CATALYSIS OF BLOCKED ISOCYANATES WITH NON-TIN CATALYSTS

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Dr. Loren Hill

Yes, Loren there is life after HMMMM
### COMPARISON MELAMINE-BLOCKED NCO

<table>
<thead>
<tr>
<th></th>
<th>HMMM</th>
<th>BL. NCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUNCTIONALITY</td>
<td>2-5</td>
<td>2-3</td>
</tr>
<tr>
<td>CATALYST</td>
<td>ACID</td>
<td>DBTDL</td>
</tr>
<tr>
<td>CURE TEMPERATURE, ºC</td>
<td>60-200</td>
<td>100-120 M*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130-200</td>
</tr>
<tr>
<td>VOC</td>
<td>MeOH/</td>
<td>EtOH M*</td>
</tr>
<tr>
<td></td>
<td>HCHO</td>
<td>KETOXIME</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PYRAZOL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GLYCOL</td>
</tr>
<tr>
<td>OVERBAKE</td>
<td>SELFCOND</td>
<td>FLEXIBILITY</td>
</tr>
<tr>
<td>CHEMICAL SENSITIVITY</td>
<td>ACID</td>
<td></td>
</tr>
<tr>
<td>M* malonate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SL2226
BLOCKED ISOCYANATES

ROH

\[ \text{ROH} \]

\[ \text{ROH} \]

\[ \text{RO-C} \]

\[ \text{RO-C} \]

\[ \text{RO-C} \]

\[ >\text{C=NOH} \]

\[ \text{RO-C} \]

\[ \text{RO-C} \]

\[ \text{RO-C} \]

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INTERNALLY BLOCKED ISOCYANATES

URETDLIONE

CYCLIC UREA
### APPLICATIONS FOR BLOCKED ISOCYANATES

<table>
<thead>
<tr>
<th>Application</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Coating</td>
<td>IPDI/LACTAM</td>
</tr>
<tr>
<td></td>
<td>URETDIONE</td>
</tr>
<tr>
<td>Cationic Electrocoating</td>
<td>Alcohol/TDI</td>
</tr>
<tr>
<td></td>
<td>Alcohol/MDI</td>
</tr>
<tr>
<td>Coil Coating</td>
<td>IPDI/HDI BL.</td>
</tr>
<tr>
<td>Automotive Clearcoats</td>
<td>Malonate</td>
</tr>
<tr>
<td>Stone Chip Resistant Primer</td>
<td>Ketoxime</td>
</tr>
<tr>
<td>Wire Coating</td>
<td>Phenol</td>
</tr>
</tbody>
</table>
REACTION OF BLOCKED ISOCYANATE

$RNHCOO\text{-}BL \rightleftharpoons k_1 \quad RNCO + BL \quad k_2$

$RNCO + R'OH \quad k_1 \quad RNHCO\text{-}OR'$

$RNHCO\text{-}BL + R'OH \quad k_1 \quad RNHCO\text{-}OR' + BL \quad k_2$
SIDE REACTIONS OF BLOCKED ISOCYANATE

\[ RNHCOO{-}BL \rightleftharpoons RNCO + BL \]
\[ RNCO + HOH \rightarrow RNHCOOH \]
\[ RNHCOOH \rightarrow RNH_2 + CO_2 \]
\[ RNH_2 + RNCO \rightarrow RNHCONHR \]

BIURET

ALLOPHANATE
BLOCKED ISOCYANATES

ROH ELECTROCOATING 180°C

WIRE COATING >200°C

POWDER COATING >180°C
BLOCKED ISOCYANATES

TOP COATS >130°C

TOP COATS >140°C

TOP COATS >100°C
BLOCKED ISOCYANATE RESPONSE TO CATALYST

MEK RESISTANCE

CATALYST, Me %
CARBITOL BLOCKED ISOXYANATE
CATALYST SELECTION, Me 0.18%

- No catalyst
- DBTDL
- Ti IV eth.aceto
- Al dionate
- Zn ethylhex.
- Co ethylhex.
- Bi ethylhex.

MEK

170°C  150°C
PHENOL BLOCKED ISOCYANATE
CATALYST SELECTION, 0.22 % Me

MEK RUBS

No catalyst
Ce naphth.
Ti IV eth.aceto
Zr dionate
Al dionate
Zr ethylhex.
Ca ethylhex.
Cr III ethylhex.
DBTDL
Bi ethylhex.
Mn naphth.
Zn ethylhex.

20 MIN. 130°C

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URETDIONE BLOCKED ISOCYANATES

\[
\begin{align*}
\text{R-N} & \quad \text{N-R} \\
\text{O} & \quad \text{C} \\
\text{C} & \quad \text{N} \\
\text{O} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{C} \\
\text{H} & \quad \text{N-R} \\
\text{C} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
2 \text{R'-OH} & \quad \rightarrow \quad 2 \text{RNCO} \\
2 \text{R'-OH} & \quad \rightarrow \quad 2 \text{RNHCOOR'}
\end{align*}
\]
URETDIONE BLOCKED ISOCYANATE
CATALYST SELECTION

CURE TEMPERATURE, °C

MEK

170 180 190 200

NO Zn Sn DBU DBTDL Bi

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ACKNOWLEDGEMENT

TECHNICAL SERVICE DEPARTMENT

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