

# **Specialty Plasticizers: Current Technology and New Developments**

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# Overview

- Introduction to Genovique Specialties
- Background
  - Compounding and definitions
  - EH&S
- Benchmarking study in plastisol
- Examples - Benzoates esters (high solvators)
  - Screen ink
  - Resilient flooring – Formulary approach
- Summary



# **Introduction to Genovique Specialties Corporation**



# Long History for a New Company

- Based in Rosemont, IL (Chicago metropolitan area)
- Technology leader in high-performance specialty polymer and food additives
- Global company established in 1931
- 1<sup>st</sup> esterification process in Chattanooga, TN 1963
- Purchased Chestertown, MD facility 1994
- Purchased Kohtla-Järve, Estonian Plant 1995
- Acquired by Arsenal Capital Partners in 2005
- Joint venture in Wuhan, China established 2006
- Genovique Specialties Corporation launched October 2008



# Plasticizers for Vinyl Applications

- Benzoflex<sup>®</sup> plasticizers are, as a class, high solvators for vinyl
  - Dipropylene glycol dibenzoate: 40+ years of use in vinyl flooring
  - Dipropylene/Diethylene glycol dibenzoate
  - Blend of three dibenzoates Blend 2088: Established industry benchmark high solvator in Europe
  - Propylene glycol dibenzoate: Resilient flooring wear/clear layers, improved stain resistance
  - TMPD benzoate/isobutyrate blends 1046/6000: Low stain, lower plastisol viscosity
  - TMPD dibenzoate: Plastisol screen ink
  - Isodecyl benzoate and 2-ethylhexyl benzoate: Plastisol viscosity control



# New Specialty Plasticizers

- **Benzoate Blend 532: New! High solvator dibenzoate for resilient flooring application**
- **Benzoate Blend 953: New! High solvator for vinyl applications**
- **Benzoate 502: New! Moderate solvator for demanding plastisol applications (Stain and bleed resistance)**



# Other Plasticizers for Vinyl Applications

- Admex<sup>®</sup> polymeric plasticizers
  - Line of products from low to high molecular weight polymerics
  - Permanent products for plastisol process, film and extruded applications
- Generic plasticizers



# Background



# Model Flexible PVC Compound

- PVC Resin
  - Primary - General purpose, dispersion
  - Secondary - Copolymer, blending
- Plasticizer: *Solid or liquid organic material incorporated to soften the polymer and make it more workable.*
  - Primary (general purpose)
  - Specialty (adds performance to primary plasticizer)
- Heat stabilizer(s)
- Other - filler, pigment, lubricants, biocide, uv stabilizers, process aides, polymers



# Chemical Classes Of Plasticizers

- Phthalates (ortho, iso and tere)
- Abietates (terpenes)
- Adipates
- Azelates
- Benzoates
- Citrates
- Epoxy
- Glutarates
- Glycol esters
- Hydrocarbons
- Hexahydrophthalates
- Chlorinated paraffin
- N and Isobutyrate
- Pentaerythritol esters
- Phosphates
- Polyesters
- Ricinoleates
- Sebacates
- Sulphonamides
- Sulfonates
- Trimellitates
- Soy and other oil derivatives
- Ethers



# Plasticizer Types

- **General purpose**
  - Examples: DOP, DINP
  - Combination of cost and performance
- **Specialty**
  - Examples: **Benzoates**, phosphates, polymerics, adipates, azelates, other phthalates, etc.
  - Added value over General purpose
- **Secondary**
  - Examples: Oils, chlorinated paraffins
  - Reduces costs



# Specialty Plasticizers

- **High Solvators** - polar, aromatic
  - Fast fusion, compatible, stain resistance
- Low temperature flexibility - non-polar, aliphatic
- Permanence - polymeric, higher molecular weight esters
  - Low volatility, migration resistant
- Flame retardant - phosphorous, other



# Plasticizer Properties











Plasticizer	Plasticizer Acronym/Trade Name	Molecular Weight	Specific Gravity	Small's Solubility Parameters
Dibutyl Phthalate	DBP	278.3	1.046	9.41
Diisobutyl Phthalate	DIBP	278.3	1.040	9.20
Butyl Benzyl Phthalate	BBP	312.4	1.119	9.88
DEG/DPG Dibenzoate	Blend 50	328.0	1.154	9.72
DEG/DPG/TEG Dibenzoate	Blend A	332.0	1.160	9.80
DPG Dibenzoate	DPGDB	342.3	1.129	9.61
Diisoheptyl Phthalate	DIHP	362.0	0.994	8.93
Alkyl Benzyl Phthalate	ABP	368.0	1.070	9.55
Diocetyl Adipate	DOA	370.6	0.924	8.46
Alkylsulphonic phenyl ester	ASE	376.0	1.050	
Di 2-ethyl hexyl Phthalate	DEHP	390.6	0.982	8.84
Diocetyl Phthalate	DnOP	390.6	0.978	8.90
Diisoctyl Phthalate	DIOP	390.6	0.982	8.73
Diocetyl Terephthalate	DOTP	390.6	0.984	
Diisononyl Adipate	DINA	398.6	0.917	
Acetyltributyl Citrate	ATBC	402.0	1.048	9.04
Diisononyl Phthalate	DINP	418.6	0.973	8.88



# Non Phthalates

- In EU a drive to non phthalates exists
  - Labeling
  - REACH
  - ECHA
- In US there is a heightened sensitivity to phthalates



Products	Risk Phrases	Symbols	Products	Risk Phrases	Symbol
DEHP	Category 2 reproductive toxicant R60 : <b>May impair fertility.</b> R61 : <b>May cause harm to the unborn child.</b>		DPGDB	R 51/53 – <b>Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.</b>	
DBP	Category 2 reproductive toxicant R50: <b>Very toxic to aquatic organisms.</b> R60 : <b>May impair fertility.</b> R61 : <b>May cause harm to the unborn child.</b>	 	2EHB	None	None
			TMPD Benzoate isobutyrate Blend 1046	R38 – <b>Irritating to skin.</b> R43 – <b>May cause sensitization by skin contact.</b>	
			PGDB	None	None
BBP	Category 2 reproductive toxicant R50/53 : <b>Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.</b> R60 : <b>May impair fertility.</b> R61 : <b>May cause harm to the unborn child.</b>	 	Blend A	R52/53 – <b>Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.</b>	None
			TMPD Benzoate Isobutyrate Blends, 6000	R38 – <b>Irritating to skin.</b> R43 – <b>May cause sensitization by skin contact.</b>	
DIBP <i>December 1, 2010</i>	Category 2 reproductive toxicant R61 : <b>May cause harm to the unborn child.</b> R62 : <b>Risk of impaired fertility.</b>		Dibenzoate 904	None	None
			Benzoate 532	R52/53 – <b>Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.</b>	None
DIHP <i>December 1, 2010</i>	Category 2 reproductive toxicant R61 : <b>May cause harm to the unborn child.</b>				



# Benchmark Study: Plastisol



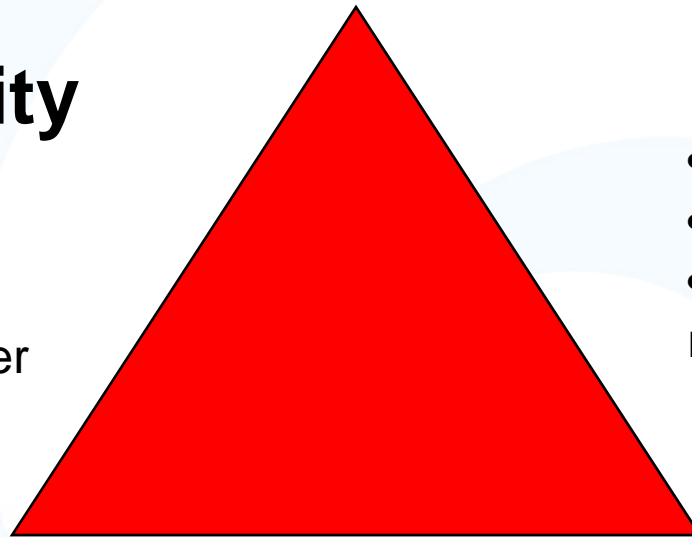
# Basic Vinyl Evaluation Performance Parameters

## Compatability

- Solubility Parameter
  - Small's
  - Hansen's
- Interaction Parameter
- Loop spew

## Permanence

- Molecular Weight
- Volatility
- Extraction, migration resistance



## Efficacy, Efficiency

- Tg Suppression
- Tensile, hardness, LTF, FR, Density

## *Processability* –

Plastisol Viscosity, Rheology, Gel/Fusion, Dry Blend, Melt Process etc.



