



# SCHENECTADY INTERNATIONAL INC.

Xiamen Pharmaceutical Stopper Seminar

November 2003

***Phenolic Resins for Curing Elastomers***

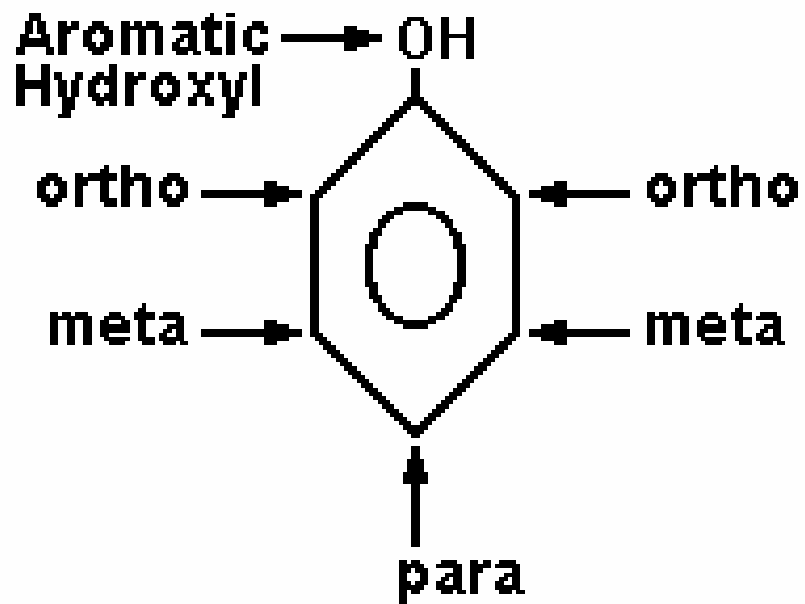
*Presented by James Lamb*

***Global Business Manager – Performance Resin Division***



# Phenolic Resin Chemistry

## *Nomenclature*



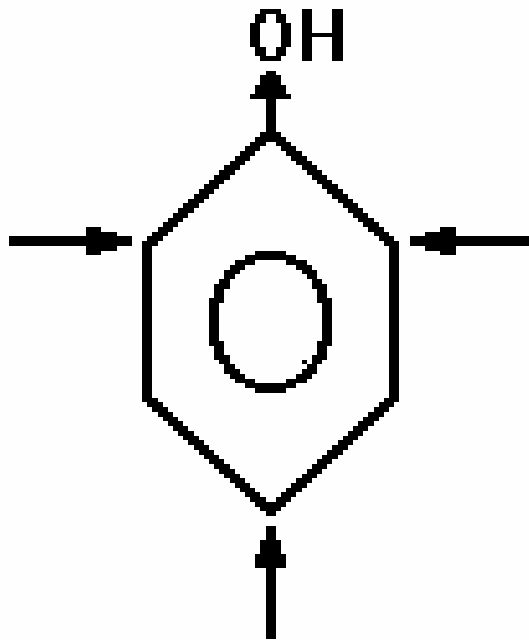
### Functional Groups

- (1) Aromatic Hydroxyl group
- (2) ortho positions
- (2) meta positions
- (1) para position



# Phenolic Resin Chemistry

## *Functionality*



Ortho and para directed reactions

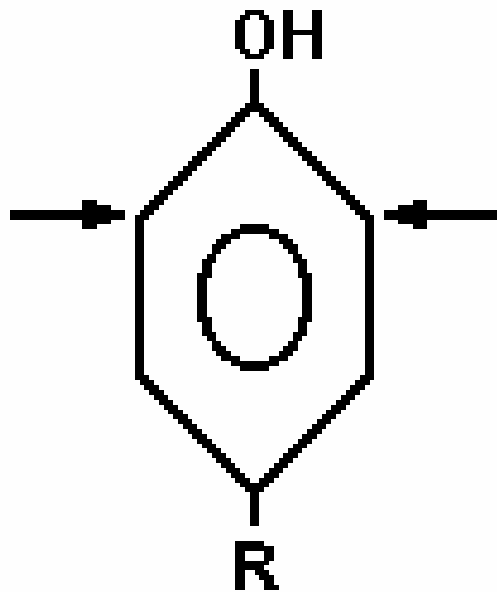
Tri-functional

Capable of highly branched polymers



# Phenolic Resin Chemistry

## *para-Alkylphenols*



Para-substituted phenol is di-functional

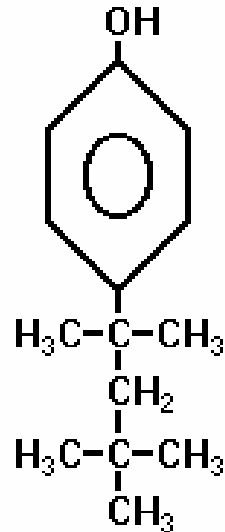
Reactions produce linear polymers

Alkyl group affects solubility and compatibility

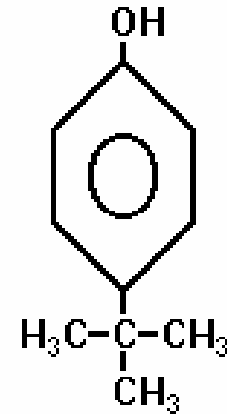


# Phenolic Resin Chemistry

## *Monomers used in rubber*



**p-tert.  
Octyl  
Phenol**



**p-tert.  
Butyl  
Phenol**

# Phenolic Resin Chemistry

## *Formaldehyde Reactions*

Monomers react with formaldehyde under different conditions to make different products

Reacting under acid conditions yields thermoplastic resins (Novolaks)

Reacting under base conditions yields reactive resins (Resoles)

