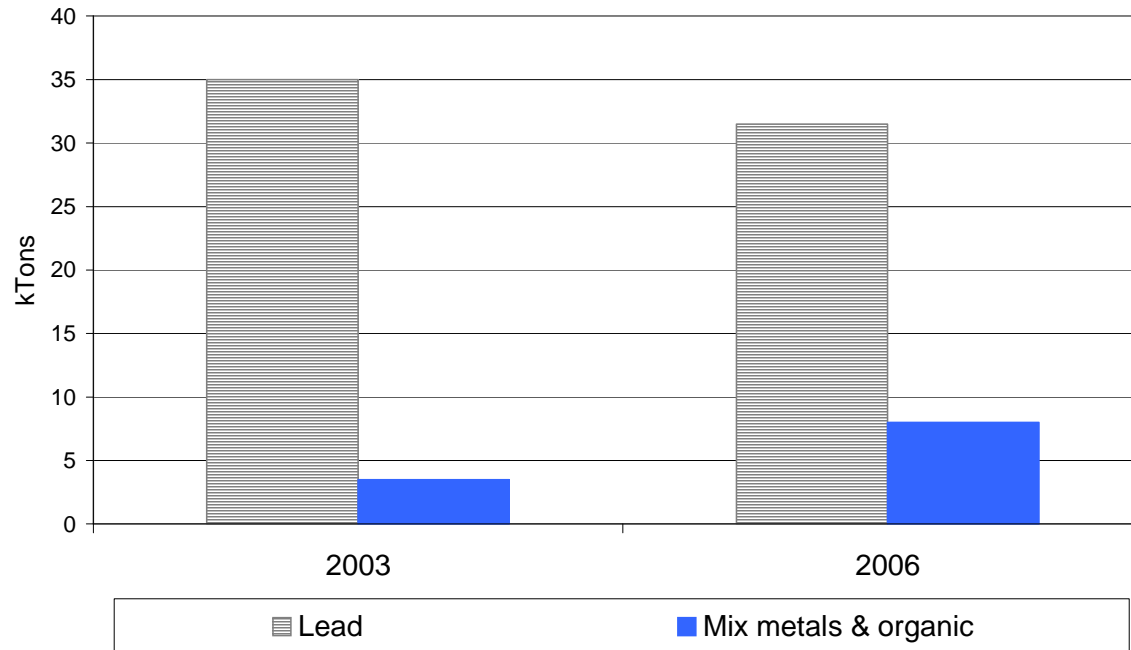
# PVC heat stabilizers (all applications)

- Lead is still the most widely used (# 50% of WW volume)
- Lead is n°1 everywhere except in North-America, where tin is predominant



- EU: Vinyl 2010 for Pb phase-out  
2010: -50% / 2015: -100%
- TEPPFA: Pb for pipes & fittings:  
2005: -25% / 2010: -100%
- ASIA (& rest of the world) should follow Europe with progressive elimination of lead.

# PVC heat stabilizers (PIPES)



- Definite move to lead free stabilizers in PVC pipes
- One of the most cost competitive market
- Pipe manufacturers are expecting high performance & cost competitive lead-free stabilizers. Current price/performance ratios of CaZn are not viewed as attractive enough to accelerate the lead phase-out.

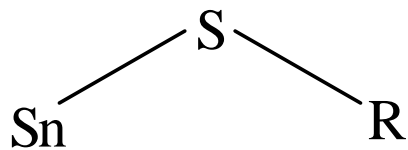
# The blocked thiol technology by Rohm and Haas

- Lead and tin based stabilizers, the oldest and best known PVC stabilizer technologies
- Rohm and Haas: high experience and technical know-how on tin stabilizers
- Stabilization mechanism with tin stabilizers involves the mercaptan moiety to substitute the labile chlorine
- But free mercaptans can not be used as such... despite highly efficient stabilizing properties, they can create offensive odor, and they are non-compatible with lead based stabilizers (cross staining when handling both systems on the same equipment, and for recycling purposes)

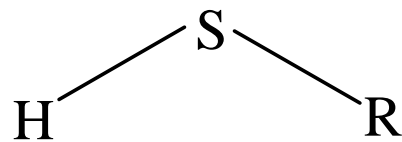
► solution is the « blocked thiol » technology