# Formulation

<u>Raw Material</u>	<u>PHR</u>
Dispersion Resin	85
Blending Resin	15
Primary Plasticizer	40
2,2,4-Trimethyl-1,3-Pentenediol Diisobutyrate	10
Blend of Isoparaffinic and Cycloaliphatic Solvents	5
ESO	2
Ca/ Zn Stabilizer	3
<b>Total</b>	<b>160</b>

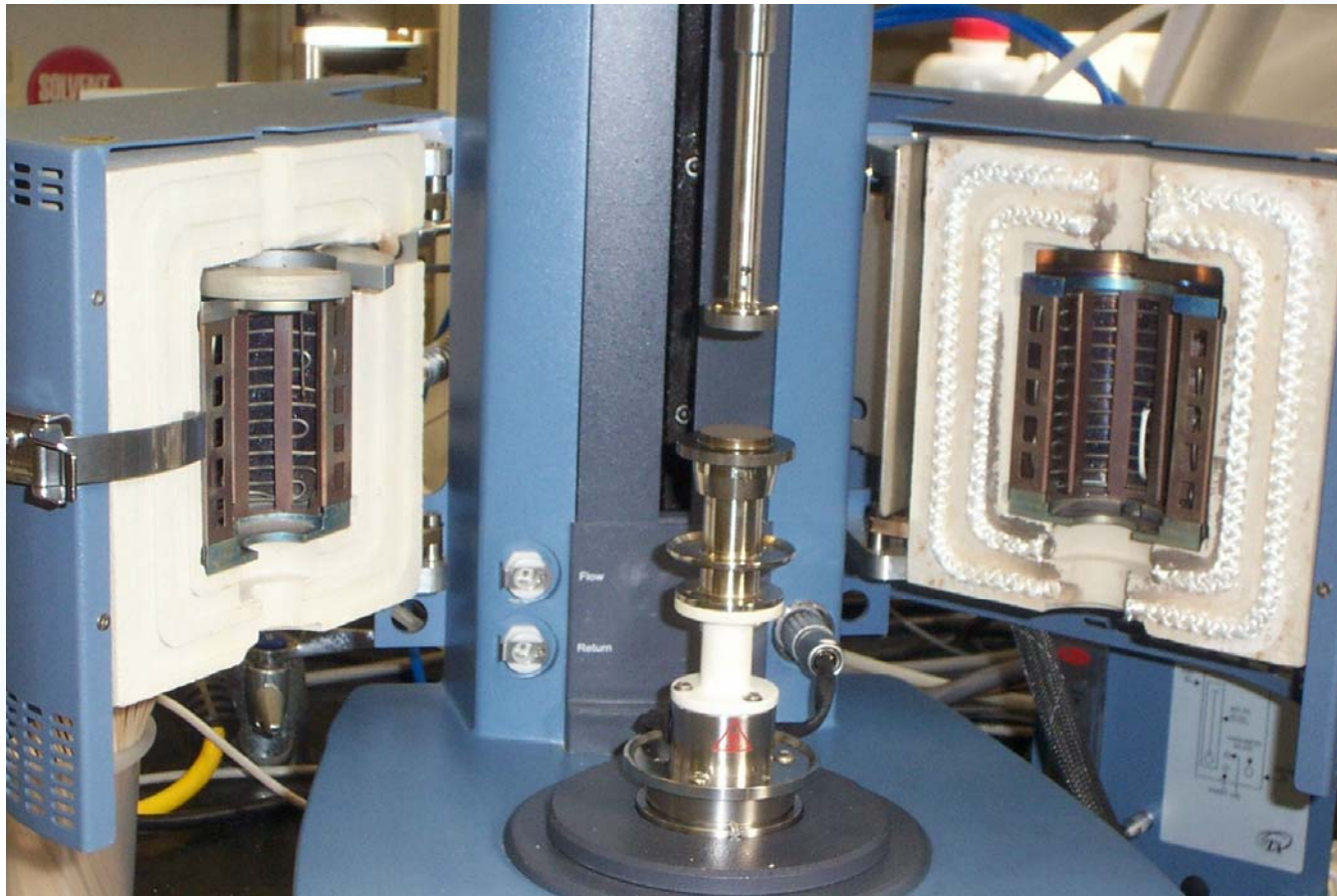


# Plasticizers in Screen

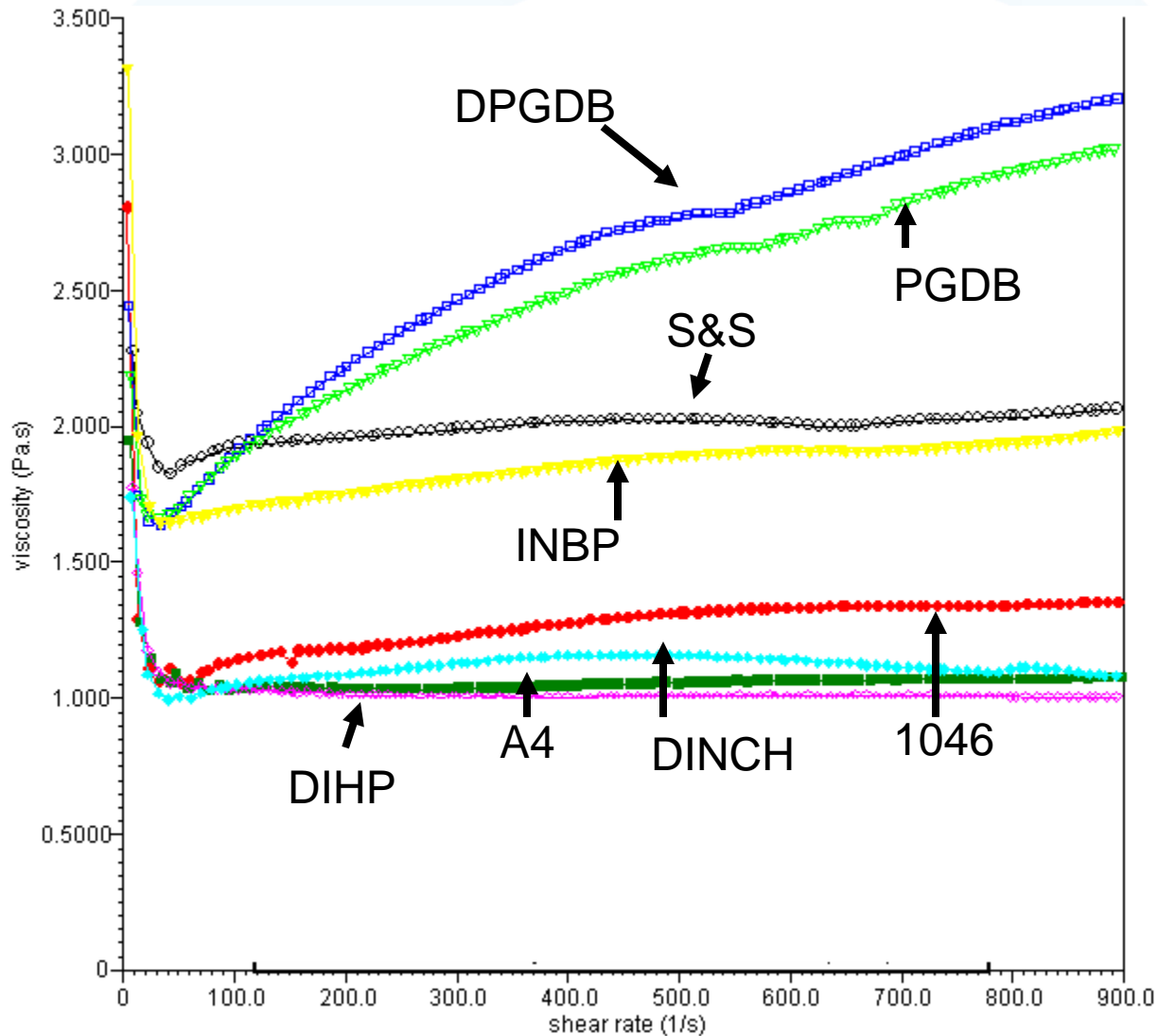
- Specialties, Non phthalates
  - DPGDB, Blend 953, Blend A, PGDB, Blend 1046
  - Caster oil mixed ester, S&S
  - Diisononyl-1,2-cyclohexane dicarboxylate, DINCH
  - Acetyl tri-n-butycitrate, A4
- Phthalates
  - Isononyl benzyl phthalate, INBP
  - Butyl benzyl phthalates, BBP
  - Diisoheptyl phthalate, DIHP
  - Di-2-ethylhexyl phthalate, DOP
  - Diisononyl phthalate, DINP
  - Disobutyl phthalate, DIBP
  - Di-n-butyl phthalate, DBP
  - Dioctyl terephthalate, DOTP



