NEW GENERATION OF MULTIFUNCTIONAL CROSSLINKERS

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INTRODUCTION

Crosslinking is a most interesting process, attractive for the chemist, informative for the physicist and helpful for the user – in the joint development of tailored PSAs. This applies mostly also for acrylate based PSA dispersions.

In general PSAs are used increasingly for coating of labels, PSA tapes, decorative films and similar self-adhesive articles. The PSAs have to have certain properties. Besides a good surface adhesion the PSAs should have good stability against light, oxygen, moisture and plasticizer and the adhesion characteristic should be constant over a very large temperature range.

The crosslinking of PSAs is a useful process in the repertoire of general procedures and is recognized like a red line going through the many applications in the areas of PSAs. In the nomenclature „crosslinking“ is the correlation of a network which relates to a net of interconnected chains. Polymeric networks or crosslinked systems consist of interconnected macro molecules, which expend into all three dimensions.

The individual molecule chains in a crosslinking are interconnected into „infinitely“ large molecules. Due to the huge length of the starting polymeric chains, only small amounts of a crosslinking additive are needed to accomplish complete crosslinking, i.e. a crosslinking covering the total volume of the PSA. The larger the starting molecules, the larger the probability that they participate in the network concentration at a given amount of crosslinking additive. Therefore, preferrably parts with lower molecular weight remain without ties to the network when low crosslinking degree applies because of the normally polydispersal characteristic of polymers.

GOAL OF CROSSLINKING

The physico-chemical and mechanical properties of PSAs based on acrylate acid esters are determined to a large degree by the type and amount of crosslinking agent which is added to the copolymer. It is known that an acrylate copolymer which has no crosslinking or is crosslinked only by hydrogen bridges, has no sufficient thermo-mechanical stability and is practically useless as a PSA.

The crosslinking can be considered as a critical factor in the formulation of the PSA in the application stage. The generated crosslinked connections inhibit the mobility of the polymer molecules extensively by chemical bondings in the network of the polymeric PSA. A crosslinked PSA therefore can not melt anymore. Perhaps it becomes somewhat softer at increased temperature, but does not melt. Rather it undergoes decomposition above a certain temperature.
There are two parameters of importance in the crosslinked PSAs and should not be mixed up in their meaning:

Degree of crosslinkage  
Density of crosslinkage

The crosslinking therefore has to take place in the way that the degree of crosslinkage may be high, the density of the crosslinkage, however, has to stay definitely low. The degree of crosslinkage is a measure for the interconnected bonding of the PSA molecules in the three-dimensional network. The following drawing illustrates that:

![Diagram of low and high density of crosslinkage]

LOW DENSITY OF CROSSLINKAGE       HIGH DENSITY OF CROSSLINKAGE

The degree of crosslinkage should be as high as possible to keep the melting and the solubility of the PSA at a minimum. With increasing density of the crosslinkage the cohesion increases, but the crosslinking process causes a decrease in volume, that means a shrinkage during crosslinking, which negatively affects the adhesion. Furthermore, an exceeding density of crosslinkage causes a loss in tacking and leads to porosity: consequentially a good PSA should have a high degree of crosslinkage, but a low density of crosslinkage.

With the help of chemical bondings or procedures an increase in cohesion may be accomplished during the drying of the PSA coating in the drying step. Logically the tackifying properties of the PSA coat, such as tack and peel adhesion decrease:

![Graph showing tack, peel adhesion, and shear resistance vs. crosslinkage density]

CROSSLINKAGE DENSITY
The time span, which can be utilized after the crosslinking agent containing PSAs are set up, is called pot life. After a second time span the so called gel point is reached, and the PSA can no longer be modified. This process is illustrated below:

The curve in general applies for each crosslinking agent containing PSA system. That means that a fast crosslinking system has actually a short pot life, and a slow crosslinking system has a long pot life. Fast crosslinking PSA systems for industrial use with short pot life are often used with two-component application-equipment, which mix and add the reactive components right before the coating.