# The blocked thiol technology (cont')

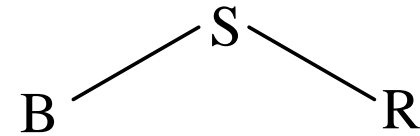
- **Patented technology:**
  - Take advantage of the efficiency of mercaptans as heat stabilizers
  - Link the mercaptan to an organic moiety to suppress adverse effects of free-mercaptans



*Tin mercaptides*



*Free mercaptans*

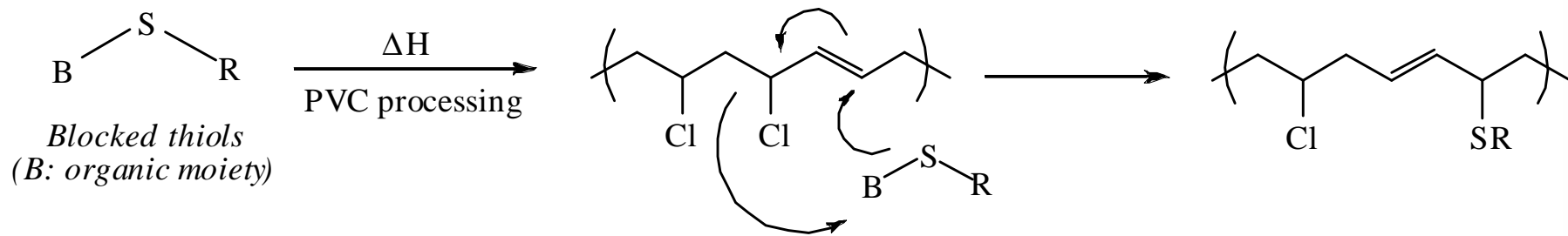


*Blocked thiols  
(B: organic moiety)*

# The blocked thiol technology (cont')

- The « blocked thiol » activation:

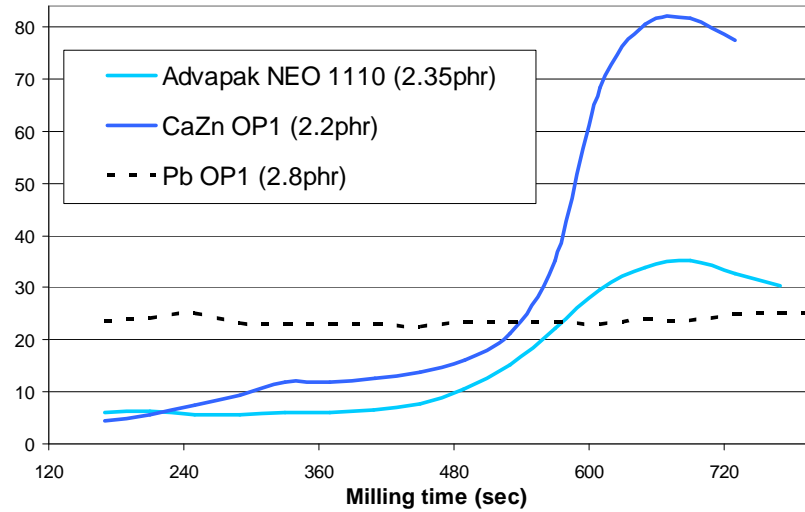
During processing of PVC, shear and temperature induce the generation of the highly active stabilizing components that immediately react with the PVC chain (concerted mechanism).



- Additional stabilization mechanisms are proposed; the “reverse reaction mechanism” is usually admitted as part of the thiols stabilizing role, resulting in particular in the absence or in delayed cross-linking observed when using thiol stabilizers.