Resole resins can be used for curing of elastomers



# Phenolic Curing Resin

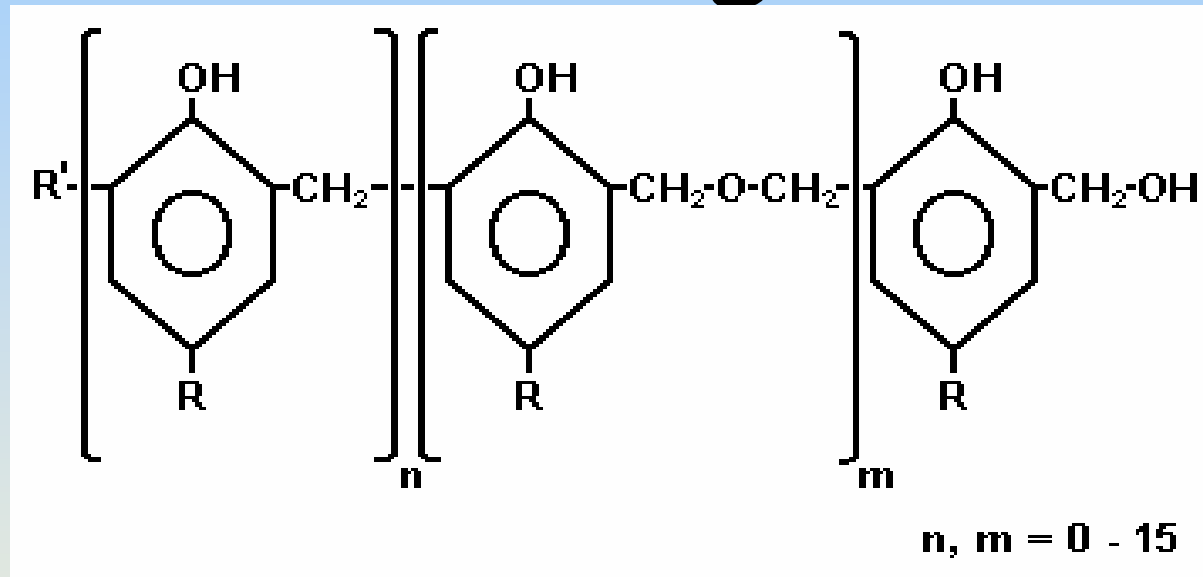
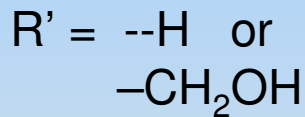
## *Description*

- Complex polymer with multiple reactive sites (resole resin)
- Undergoes multiple reactions simultaneously
- Activated by halogens (resinous, elastomeric, or metallic salts)
- Requires zinc source for best results



# Phenolic Resin Chemistry

## *SP-1045 Curing Resin*



Amorphous structure of various length chains

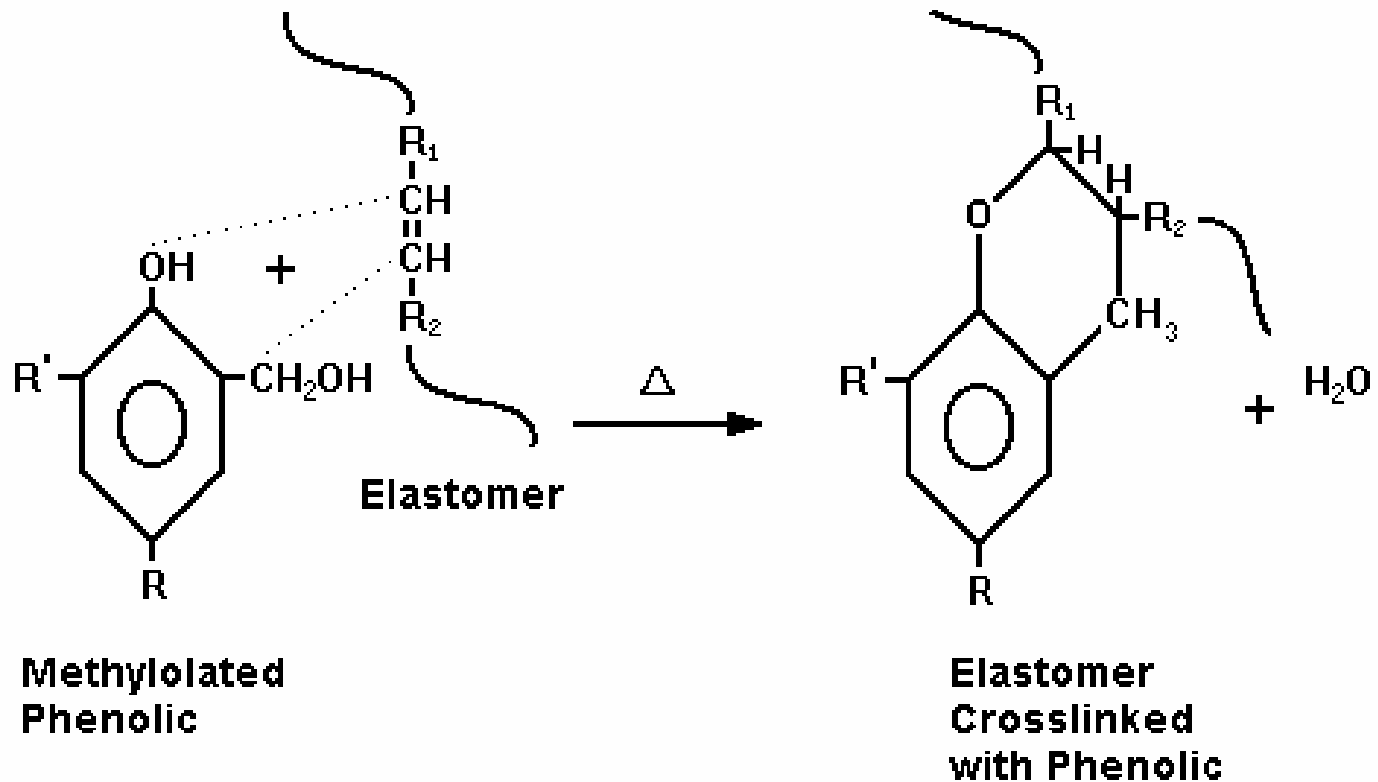
Multiple reactive sites, complex structure

