Novel Room Temperature Cure Compositions For Use In Polyisoprene Latex

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Acknowledgments

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- Technical colleagues at Robinson Brothers who conducted the work:
  - Mr Ranvir Virdi
  - Dr Boyd Grover
  - Dale Stroyde
- Distributing partners for Robac products in USA – Swan Chemical Inc.
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  • Polyisoprene latex and natural rubber latex
  • Issues with conventional rubber accelerators
  • Benefits of safer accelerators
  • Previous work. Technical performance of safer systems
  • Challenges facing compounders
  • Aims of current work
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  • Formulation
  • Activation using metal xanthates
• Results
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  • Migration studies
  • Nitrosamine testing
• Conclusion
Introduction: Synthetic Polyisoprene

- The global usage of synthetic polyisoprene latex (IR) was ~ 12kT per annum in 2014, showing 15% year on year growth since 2010
- Demand driven by high performance synthetic alternatives to natural rubber latex, particularly in the glove, condom and medical device application
- Synthetic Polyisoprene offers the benefits of natural rubber but eliminates the risk of type 1 allergy
Physico chemical properties of natural rubber latex (NRL) and synthetic polyisoprene latex (PI)

<table>
<thead>
<tr>
<th>Property</th>
<th>Natural Rubber Latex</th>
<th>Polyisoprene Latex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>Havea Brasiliensis Tree</td>
<td>Synthesis from isoprene monomer</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>$1 \times 10^5 - 1 \times 10^6$</td>
<td>$1.5 \times 10^6 - 2.5 \times 10^6$</td>
</tr>
<tr>
<td>Distribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural Difference</td>
<td>99% cis 1,4 polyisoprene</td>
<td>90-96% cis1,4 polyisoprene 4-10% isomers of 3,4, 1,2 polymer and trans 1,4 polymer</td>
</tr>
<tr>
<td>Stabilisation</td>
<td>Proteins – amino acids</td>
<td>Synthetic surfactant stabilised</td>
</tr>
<tr>
<td></td>
<td>(ammonia, zinc oxide, thiuram addition)</td>
<td></td>
</tr>
<tr>
<td>Concern</td>
<td>Type 1 allergic reaction</td>
<td>Zero Type 1 allergic reaction</td>
</tr>
<tr>
<td>Cross-linking efficiency</td>
<td>Very efficient</td>
<td>Variable efficiency</td>
</tr>
</tbody>
</table>

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Introduction: Synthetic Polyisoprene

• Synthetic Polyisoprene does not contain the proteins that are found in natural rubber. As such the risk of type 1 allergy is eliminated

• However, many of the accelerators used in natural rubber are also used to vulcanise synthetic polyisoprene

• These traditional accelerators can leave residue in the rubber that can give rise to Type 4 allergy and generate carcinogenic nitrosamines
Issues generated by using conventional rubber accelerators in lattices

RISK = HAZARD X EXPOSURE

• Residual accelerator migration to surface of films – causes irritant dermatitis
• Carcinogenic materials – MBT to be listed on Proposition 65.
• Residual nitrosatable matter – generates nitrosamines (documented widely)
• Type IV allergy – delayed contact dermatitis
• Heavy metals – toxicological / environmental issues at the end of product cycle
• Volatile nitrosamine exposure in manufacture, warehouse and disposal
The Robac solution

- Nitrogen free accelerators: impossible to nitrosate
- Chemically bound to matrices (non-extractable)
- Complete consumption during vulcanisation = no residues and no Type IV allergy
- Highly soluble, large molecular volume = limited migration, reduced skin penetration
- Safer, longer, thermally stable branched secondary amine = no decomposition, difficult to nitrosate

Risk = Exposure x Hazard
No residue = No hazard = No Risk
Robac AS100 (DIXP)

Benefits

• Contains no nitrogen atoms
  No nitrosatable matter
  Formation of N-nitrosamine not possible
• Fully consumed during vulcanisation process
  Leaves no accelerator residue therefore no Type IV allergic reaction
• FDA Approved

Chemical Properties

• Sulfur donor or accelerator with elemental Sulfur
• Produces mono-, di- and polysulfidic cross-links in equal proportions
• Highly soluble in polymer matrix
• Non-polar accelerator
• Better migration to reaction site
• No metal atoms, no metal staining observed
Benefits

• Branched, sterically hindered, high molecular weight, long chain dithiocarbamate
• High molecular weight and branching results in less skin penetration
• No dermal or delayed contact hypersensitivity
• BfR Special Category Approval
• Safer parent 2° amine – diisononyl amine is difficult to nitrosate

Chemical Properties

• Acts as accelerator to give di-polysulfidic cross-links
• Balanced hydrophilic-hydrophobic properties
• Aids better migration into micelle site where chemical cross-linking takes place
• Thermally stable
  • Decomposition temperature >250°C
Historical Work

- Over the last 20 years Robinson Brothers have actively developed safer systems and reported our findings at various international conferences.
- In 2010, we reported on our work in polyisoprene latex but further improvement was required to overcome processing issues including:
  - Temperature during vulcanization
  - Extended reaction times at lower temperature
  - Choice of accelerator system
  - Making the formulation work in real life systems, not just flowed films
  - Variable vulcanisate properties
Challenges facing the compounder in dipped film forming technology in PI latex.