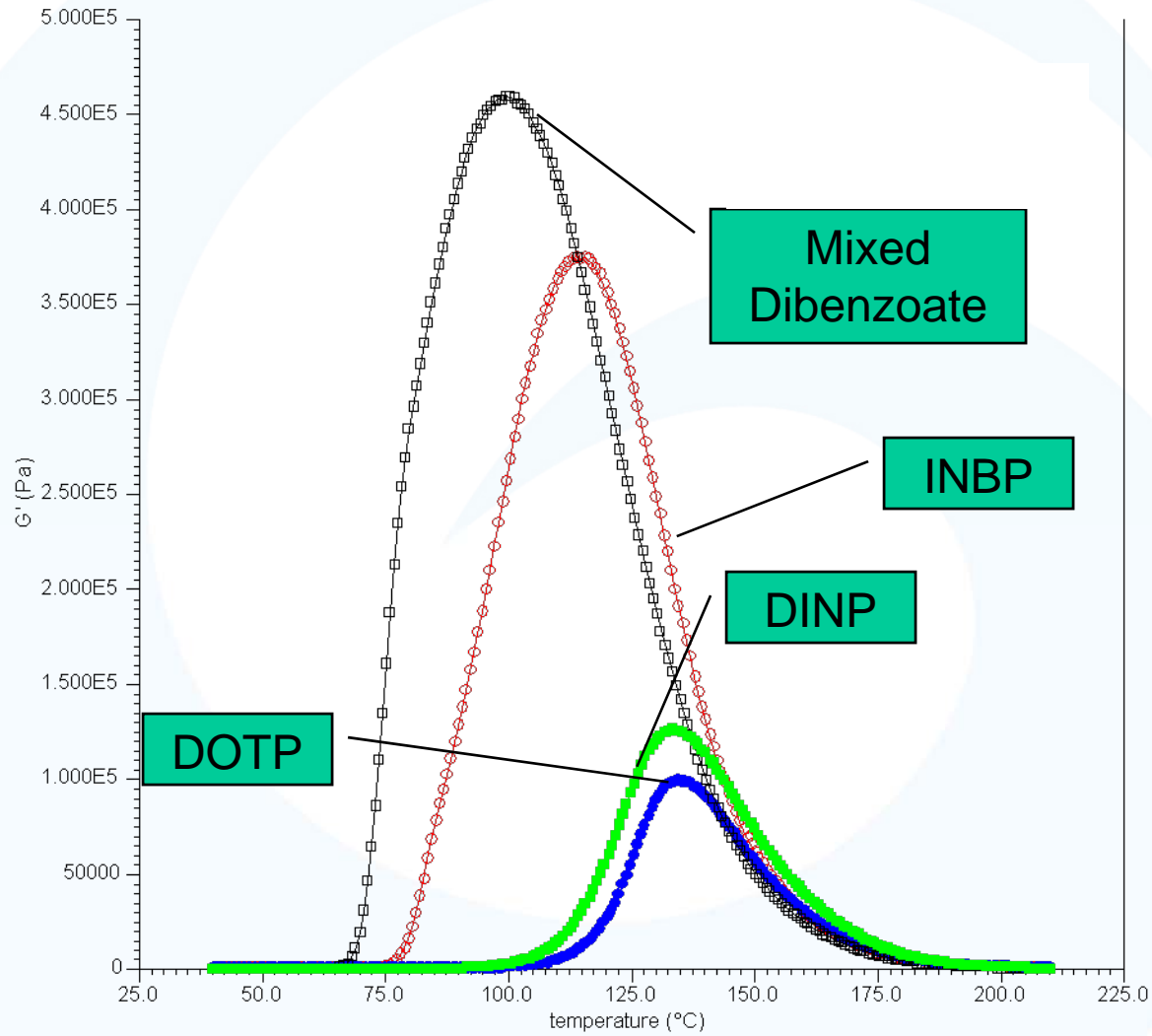
# TA AR2000 Rheometer



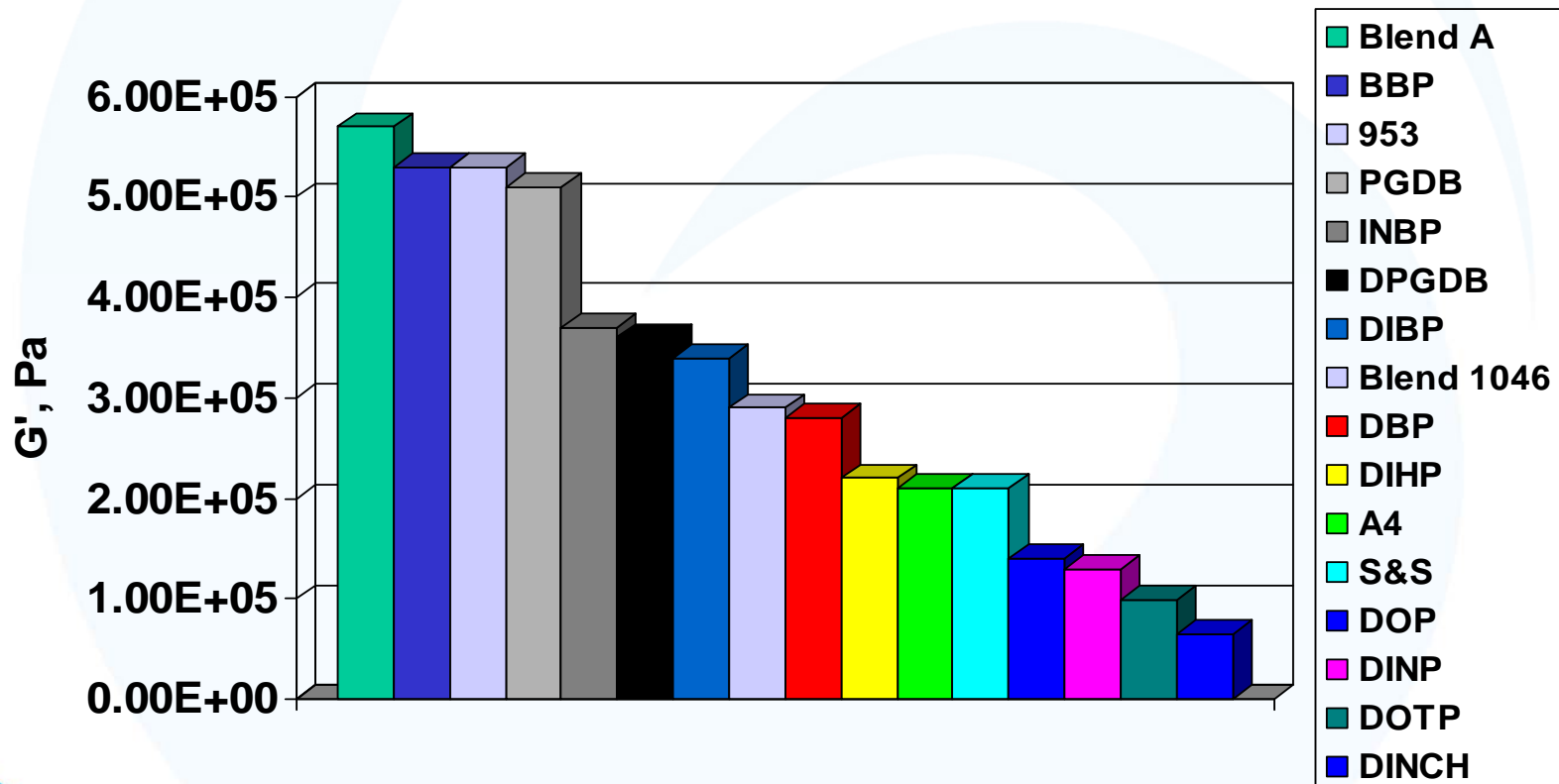
# Plastisol Rheology: One Day Data



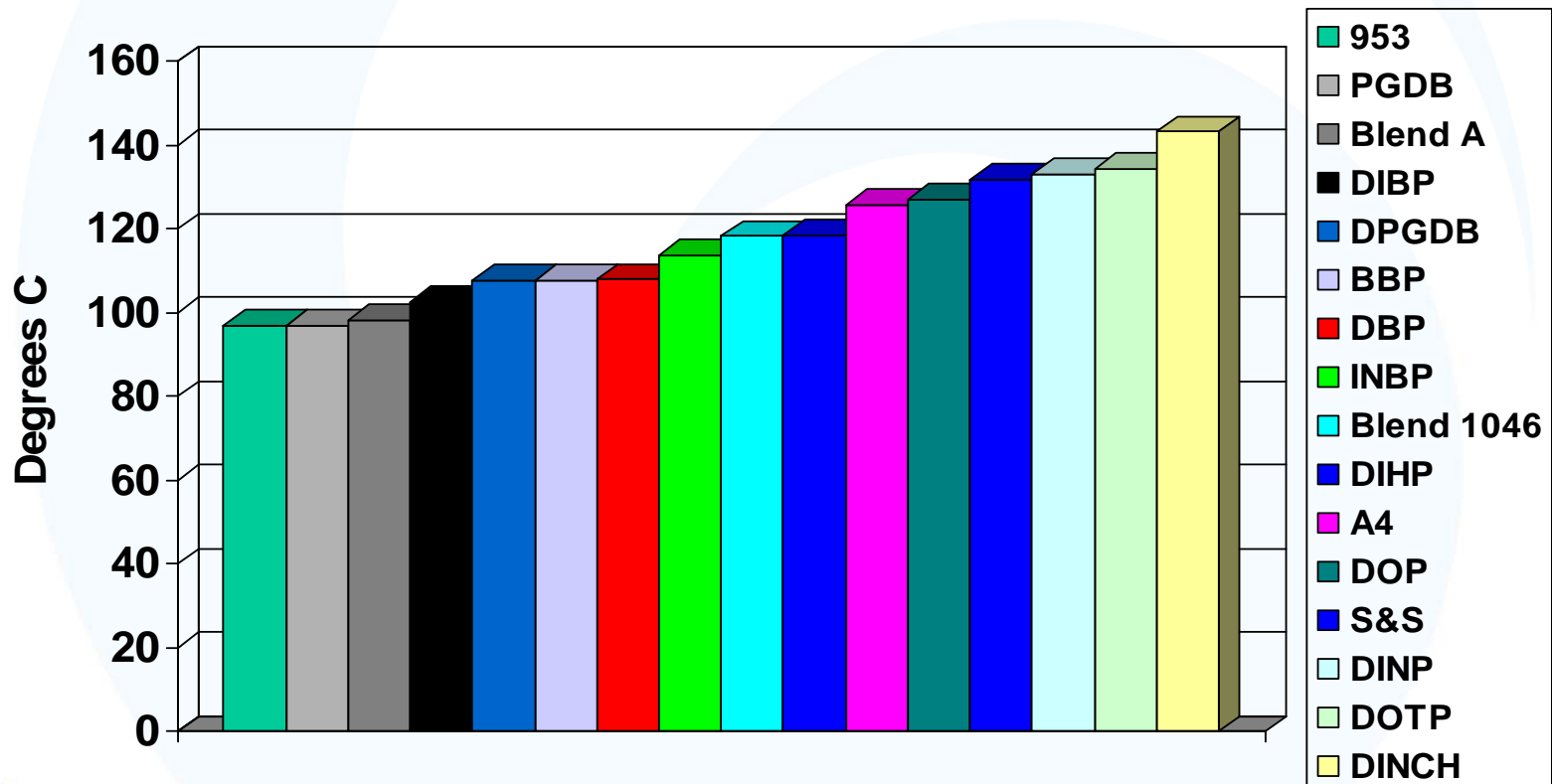
# Gel/Fusion Curve



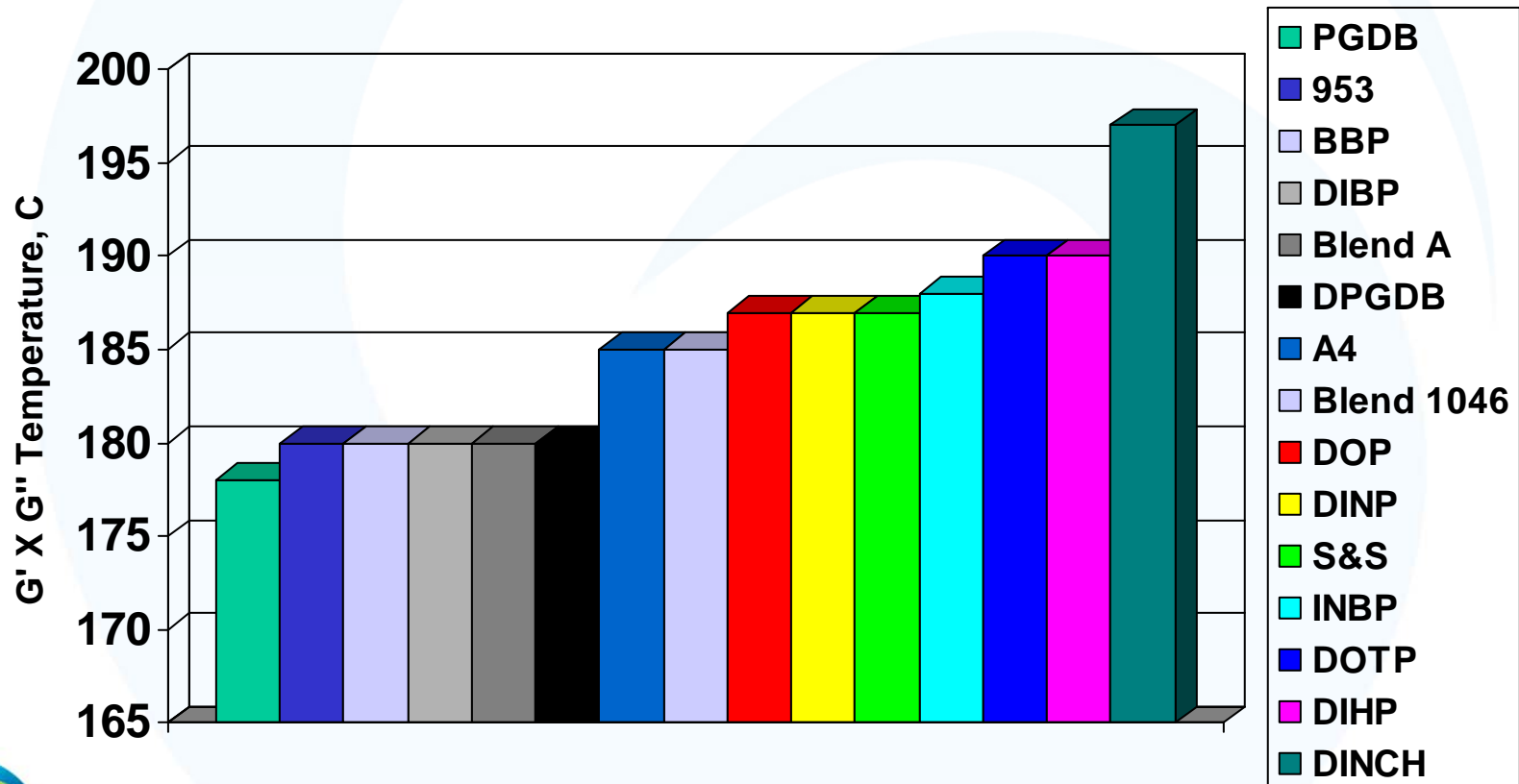
# Gel/Fusion Curve Peak (G'), Pa



# Gel Fusion