Methylene or ether bridged monomeric units



# Phenolic Resin Reactions

## *Unsaturated Elastomers*

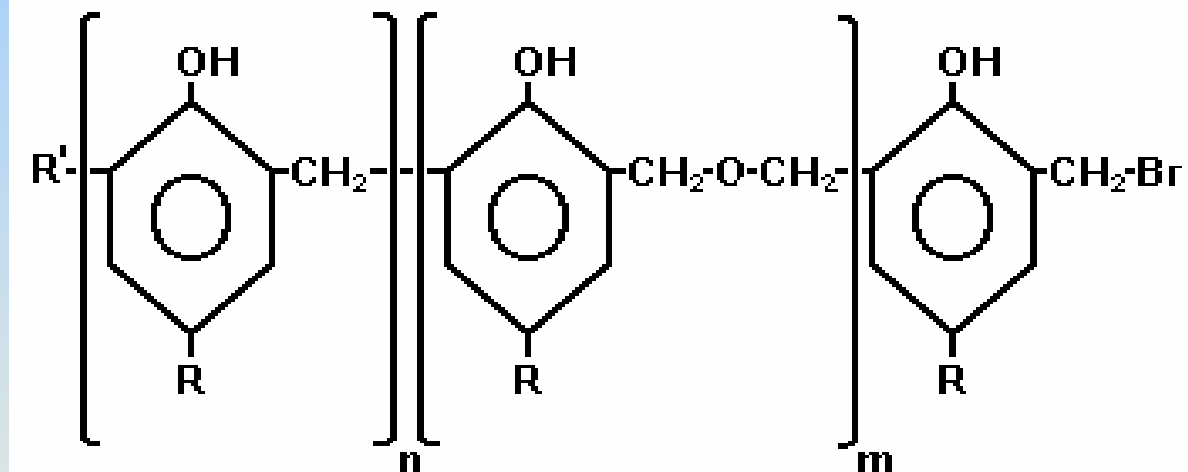


Chroman Ring Structure



# Phenolic Resin Chemistry

## SP-1055 Curing Resin



$R' = -H,$   
 $-CH_2H,$   
 or  $-CH_2Br$

$R = C_8H_{17}$

$n, m = 0 - 15$

Bromine can be added to resin

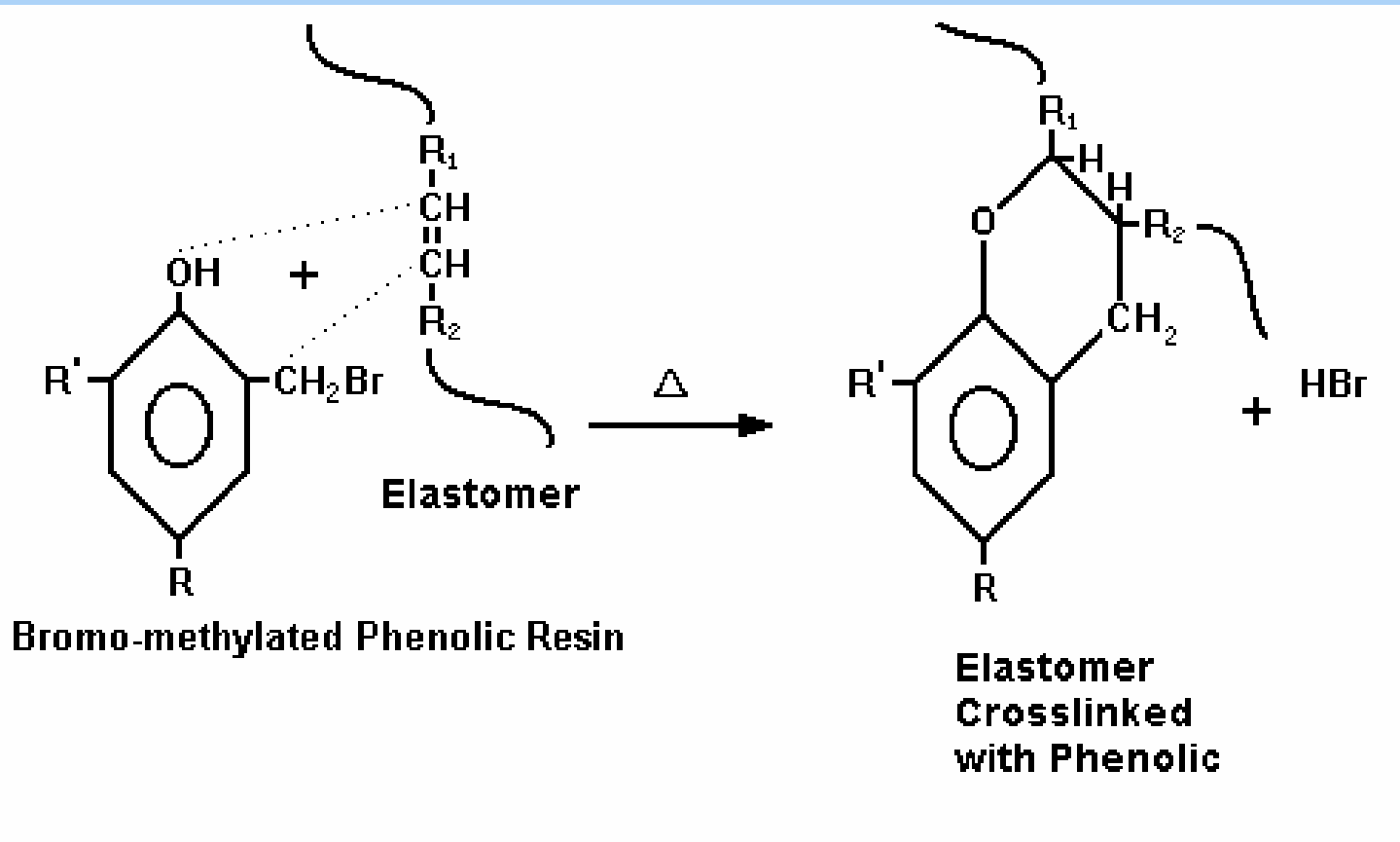
Increases rate of reaction with labile halogen