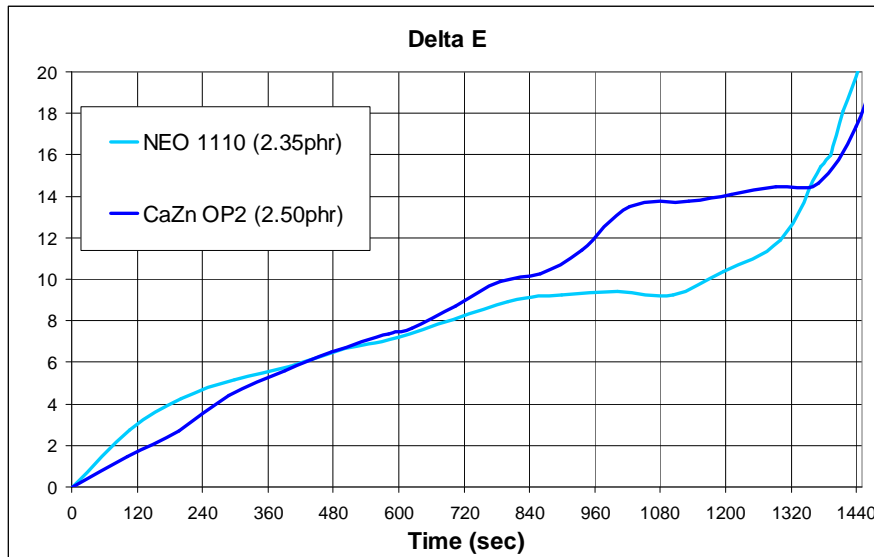
# Advapak™ NEO: efficient thermal stabilizer

Dynamic stability (Yellow Index)



- Thermal stability tests (2-roll mill and Metrastat oven). Advapak™ NEO products demonstrate better early color and mid term stability compared to tested commercial CaZn one-packs.

Delta E



Pressure pipe formulation:

PVC K68 (100) – TiO<sub>2</sub> (0.2) – CaCO<sub>3</sub> (2)

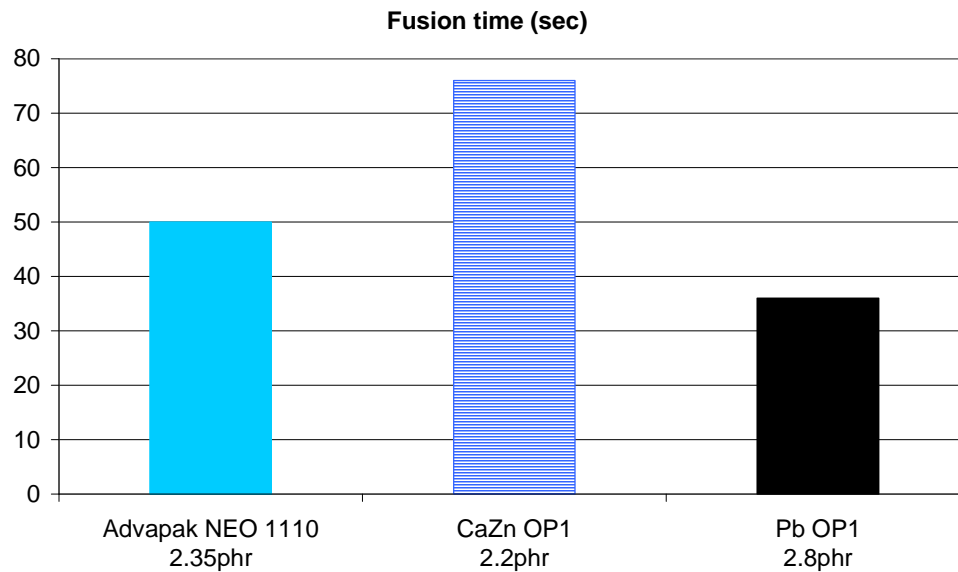
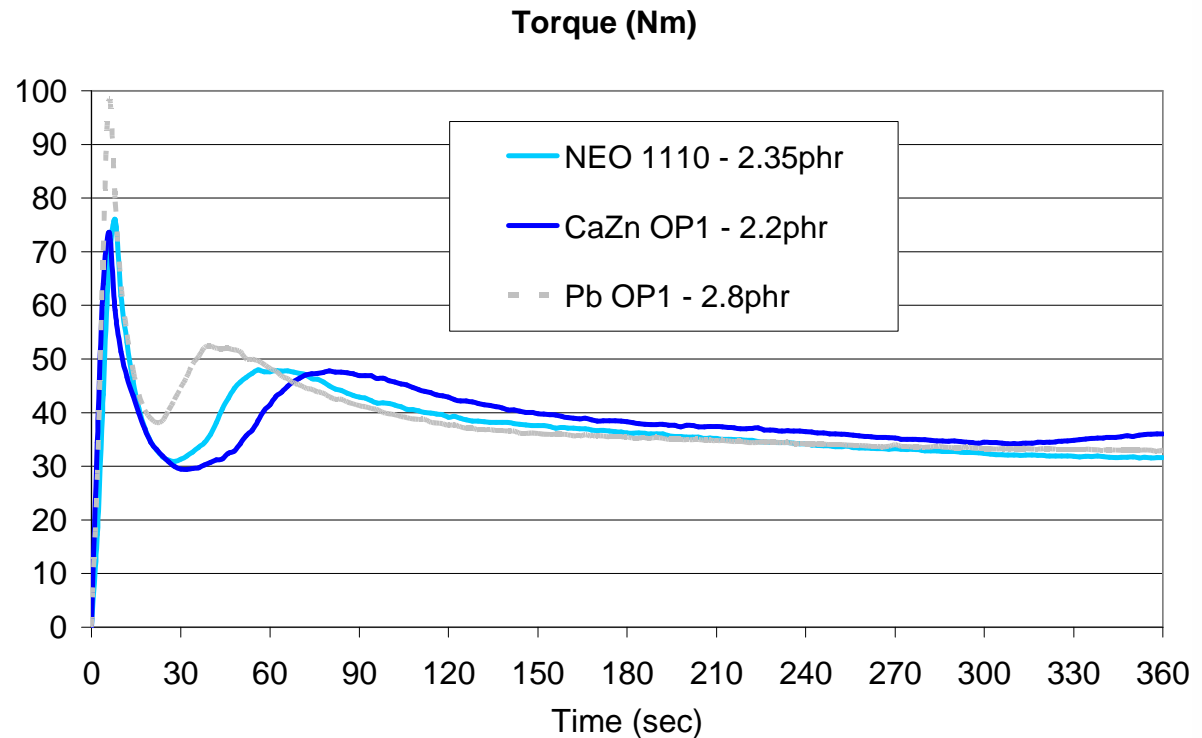
2-roll mill dynamic test 200°C