Temperature at Peak (G')



# G' and G'' Cross Temperature



# Examples of High Solvator Use



# Textile Printing Inks



# Plastisol Screen Ink Evaluation

- Plastisol screen ink study published in the early 1990's when TMPD Dibenzoate, was introduced
- Protocol
  - Formulation – Starting formulation
  - Tests
    - Bleed data
    - Tensile development
    - Viscosity

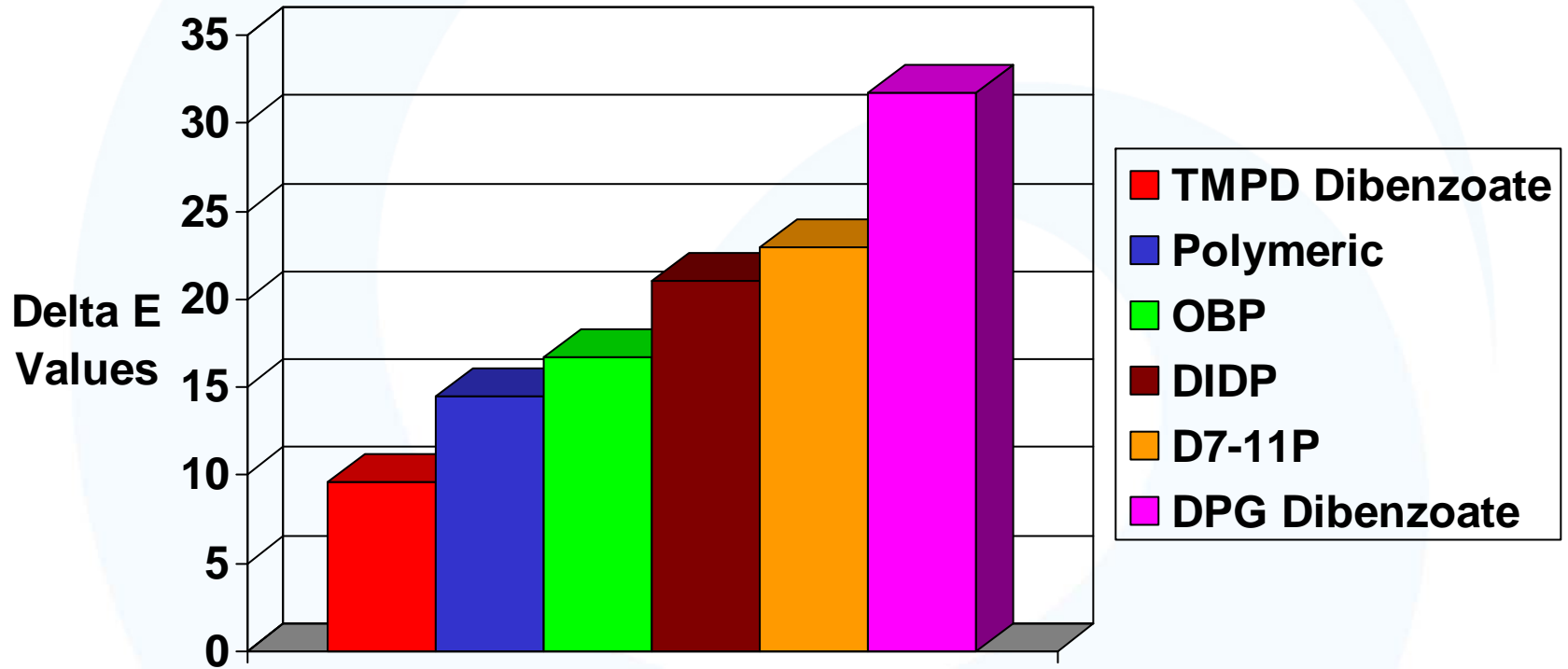


# Plastisol Formulation

Ingredients	Parts by Weight
Dispersion resin, Low Mw	100.0
Plasticizer	82.5
Isodecyl benzoate	27.5
CaCO <sub>3</sub>	100.0
TiO <sub>2</sub>	50.0