Selecting Accelerators

- Very efficient cure system that can function effectively at lower temperature is required.
- Accelerators with lowest toxicity profile should be considered.
- Additional parameters to consider:
  - Stability of accelerators
  - Commercial availability
  - Effectiveness and functional efficiency during vulcanisation at lower temperature
  - Meeting regularity demands
  - Cost
Current Work

Since 2012 Robinson Brothers have actively searched for improved methodologies for the effective and efficient vulcanization of polyisoprene latex. The main objectives were:

- Develop a safer vulcanization system reducing the risks of type 4 allergy and hazardous nitrosamine formation
- Improve the vulcanisate properties
- Decrease the maturation time
- Lower the temperature of vulcanization
- Utilise aqueous coagulant dipping
Experimental

Maturation study
• 24 hours was carried out at 30-35°C and then during storage, up to 10 days at 18-22°C. Cross-link density of the compounded latex during maturation were monitored using a modified solvent swell index in toluene and using the isopropanol index test.

Viscosity measurements
• Brookfield DV-E LV viscometer operating at 60 rev/min, using spindle RV2 or RV3 at 20°C.

Thin Films
• Dipping procedure utilising aqueous calcium nitrate coagulant solution, aqueous gel leaching an oven curing.

Tensile
• Determined to BS903: Part A2 Type 1 Dumbells using Intron 4302 tensile testing with machine with Blue Hill software. Wallace Thin Film Grips (TFG) were used to pull the dumbbell samples under 500N load cell.
Experimental

Materials

- 60% Sulfur, 50% Zinc oxide and 50% Antioxidant as aqueous dispersions. Supplied by Aquaspersions
- Zinc isopropyl xanthate (ZIX). Supplied by Akrochem. Converted to 30% dispersion
- KratonTM IR-401. Supplied by Kraton
- MIDSISOLEX. Supplied by Medline Industries

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- Robac AS100. diisopropyl xanthogen polysulphide (DIXP) as 60% emulsion
- Robac arbestab Z. zinc diisononyl dithiocarbamate (ZDNC) as 35% dispersion
- Sodium isopropyl xanthate (SIX) as 24% solution
The following formulations were examined to assess the curing activity of ZDNC and DIXP in isolation and in combination with metal xanthate.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations (Dry Weights)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>PI latex, cis 1,4 content 88-92%</td>
<td>100</td>
</tr>
<tr>
<td>Potassium Caprylate</td>
<td>0.5</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1.0</td>
</tr>
<tr>
<td>ZDNC</td>
<td>0.5</td>
</tr>
<tr>
<td>DIXP</td>
<td>-</td>
</tr>
<tr>
<td>SIX</td>
<td>0.3</td>
</tr>
<tr>
<td>ZIX</td>
<td>-</td>
</tr>
</tbody>
</table>
Results Effect of Storage

Salient Points
- Viscosity remains constant
- Bin stability is good up to 30 degC and 30 days
- Linear Swell in Toluene not a useful test

<table>
<thead>
<tr>
<th>Storage Time after maturation at 35°C</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Isopropanol index</td>
<td></td>
</tr>
<tr>
<td>24hrs at 35°C</td>
<td>1</td>
</tr>
<tr>
<td>Linear Swell in Toluene (%)</td>
<td></td>
</tr>
<tr>
<td>24hrs at 35°C</td>
<td>Gelled</td>
</tr>
<tr>
<td>Brookfield Viscosity (Centipoise) at 18±2°C</td>
<td></td>
</tr>
<tr>
<td>24hrs at 35°C</td>
<td>32</td>
</tr>
<tr>
<td>30 days at 18±2°C</td>
<td>33</td>
</tr>
</tbody>
</table>