In order to reach the PSA crosslinking, various multifunctional chemical compounds with respectively reactive groups are used as the following list illustrates:

* Metal acidesters
* Metal chelates
* Metal salts
* Polyfunctional isocyanates
* Organofunctional silanes
* Polycarbodiimides
* Polyfunctional ethylene imines
* Polyfunctional propylene imines
* Amino resins
* Epoxy resins
* Peroxides
* Monomers with crosslinking properties

We will now dive into the world of propylenimines.
MULTIFUNCTIONAL PROPYLENIMINE DERIVATIVES

In order to achieve an optimum of crosslinking efficiency the known terrain of crosslinkers was widened by the introduction of a new generation of crosslinkers namely multifunctional propylenimines.

They are chemicals derived from 2-Methylaziridine (a highly reactive and versatile material) containing saturated instable rings with nitrogen atoms:

\[
\begin{align*}
\text{CH}_2 & \text{CH} \\
\text{CH}_3 & \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 & \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \text{CH} \\
\text{N} & \text{CH} \\
\end{align*}
\]

\[
x + y \geq 2
\]

Such compounds react with the carboxyl groups or isocyanate groups of the polymer by opening the ring. This classifies them as crosslinkers.

The crosslinking of carboxyl group containing pressure sensitive adhesives is carried out under room temperature, an increase of temperature accelerates the crosslinking process. Because of the high reactivity of polyaziridines the pot life of propylenimine containing PSA formulations is quite limited and lies in the range of 4 ... 8 h which is lower than the pot life of polyisocyanate containing adhesives. This problem can be overcome by mixing the adhesive mass and the crosslinker directly prior to the coating step. In comparison to metal acid esters or metal chelates the crosslinking yield of multifunctional propylenimines is so high that no afterreactions like brittleness or a decline of peel resistance due to ongoing crosslinking occur.
Reaction Mechanism of Crosslinking

The crosslinking of pressure sensitive adhesives with multifunctional propylenimines is mainly based on the carboxyl groups offered by the vinylcarboxonic acids within the polymeric chain. The oxygen of the nucleophilic carboxyl group causes the opening of the tense propylenimine rings while the hydrogen atoms accompanying the carboxyl groups protonate the nitrogen atoms:

For such a crosslinking variation speaks the following consideration:

Facing the carbon-cation-structure the variant 2 seems to be the most realistic path backing the reaction mechanism shown above. Multifunctional propylenimine groups containing compounds are known for over 32 years. Along with the progress in the field of organic synthesis the chemical structure of propylenimine crosslinkers was adapted to the developments in polymer chemistry. The application of such crosslinkers is product oriented and only mentioned for special formulations. In the early eighties 3M was particularly active in
this sector presenting new ideas about structure and application of polyfunctional propylenimines.

The state of the art in the field of multifunctional propylenimines covers the following literature:

[1] describes a procedure for the synthesis of polyfunctional propylenimine compounds. Reactants are \( \alpha,\beta\)-Alkylenimin (Propylenimin) and Poly(acylchloride)-semiester.

[2] comprises the substance claim on compounds characterized by the general formula:

\[
\left[ R_4 \begin{array}{c} \text{N} \\ \text{[A]} \end{array} X \right] \text{Si} \rightarrow R_{4-m}
\]

[3] describes a procedure for the crosslinking of polyesters containing anhydride and carboxyl groups by using multifunctional propylenimines.

[4] describes boranes containing propylenimine groups characterized by the general formula:

\[
\begin{pmatrix}
 R \\
 B \text{N} \\
 \text{CH-R_2}
\end{pmatrix}
\]

and their making procedures.

[5] reveals radiation curable resins containing propylenimine group based compounds characterized by the general formula:

[6] shows products from the reaction between polyfunctional epoxy resins and tri[2-(1-aziridinyl)ethyl]trimellitate or bis(2-methylaziridinylethyl)sulfone.
[7] claims propyleniminesilanes characterized by the general formula:

\[
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4 \\
\text{N}(-\text{C}_n\text{H}_{2n})\text{X} \\
\text{Si} - \text{R}^+ - \text{m}
\end{array}
\]

[8] describes bifunctional propylenimine compounds:

\[
\begin{array}{c}
\text{X} \\
\text{N} - \text{C} - \text{R} \\
\text{C} - \text{R} \\
\text{H}
\end{array}
\]

where X = organic group, selected from an alkylen-, cycloalkylen-, alkylenycloalkylen-, alkylenthioalkylen-, alkylensofoalkylen-, alkylenoxyalkylen- and alkylenarylalkylen group with C_{2-20} -atoms. The aziridinylring contains at least one functional group (R) like a carboxyl-, cyano-, nitrogroup etc.