Metrastat oven 205°C

# Rheology

- Brabender data  
190°C/60rpm  
6min, 65g dry-blend

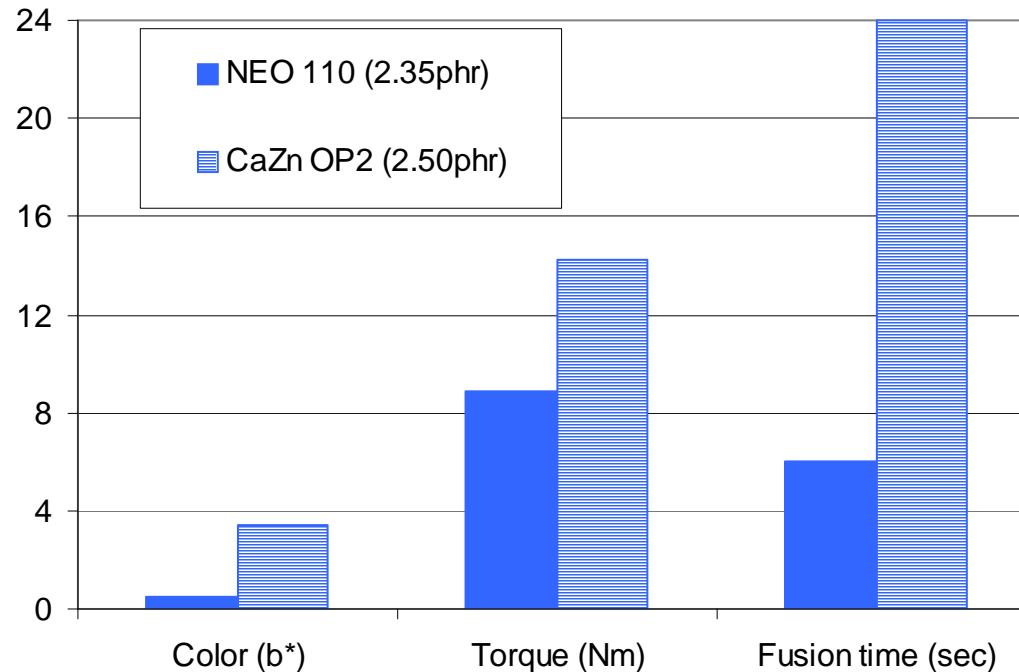
Fusion time  
Torque



- The tested commercial CaZn has much slower fusion than lead
- NEO, with closer rheology to lead, can be easily adjusted

# Enhanced recycling properties for pipes

- Advapak™ NEO products are designed to limit impact on color and rheology when using recycled PVC