Increases complexity of cure mechanism



# Phenolic Resin Reactions

## *Unsaturated Elastomers - Br*



Chroman Ring Structure



# Phenolic Curing Resin *Characterization*

- Capillary Melting Point – measure of crystalline nature of resin (related to Tg)
- Ball & Ring Softening Point – measure of melt viscosity of resin
- Methylol Content – measure of reactivity
  - Ortho- position required for desired reactions
  - Ether is counted as methylol by test method
- Bromine Content – Percent by weight



# Phenolic Curing Resin

## *Available Grades*

<i>Resin</i>	<i>Capillary Melt Point</i>	<i>Ball &amp; Ring Softening Point</i>	<i>Methylol, %</i>	<i>Bromine, %</i>
<i>SP-1044 (PTOP)</i>	<b>135-150 °F</b>	<b>80 - 90 °C</b>	<b>7.5 - 9.5</b>	<b>None</b>
<i>SP-1045 (PTOP)</i>	<b>140-150 °F</b>	<b>80 - 95 °C</b>	<b>8.0 - 11.0</b>	<b>None</b>
<i>HRJ-10518 (PTOP)</i>	<b>140-150 °F</b>	<b>80 - 95 °C</b>	<b>6.0 - 9.0</b>	<b>None</b>
<i>SP-1055 (PTOP)</i>	<b>140-158 °F</b>	<b>85 - 95 °C</b>	<b>10.0 - 14.0</b>	<b>3.6 - 4.0</b>
<i>SP-1056 (PTOP)</i>	<b>140-158 °F</b>	<b>80 - 90 °C</b>	<b>9.0 - 11.0</b>	<b>6.0 - 7.5</b>
<i>HRJ-1367 (PTBP)</i>	<b>160 °F (typical)</b>	<b>92 - 100 C</b>	<b>14.0 - 18.0</b>	<b>None</b>

# Phenolic Curing Resins

## *Function*

- Phenolic resins can be used to vulcanize (crosslink) elastomers
- Methylol and hydroxyl groups of resin react with unsaturated sites of elastomer
- Properties of vulcanized elastomer changed
  - Reduced thermoplasticity
  - Improved abrasion resistance
  - Increased tensile strength



# Phenolic Curing Resin

## *Benefits*

- Forms covalent carbon-carbon bonds which are not easily broken
- Ideal for repeated heat cycles
- Acts as plasticizer until cure initiated
- Resin can be halogenated for rapid cure



# Phenolic Curing Resin

## *More Benefits*

- Does not require amine accelerators
- Can tolerate autoclave temperatures
- Low extractables compared to sulfur cure systems



# Phenolic Curing Resin *Rubber Formulation*

- Elastomer (butyl or halobutyl rubber)
- Reinforcing material (Clay, Carbon black)
- Modifiers (Wax, oils)
- Minerals (Zinc Oxide, Magnesium oxide)
- Phenolic Resin SP-1045 or SP-1055





# Phenolic Curing Resin *Bladder Formulation 1*

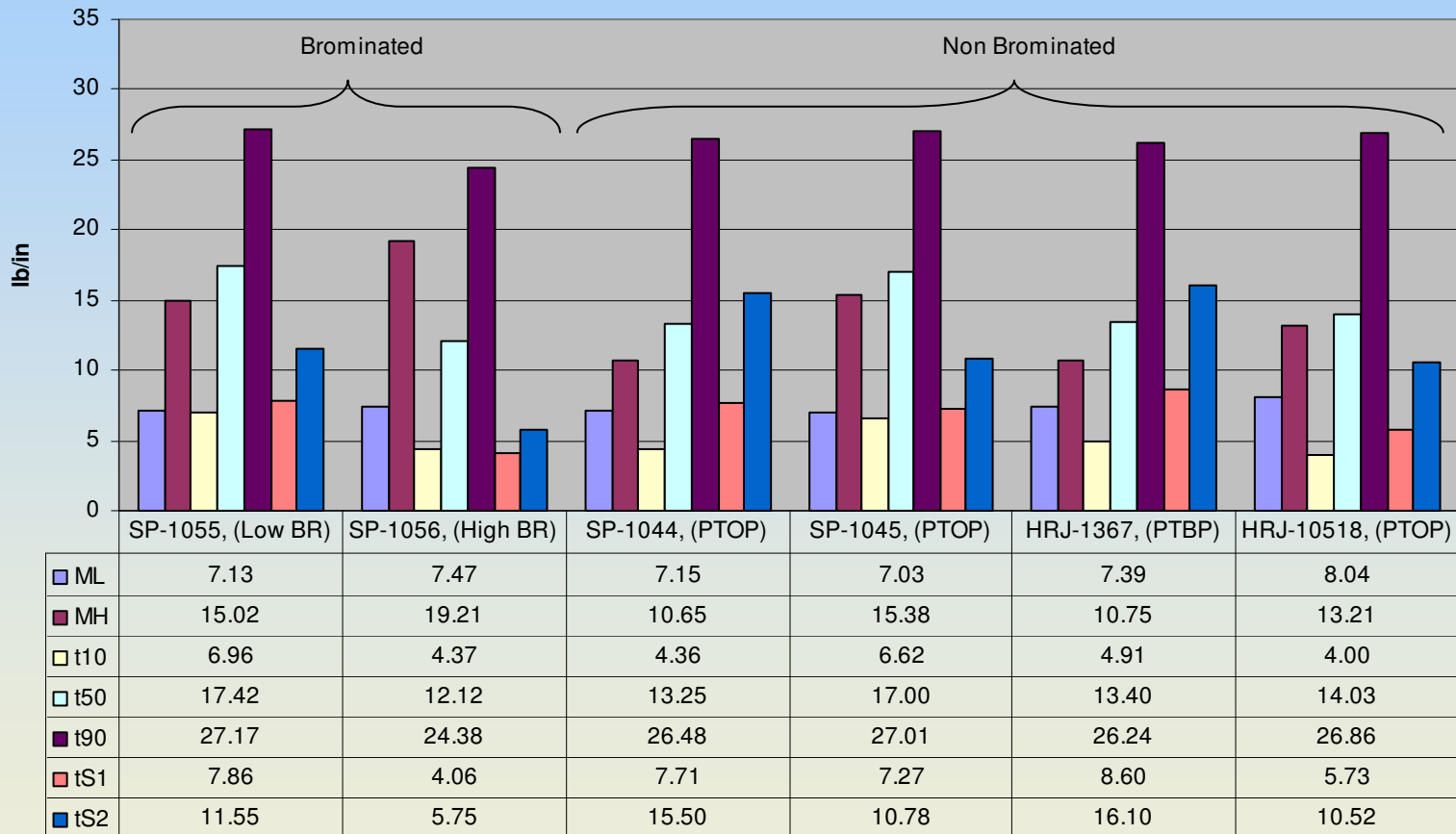
- Butyl 268 Elastomer 100
- HAF Carbon Black 50
- Castor Oil 5
- Zinc Oxide 5
- Curing Resin with Br 10



