





Formulation Adjustments for Biobased Plasticisers

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Biobased plasticisers are becoming competitive



- Formulators have been challenged to replace traditional plasticisers
- Cost has been an important barrier for new products
- New biobased materials, especially in Brazil, have been competitive, motivating faster replacements
- Results presented draw on 5 years experience of actual industrial usage

Question: What is the main limitation for business development of newer bio-based chemicals or additives?



Source: SpecialChem Feb 1, 2014

Laboratory Experiments



- Various plasticisers
 - DEHP (Di-Ethyl-Hexyl Phthalate) or DOP (Di-Octyl Phthalate)
 - DINP (Di-IsoNonyl Phthalate)
 - DOA (Di-Octyl Adipate)
 - Octyl Epoxy Soyate
 - Methyl Epoxy Soyate
 - Nexo B5
- (Complex Esters of Soybean Oil, PATENT US 8623947)
- Nexo MB50
- In various plastisol formulations for coated fabrics applications
 - Top, crystal clear
 - Top, typical synthetic leather formulation, white
 - Expanded layer
 - Base and top layers for low temperature flex test
- Compared both directly and after adjustments

Gel Rates



 Gel rates obtained, consistent with viscosity and efficacy of selected plasticisers



Viscosity Ageing



• Viscosities of paste, same plasticizer content, top coat



Viscosity

Component	phr
NORVIC P75 LMT	100
CaZn Stabiliser	2
Plasticiser	60*

^{*} For non-epoxy plasticisers 3 phr of ESBO

Obs.: Brookfield Viscosity, ASTM D 1824 - 95 (2010), 20 rpm, 23 °C

Viscosity Ageing



• Viscosities of paste, same plasticizer content, base coat



Viscosity

Component	phr
Solvin 367 NK	100
Plasticiser	60
Kicker KZn	2
CaCO3	20
MB AZDC	6

Obs.: Brookfield Viscosity, ASTM D8124 - 95 (2010), 20 rpm, 23 °C

Viscosity Ageing - Adjustments



• Viscosities of paste, same plasticiser content, adjusted resin combination, top coat

	DOP	Nexo B5, adj	Nexo MB 50
NORVIC P75 LMT	70	100	70
SOLVIN 367 NK	30	-	30
DOP	55	-	-
ESBO	5	-	-
Nexo B5	-	60	-
Nexo MB50	-	-	60
CaZn Stabiliser	2	2	2
CaCO ₃	30	30	30
MB TiO ₂ / pls (70/30)	8	8	8
Ultramar Blue GP58	0.050	0.050	0.050
Ultramar Violet V5	0.006	0.006	0.006

Viscosity

Obs.: Brookfield Viscosity, ASTM D1824 - 95 (2010), 20 rpm, 23 °C

Viscosity Ageing - Adjustments

 Viscosities of paste, same plasticiser content, adjusted resin combination, base coat

		Nexo B5	Nexo MB	
	DOF	Adj	50 Adj	
SOLVIN 367 NK	50	80	70	
SOLVIN 370 HD	50	20	30	
DOP	60	-	-	
ESBO	5	5	5	
Nexo B5	-	60	-	
Nexo MB50	-	-	60	
KZn Kicker	2	2	2	
CaCO ₃	40	40	40	
ADC (diluted 1:1 in pls)	4.5	4.5	4.5	
MB TiO ₂ / pls(70/30)	5	5	5	

Viscosity

Obs.: Brookfield Viscosity, ASTM D1824 - 95 (2010), 20 rpm, 23 °C

Film Transparency

- Transparency was evaluated based on presence of bubbles
 - Formulations:

#	Plasticiser
1	DOP
2	DINP
3	DOA
4	Octyl E.S.
5	Methyl E.S.
6	Nexo B5
7	Nexo MB50

Component	phr
NORVIC P75 LMT	100
CaZn Stabiliser	2
Plasticiser	60*

* For non-epoxy plasticisers 3 phr of ESBO

Thermal Stability

• Epoxy materials improve stability significantly

Thermal Stability – adjustments

• Stabilizing was similar at 5 minutes for Nexo B5 with 0.5 phr CaZn stabilizer when compared to 3 minutes in the DOP formulation