## Delta color:

b\* difference on films using fresh dry-blends and 100% recycled material

## Delta torque:

fusion torque difference after 3 recycling cycles using 100% recycled material

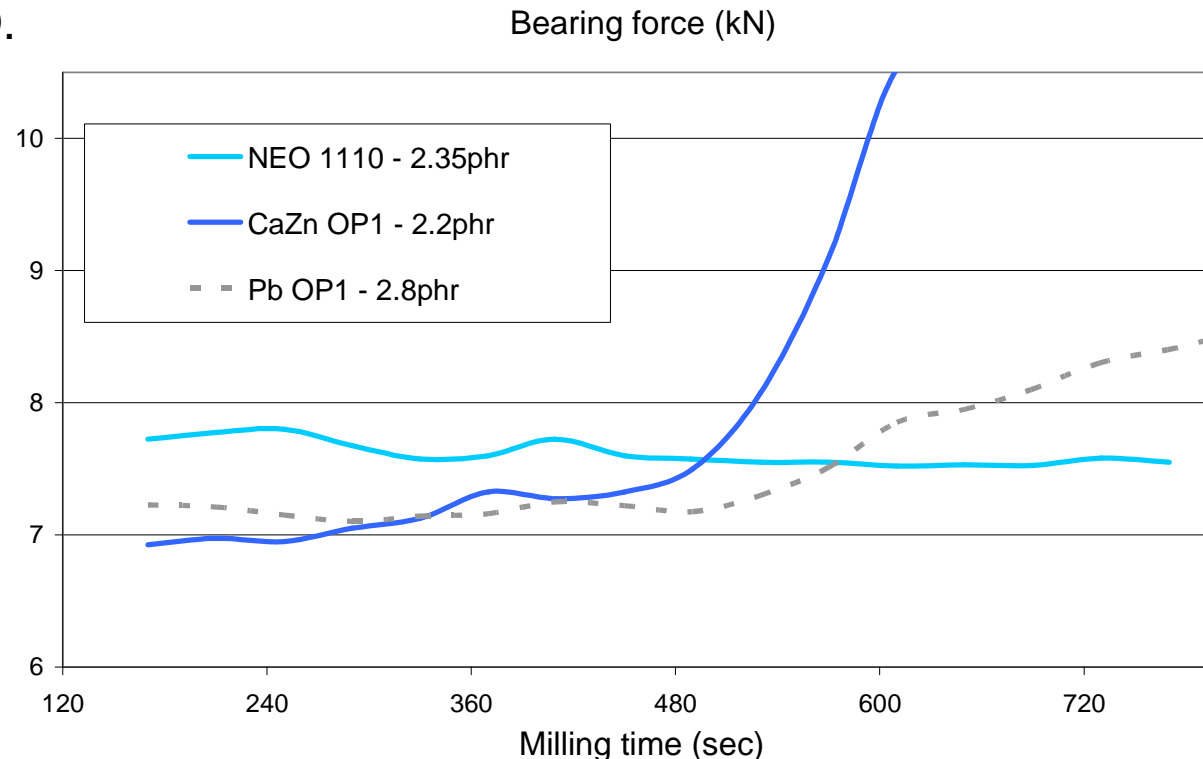
## Delta fusion time:

fusion time difference after 7 recyc. cycles using 20% recycled mat.

# Enhanced recycling properties for pipes (cont')

The ability of Advapak™ NEO not to impact rheology after several processing cycles is directly linked to the absence, or delayed, cross-linking with the blocked thiol technology.

This is visible on bearing force curves (two roll mill). While the bearing force of the standard lead and CaZn increase with milling time, the curve stays flat with NEO.



# Advapak™ NEO: pipe extrusion data (1/3)

Extruder Bausano MD2 / 46B20-A / Pipe diam. 60 mm / 2mm thick  
S\_PVC K68 (100), TiO2 (0.2phr), and CaCO3 (2phr).