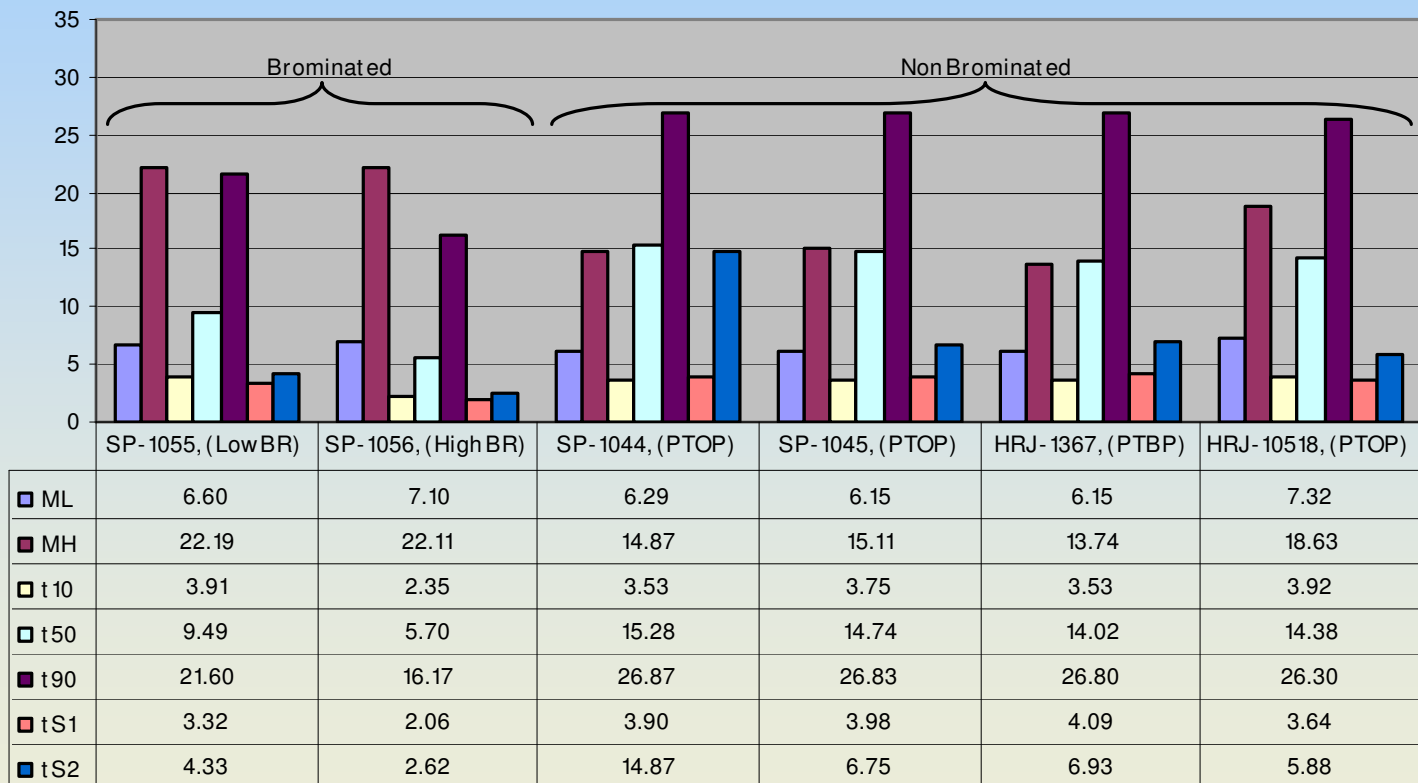
# Phenolic Curing Resin *Bladder Formulation 2*

- Butyl 268 Elastomer 100
- HAF Carbon Black 50
- Castor Oil 5
- Zinc Oxide 5
- Neoprene W 5
- Curing Resin without Br 10