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Results Tensile Properties

<table>
<thead>
<tr>
<th>Tensile Properties</th>
<th>Formulations</th>
<th>ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Initial Tensile Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>1.2</td>
<td>6</td>
</tr>
<tr>
<td>Strain at Break (%)</td>
<td>&gt;1250</td>
<td>&gt;1250</td>
</tr>
<tr>
<td>Stress at 300% Strain (MPa)</td>
<td>0.58</td>
<td>0.72</td>
</tr>
<tr>
<td>Stress at 500% Strain (MPa)</td>
<td>0.61</td>
<td>0.87</td>
</tr>
<tr>
<td><strong>After Thermal Ageing (7 days at 70°C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Strain at Break (%)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stress at 300% Strain (MPa)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stress at 500% Strain (MPa)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Tensile properties meet ASTMD3577. Standard specification for rubber surgical gloves Type II Synthetic latex gloves

Focus on formulation 5 and 6 utilizing booster SIX and ZIX

Unoptimised results
The following formulations were examined using varying amounts of cis 1,4 isomer:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations (Dry Weights)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>PI latex, cis 1,4 content 88-92%</td>
<td>100</td>
</tr>
<tr>
<td>PI latex, cis 1,4 content 96-98%</td>
<td>-</td>
</tr>
<tr>
<td>Potassium Caprylate</td>
<td>0.5</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>0.5</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1.0</td>
</tr>
<tr>
<td>ZDNC</td>
<td>0.5</td>
</tr>
<tr>
<td>DIXP</td>
<td>0.5</td>
</tr>
<tr>
<td>SIX</td>
<td>-</td>
</tr>
</tbody>
</table>
Results Effect of cis 1,4 content

Salient points
- No real changes in storage stability after 10 days
- Viscosity increase by changing cis 1,4 content – can be overcome
Results Effect of cis 1,4 content

**Salient points**
- It can be clearly seen that the ultimate tensile strength is reduced in formulation 7.
## Results: Effect of wet gel leaching

### Salient points
- Eliminating wet gel leaching improves ultimate tensile strength
- The inclusion of a post cure leach also has a positive effect

<table>
<thead>
<tr>
<th>Tensile Properties</th>
<th>Formulation 7 Cured for 20 minutes at 120°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With wet gel leaching</td>
</tr>
<tr>
<td><strong>Initial Tensile Properties</strong></td>
<td></td>
</tr>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>13.5</td>
</tr>
<tr>
<td>Strain at Break (%)</td>
<td>848</td>
</tr>
<tr>
<td>Stress at 300% Strain (MPa)</td>
<td>1.14</td>
</tr>
<tr>
<td>Stress at 500% Strain (MPa)</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Results Optimisation of Cure time

Salient point
• Cure times at 120degC can be optimized to provide optimum results
Contact Migration

- Previous studies using ZDNC and DIXP in polyisoprene latex and deproteinised natural rubber latex clearly showed that the safer accelerators could not be detected or were below the limit of detection.

- Again work performed at Robinson Brothers confirmed this to be the case during this program of work.

- The booster SIX is very water soluble and can be easily removed from the vulcanized rubber article with a post leaching step.
SIX Extractability

Graph showing the extractability of PI Latex film extracted with water with Ymin = 0.0048 and Ymax = 1.7537.
Films generated using Formulation 5 were tested against EN:71-12:2013 Nitrosamines are detected by the very sensitive HPLC MS MS system looking for the both N-nitrosamine and N-nitrosatable for the following amines:-

- NDELA, NDMA, NDEA, NDPA, NDiPA, NDBA, NDiNA, NMOR, NPIP, NDBzA, NMPhA, NEPhA

- No nitrosamines were detected

- Total Nitrosatables <0.02mg/kg
Conclusions

- The new cure compositions based on combination of ZDNC, DIXP and a metal xanthate (ZIX, SIX) can decrease the maturation time of synthetic polyisoprene latex at 30-35°C from 10 days to an economically attractive time of 24 hours. This is irrespective of variable cis 1,4 content isomer in the synthetic polyisoprene latex.

- The aqueous coagulant dipped tensile film properties, before and after thermal ageing, can meet the ASTM D3577 standard specification for rubber surgical gloves, Type II synthetic latex gloves.

- The results on vulcanised polyisoprene latex films for Nitrosamines and Nitrosatable substances fully complies with the requirements of EN71-12:2013 standard, which is one of the most stringent requirements for dipped articles.
Conclusions

• The very low level of residual accelerators in the vulcanisate do not migrate under the conditions of contact migration, which results in a film that is unlikely to cause Type IV allergy or irritant dermatitis.

• During processing of synthetic polyisoprene latex a post cure leaching stage is more beneficial than wet gel leaching as it improves the tensile film properties.

• Overall, the safer rubber accelerator combination based on DIXP, ZDNC and metal xanthate can produce vulcanisates with good tensile properties that should not give rise to irritant dermatitis, Type IV allergy or form carcinogenic N-nitrosamines and N-nitrosatable substances in the final product.
Thank you for your time

Questions?

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