Extrusion #1	Screw rpm	Back P bar	Torque Nm	Melt T °C	Temp set/act (zones/°C)						
					1	2	3	4	5	6	7
					180	180	182	185	185	193	198
NEO 1110 (2.35 phr)	34	165	294	191	179	180	181	184	184	193	198
CaZn OP2 (2.5phr)	34	170	305	190	177	180	182	185	188	196	202

Extrusion #2	Screw rpm	Back P bar	Torque Nm	Melt T °C	Temp set/act (zones/°C)							L*	a*	b*
					1	2	3	4	5	6	7			
					180	182	185	185	188	195	200			
NEO 1210 (2.54phr)	30	195	286	192	187	185	187	191	195	198	201	88.2	-0.60	10.4
CaZn OP3 (2.5phr)	27	225	318	190	185	185	184	190	192	196	200	85.7	-2.90	18.0

Under similar extrusion conditions, Advapak™ NEO demonstrate lower melt-pressure compared to the tested CaZn. Further extrusion trials have shown that this lower melt pressure allows for significantly increased output rates.

Advapak™ NEO 1210 allows excellent color hold for pipes and thus brings technical advantage for white & clear color pipes.

# Advapak™ NEO: pipe extrusion data (2/3)

Extruder Bausano MD2 / 52/23-A / Pipe diam. 72 mm / 3.3mm thick  
S\_PVC K65 (100), TiO2 (0.5phr), and CaCO3 (5phr).

Extrusion #3	Screw rpm	Back P bar	Amps	Melt T °C	Temp set/act (zones/°C)								b*	Gelation DSC
					1	2	3	4	5	6	Adap	Die		
					180	180	175	165	160	165	180	185/190/195		
NEO 1110 (2.35 phr)	40	135	19.2	183	180	179	176	166	162	169	180	185/195/195	15.4	93%
NEO 1210 (2.54phr)	40	110	19.7	184	180	179	176	166	162	169	180	185/195/195	5.8	86%
CaZn OP4 (2.8phr)	40	155	20.5	185	180	180	177	165	163	170	180	184/190/195	16.0	91%

- **Advapak™ NEO 1210:** excellent colour on pipes - preferred stabilizer for white pipes. **Advapak™ NEO 1110:** provides excellent mid and long term stability for all types of PVC pipes. The colour of the pipes with **Advapak™ NEO 1110** is equivalent to the colour with the CaZn even with a significantly lower level.

- **Advapak™ NEO 1110 Vs CaZn:** equivalent gelation - close melt T° - similar pipe colour. But: Lower melt P with **Advapak™ NEO 1110**.

This low melt P is clearly an advantage when increasing output rates.

# Advapak™ NEO: pipe extrusion data (3/3)

Extruder Cincinnati CMT45 / Pressure Pipe diam. 63 mm / 2.5mm thick  
S\_PVC K67 (100), CaCO3 (4phr), grey pigments.

	Screw rpm	Mass P bar	Torque %	Pulling m/min	Temp set/act (zones/°C)				Vicat	Gloss 60°	Gelation DSC	Melt T °C	Congo Red
					1	2	3	Die					
NEO 1110 (2.45 phr)	36	169	70	3.5	180	170	160	180/180/200/200	> 80°C	24	77%	181	t + 25%
CaZn OP4 (2.6phr)	36	178	68	3.3	180	170	160	180/180/200/200	> 80°C	20	67%	180	t

**Advapak™ NEO 1110** shows close rheology compared to the commercial CaZn, but with lower mass pressure.

Superior gelation level is achieved on NEO pipes.

Pulling speed is higher with **NEO**, and output rate could be increased further more considering the lower melt pressure (setting higher screw speed).

Both pipes have very nice aspect and overall good properties.

Pipes including **NEO** have higher residual stability.

# Lead-free stabilization for PVC pipes: The new alternative, Advapak™ NEO

- **DEDICATION TO THE PVC INDUSTRY**

Lead phase-out & increased recycling: 2 major commitments of Vinyl 2010 programme.

Advapak™ NEO: new alternative for lead replacement with excellent heat stability and good processing window

- **COST EFFECTIVENESS**

Advapak™ NEO offer very good cost-performance ratio compared to existing alternatives and help pipe producers to maintain your cost competitiveness.

- **BOOSTING RECYCLABILITY**

Advapak™ NEO: compatible with any type of stabilisers, can be combined with recycled PVC containing all types of stabilisers.

Advapak™ NEO: bring significant advantage when using recycled PVC (inhibition of cross-linking).

- **REPUTATION FOR COMPLIANCE**

Advapak™ NEO: non toxic, heavy metal free, odour less, organic based, advanced sustainable solution for PVC pipe stabilization.

Thank you.