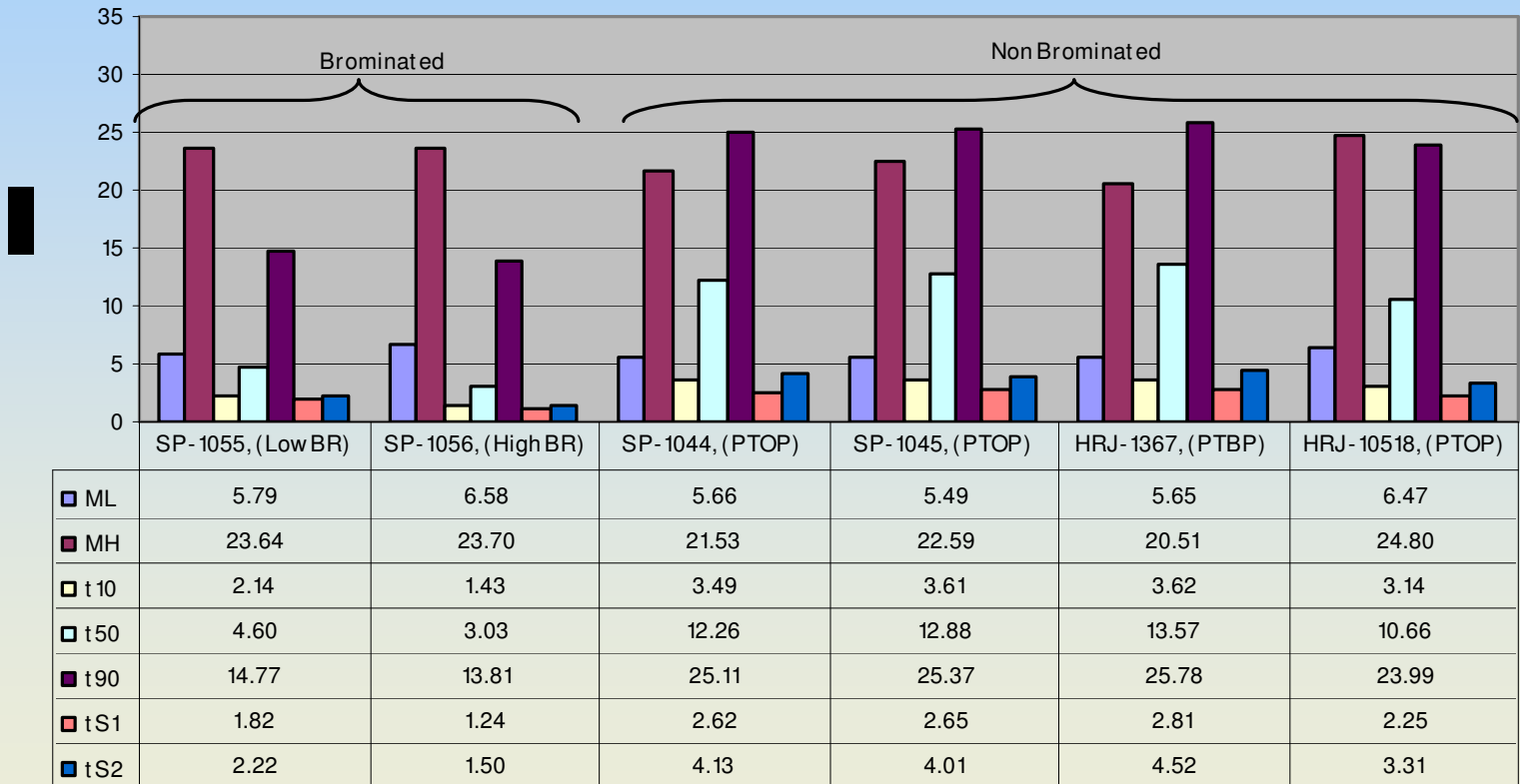
SII Heat Reactive Resin Cure  
Butyl Masterbatch  
ODR 2000, 30' @ 300°F