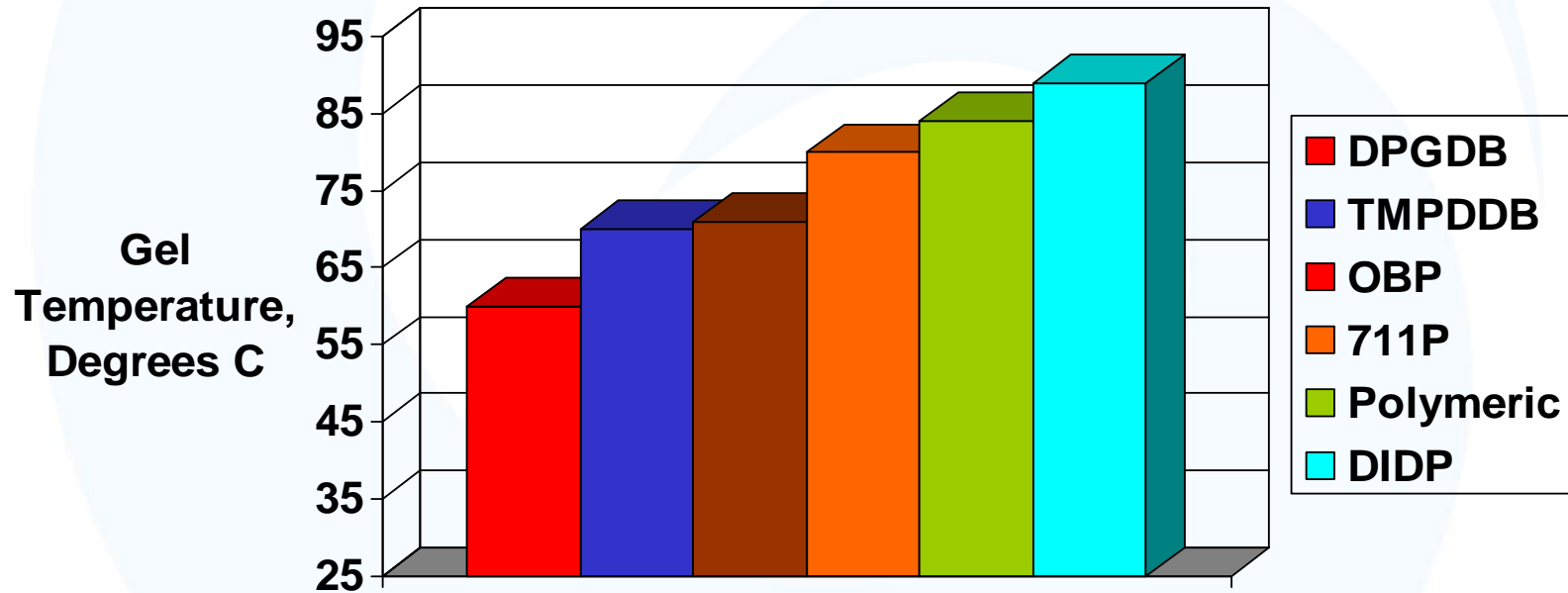
# Plastisol Ink Bleed Data



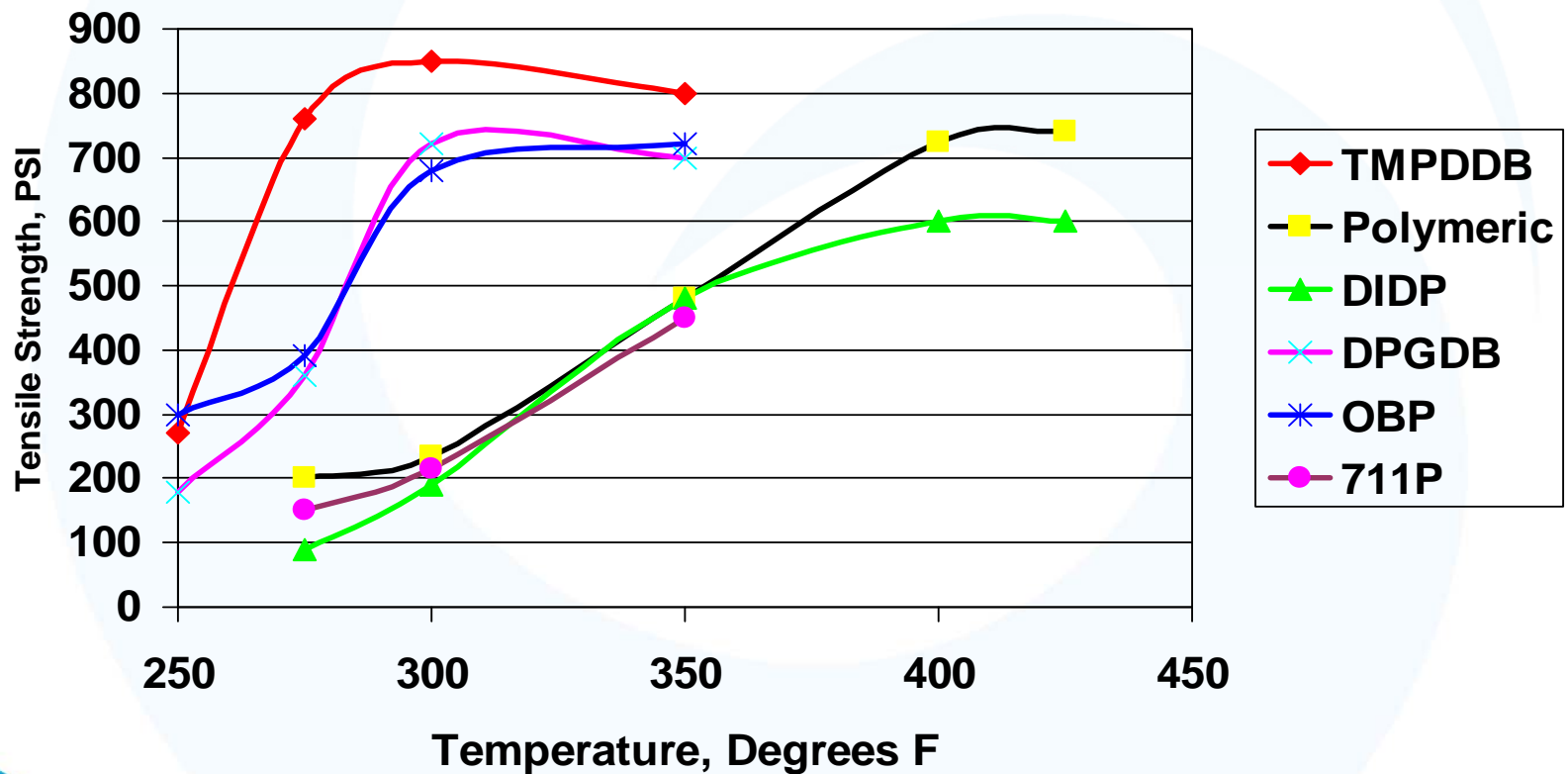
$\Delta E$  values determined against standard white plate. Samples aged 4 weeks at room temperature before reading.



# Plastisol Gel Temperatures



# Tensile Strength Development



# **Case Study: Flooring Clear Layer Plastisol Reformulation**



# Experimental Protocol

- Goal: Reformulation of wear (or clear) layer in European construct with benzoate
- A designed experiment approach used for all plastisol layers
  - EChip<sup>®</sup> DOE software used to design the experiments - mixture design
- Primary example is clear/wear layer
  - Design variables - Plasticizer type - Blend A, DINP, BBP, DIHP, TXB, Dispersion/blending ratio



# Experimental Protocol Cont.

- Wear/Clear Layer DOE
  - Response variables
    - Rheology and viscosity with Brookfield RVT, Severs and TA CLS<sup>2</sup> initial, and after aging
    - Gel-Fusion on TA CLS<sup>2</sup> (oscillatory mode (DMA))
    - UV and heat stability
    - Stain resistance
    - Plasticizer volatility
    - Tensile and tensile development versus temperature
    - Durometer
    - Plastisol preparation
  - Design - 26 unique trials, 5 replicates (quadratic)