Expansion

• Expansion rates of different formulations are shown below

SOLVIN 367 NK	100
PLS	60
KZn Kicker	2
CaCO ₃	20
Azodicarbonamide (diluted 1:1 in plasticiser)	6

Expansion – adjustments

- The use of varied concentrations of kicker and expansion agent had no significant effect on the quality and size of cells, or total expansion thickness
- Adjustment of viscosities was very effective to match or even improve expansion rates and cell quality/size of foam layers

Formulations:		B5	MB50	
	DOP	Adj	Adj	
SOLVIN 367 NK	50	80	70	
SOLVIN 370 HD	50	20	30	
DOP	60	-	-	
ESBO	5	5	5	
Nexo B5 (Complex epoxy esters)	-	60	-	
Nexo MB50 (Complex epoxy esters)	-	-	60	
KZn Kicker	2	2	2	
CaCO ₃	40	40	40	
Azodicarbonamide (diluted 1:1 in pls)	4.5	4.5	4.5	
MB TiO ₂ / plasticiser (70/30)	5	5	5	

Industrial Experience

- Exudation
 - Compatibility is key
 - Oxirane index
 - lodine index
 - Molecular weight
 - Aliphatic content
 - Attention to viscosity reducers
 - Suppliers of bio-based plasticisers should provide limits of usage
- Odour
 - Key issue is noted by operators
 - Final articles are normally not affected
 - Masking agents can be used
- Colour
 - Slight yellowing of clear and white formulations
 - Easily adjustable with blue and violet pigments
 - On other colours, almost no observable impacts
 - Care must be taken with potential interactions
 - Such as copper beta-phthalocyanine blue

Industrial experience

- Low Temperature adjustments
 - Opportunity to reduce costs

	PRC	DD A	PROD B		PROD C		PROD D		
	TA	BA	TB	BB	TC	BC	TD	BD	
NORVIC P75 LMT	100	-	100	_	100	_	100	-	
SOLVIN 370 HD	-	70	-	50	_	50	-	50	
SOLVIN 367 NK	-	30	-	50	_	50	-	50	
DOP	20	40	-	_	_	_	-	-	
DOA	40	20	40	20	30	10	20	-	
Nexo B5	-	-	25	40	35	50	45	60	
CaZn Stabiliser	2	-	2	_	2	_	2	-	
ESBO	5	_	-	_	_	_	_	-	

Obs.: Kicker, expansion agent, pigments, Calcium Carbonate added equally in all formulations

Test samples with 1.5 mm thickness, evaluated under low temperature, with the following weights:Top layer:300 g/m²Base layer:350 g/m²NWF:150 g/m²Total:800 g/m²

Industrial Experience

- Volatility
 - Inherent to plasticiser choice
 - New, wider range of options allows formulations adjustments

- Deaeration
 - Evaluate for each condition
 - Viscosity adjustments are recommended
- Thermal stability
 - Opportunity to reduce costs
- Resilience
 - Bio-based materials offer higher resilience (higher elongation and higher tensile strength) than traditional plasticisers

Conclusion

- Cost is (was) key issue for change
- Industrial usage proves viability of bio-based plasticisers
- Adjustments are necessary
- New slate of products allows greater formulation options
- Upcoming developments should improve current situation
- Biobased additives present a good opportunity for PVC to stand out as a leader in the formulation of renewable plastics

THANK YOU!

http://www.specialchem4polymers.com/communitypulse/clicknvote.aspx?id=746&lr=mpa1403238_3cnv&li=100128367

Ongoing click'n'vote With a decline in DOP demand in Europe, which plasticizer will be more in demand in 2014-15?