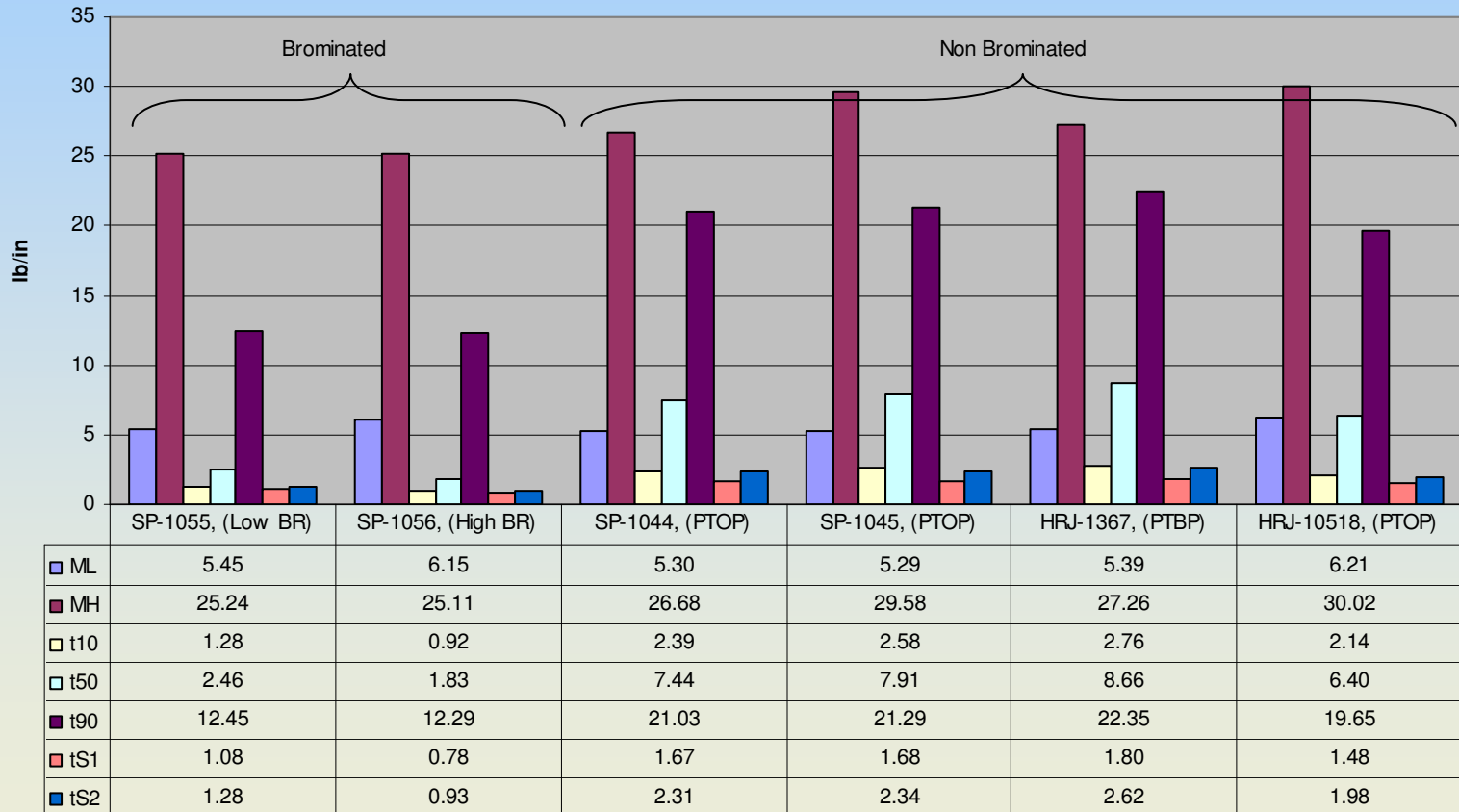
**SII Heat Reactive Resin Cure**  
**Butyl Masterbatch**  
**ODR 2000, 30' @ 325°F**



**SII Heat Reactive Resin Cure  
Butyl Masterbatch  
ODR 2000, 30' @ 350°F**



SII Heat Reactive Resin Cure  
Butyl Masterbatch  
ODR 2000, 30' @ 380°F





# Phenolic Curing Resin *Pharmaceutical Formulation*

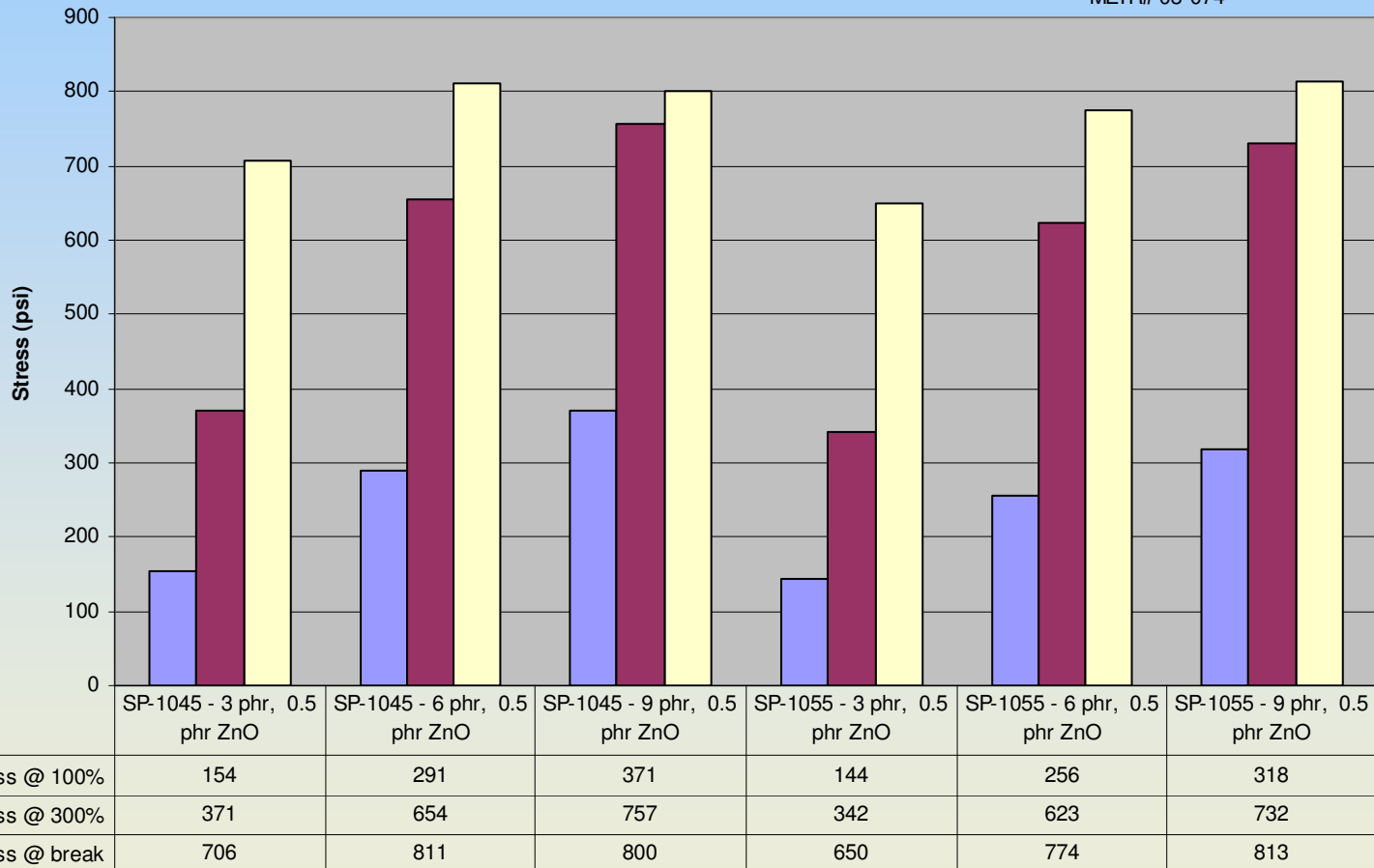
● Bromobutyl 2244	100.0
● Whitetex Clay	90.0
● AC 617A	3.0
● Zinc Oxide	0.5
● SP-1045	5.0