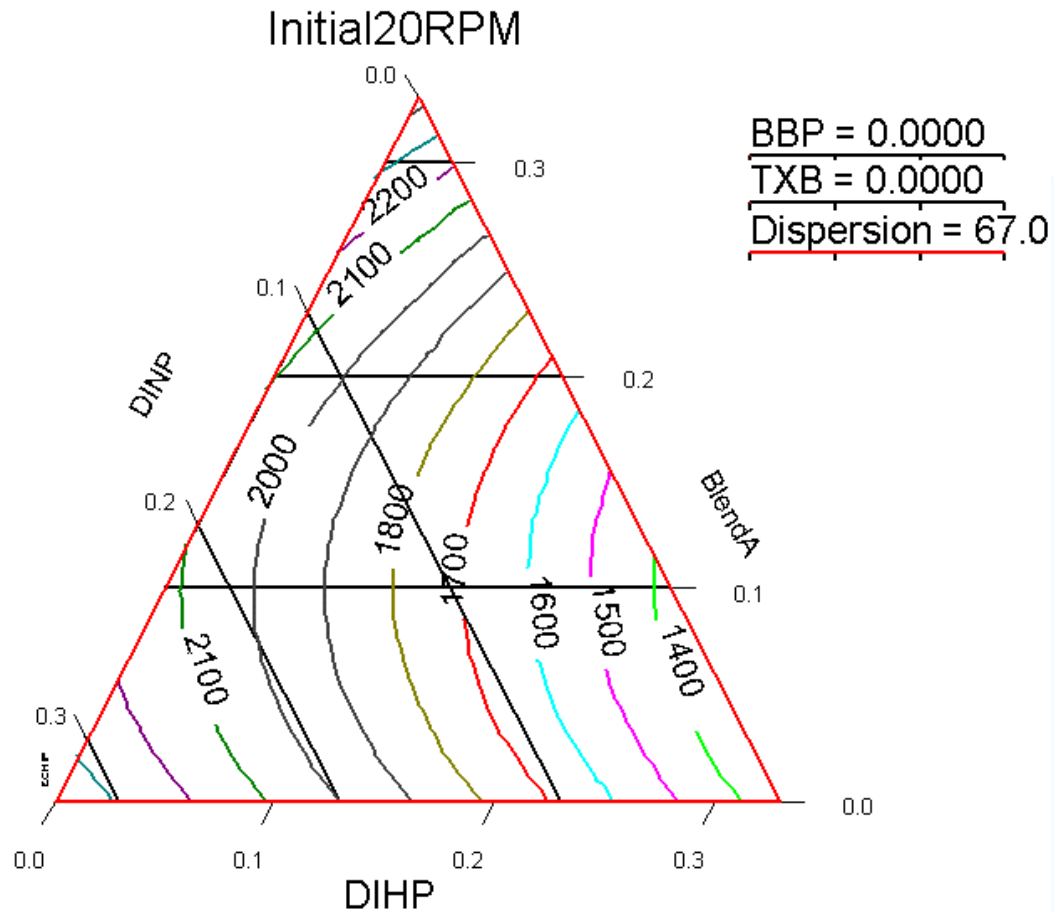


# Wear/Clear Layer Formulation

<b>Raw Material</b>	<b>PHR</b>	<b>%</b>
Dispersion Resin	70 – 100	42.82 – 61.17
Blending resin	30 – 0	18.35 – 0
Total Plasticizer	50	30.58
Epoxidized soybean oil, 6.8% oxirane	4.5	2.75
Heat stabilizer, Ca/Zn	4.5	2.75
Solvent/surfactant	4.5	2.75