- Note low resin requirement
- Note no need for halogen donor



**Stress**  
Press - 350°F

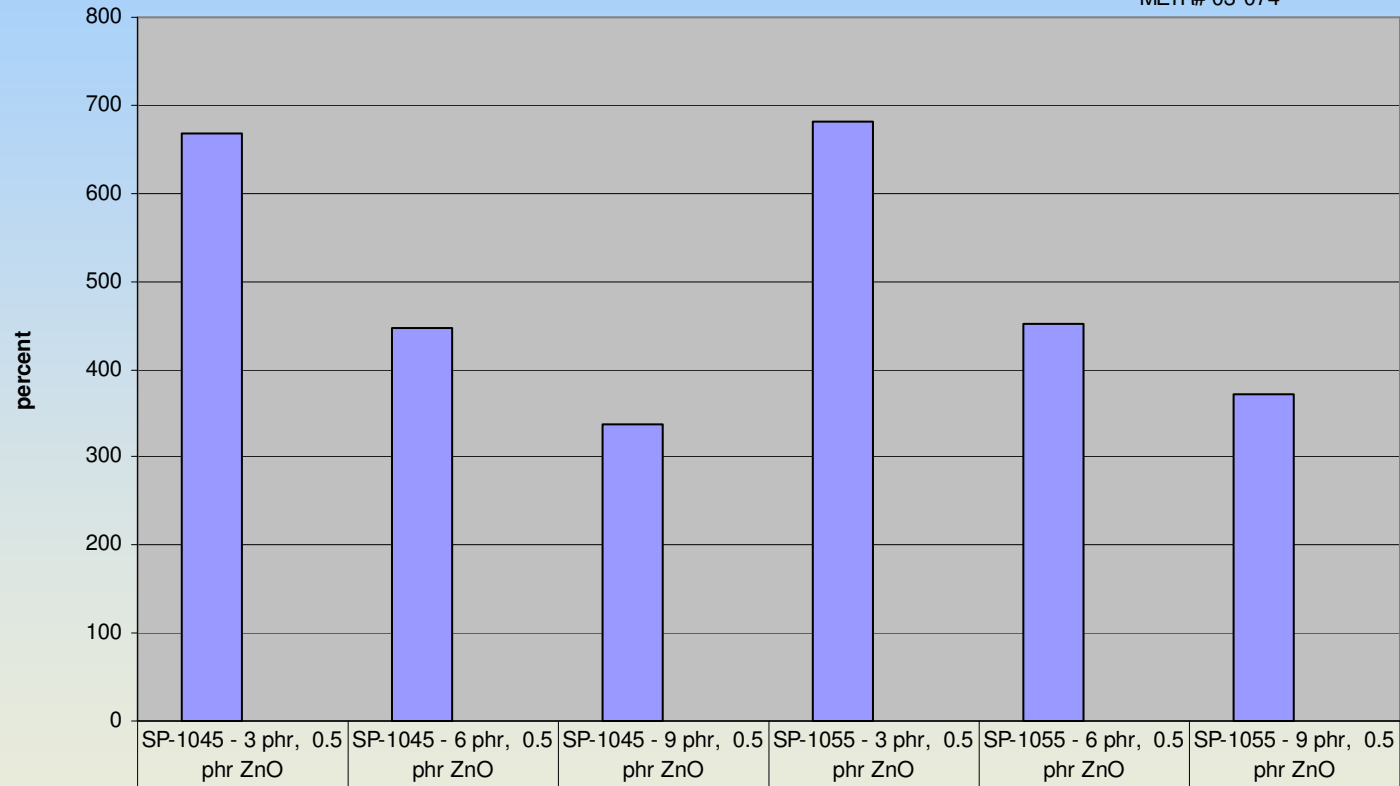
METR# 03-074





Elongation, (Strain)/Hardness  
Press - 350°F

METR# 03-074



% strain @ break	667	448	337	682	451	373
Shore "A" Hardness	50	53	58	50	57	59

# Phenolic Curing Resin *Regulatory Status*

- Commonly used in approved products
- Compliant with CFR21 177.2410  
(Durable goods for repeated use)
- Extraction studies run on products



# Phenolic Curing Resins *Market Analysis*

- Durable rubber goods
  - 20,000 MT estimated
- Thermoplastic Elastomers (TPV's)
  - >200,000 MT finished goods
- Pharmaceutical Use
  - 6000 MT of products in North America
  - 4000 MT of products in Europe
  - Increased usage globally



# References

- “The Mechanism of Phenolic Resin Vulcanization of Unsaturated Elastomers”  
Lattimer et al Paper No. 14, delivered at Dallas Meeting of ACS Rubber Division, April 19-22, 1988)
- Helpful websites
  - [www.fda.gov](http://www.fda.gov) (US FDA website)
  - [www.namsa.com](http://www.namsa.com) (Evaluation of medical devices)



# Acknowledgements

Thank you to the following for making this presentation possible:

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- Schenectady International Shanghai, Ltd.
- **ExxonMobil Chemical**





**SCHEENECTADY**

**INTERNATIONAL**

**Discussion**