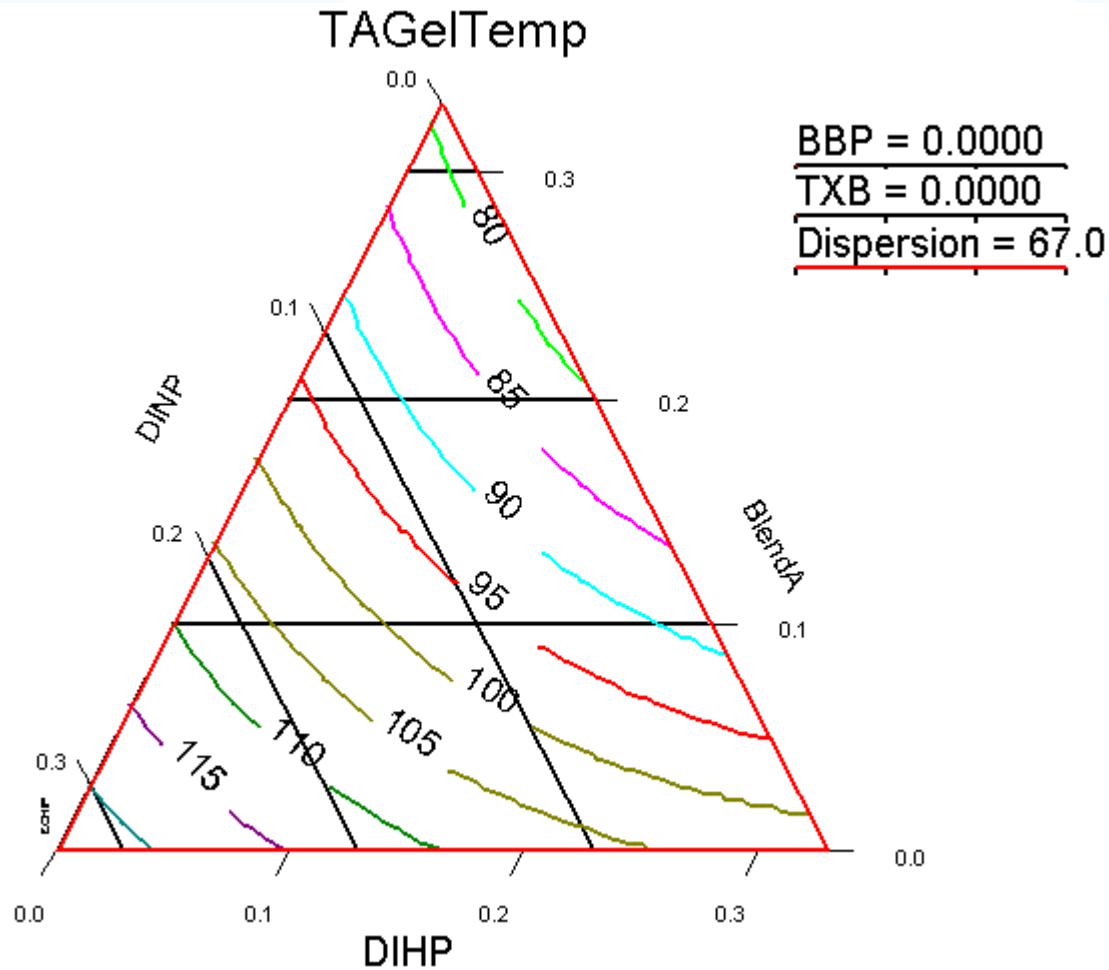


# Clear Layer Brookfield RVT Data

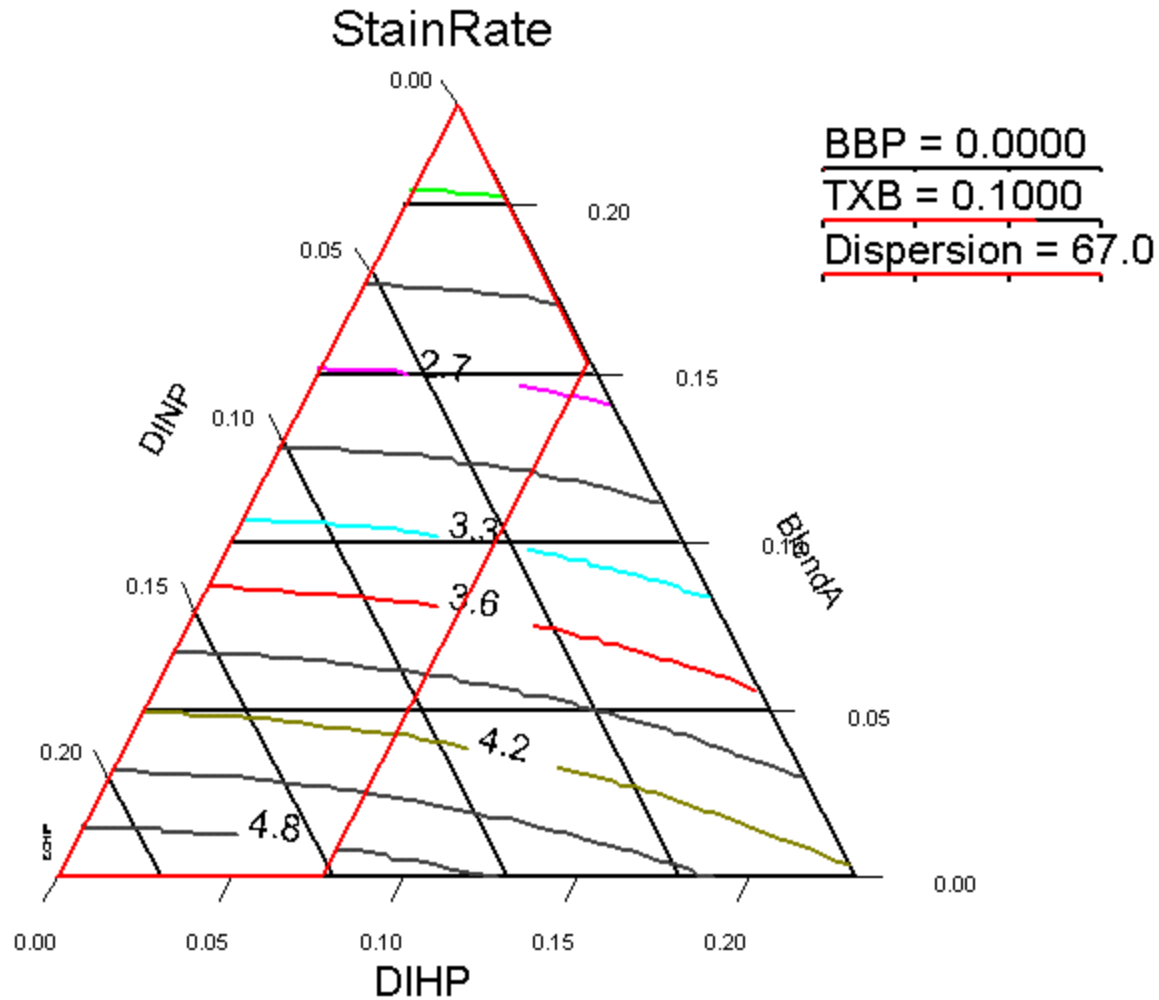




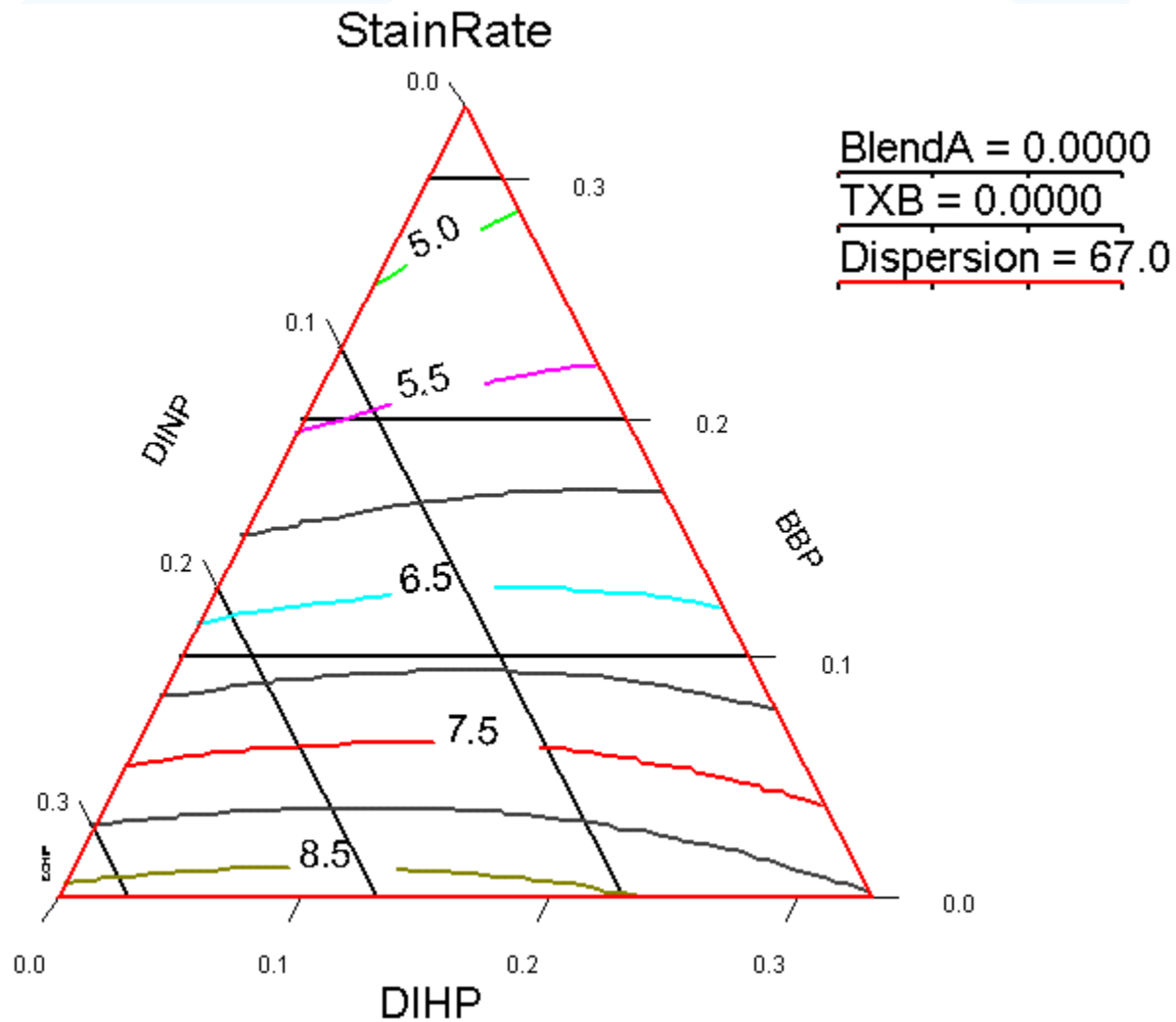
# Clear Layer Gel Temperatures



# Clear Layer Staining



# Clear Layer Staining



# Summary

- Plastics formulators and manufacturers can select from a variety of plasticizer chemistries
  - Established and developing technologies to meet changing markets
    - Regulatory, environmental, toxicological
    - Physical properties
      - Primary
      - Secondary
- Specialty plasticizers
  - Not always drop-in replacements for other chemistries
  - Can be formulated to realize full benefit
    - Performance
    - Process
- High solvator examples
  - In blends with GP plasticizers or other plasticizers to complement performance
    - Generic Plastisol
    - Resilient Flooring
  - Primary plasticizer for some applications
    - Plastisol Ink



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