These chemicals are synthesized in this way:

\[
2 \text{R}-\text{C}-\text{C}-\text{R} + \text{H}_2\text{N}-\text{X}-\text{NH}_2 \rightarrow \text{R}-\text{C} - \text{N}-\text{X}-\text{N}-\text{C}-\text{R}
\]

[9] describes polybutadiene and bifunctional derivatives characterized by the general formula:

\[
\begin{array}{c}
\text{CH}_3 - \text{H} - \text{C} - \text{CH}_2 \\
\text{H}_2\text{C} - \text{N} - \text{P} - \text{NH} - \text{CH} - \text{CH}_3 \\
\text{CH}_3 - \text{H} - \text{C} - \text{O} - \text{C} - \text{R}
\end{array}
\]

[10] describes a procedure for the crosslinking of liquid polymers (polybutadienes e.g.) containing carboxylgroups with polyethylenimine compounds yielding high molecular, solid polymers.
[11] describes bifunctional propylenimine ethers characterized by the general formula:

\[ \text{H}_2\text{C} \text{N} \text{CHCH}_2\text{OR} \text{CH}_2\text{OHCH}_2\text{N} \text{CH} \text{(C}_n\text{H}_{2n})\text{H} \]

[12] comprises a procedure for the preparation and crosslinking of special dispersions (manufacture of magnetic tapes) by using polyfunctional propylenimines characterized by the general formula:

\[ Q \left\{ \begin{array}{c}
\text{CH}_2 \\
\text{CR} \\
\text{R}^n
\end{array} \right\}_n \]

Q : n-valent inorganic or organic group  
R : H-atom or alkyl group

"CX-100" (Polyvinyl Chemical Ind.) und BPI (N,N'-Bis-propylenisophthalic acid amide) have been mentioned as crosslinkers.

[13] describes water absorbents containing carboxyl groups crosslinked with multifunctional propylenimine derivatives. Neocryl CX-100 is mentioned as an example.

[14] reveals the coating of magnetic plates with dispersions being crosslinked with polyfunctional propylenimines. Amongst other species Neocryl CX-100 is mentioned.

[15] describes the structure of removable and repositionable pressure sensitive adhesive articles. As crosslinker a bifunctional propylenimine compound namely 1,1'-(1,3-phenylendicarbonyl)bis(2-methylaziridin) is used.

Regarding their chemical structure the multifunctional propylenimine crosslinkers are going to be divided into the following groups.

**Aliphatic Propylenimine Derivatives**

This product class is prepared by reacting the corresponding multifunctional aliphatic carboxylic acid amides, carboxylic acid chlorides or bromides with 1,2-dibromopropane or propylenimine (a detailed description is given later in case of the aromatic propylenimine derivatives). For industrial quantities only propylenimine is used as starting material.
Reaction products from multifunctional carboxylic acid chlorides and propylenimine

This range of crosslinkers is also known as Bisamide Crosslinking Agents (BCA).

\[
\begin{align*}
H_2C\begin{array}{c}O \\
\text{CH}_3\end{array}\text{N}\begin{array}{c}C \text{Alkyln} \\
\text{N}\text{CH}_2\end{array}C\text{N} \hspace{1cm} \text{CH}_3
\end{align*}
\]

The process of crosslinking pressure sensitive adhesives with multifunctional propylenimines may be outlined as follows:

Here some examples for typical aliphatic propylenimines:

\[
\begin{align*}
H_2C\begin{array}{c}O \\
\text{CH}_3\end{array}\text{N}\begin{array}{c}C \text{-(CH}_2\text{)_7} \text{N} \text{CH}_2\end{array}C\text{N} \hspace{1cm} \text{CH}_3
\end{align*}
\]

1,1'-Azelaoyl-bis-(2-methylaziridine)
N,N'-Bis-propylenadipic acid amide (BPA)

N,N',N",N"'-Tetrapropyl-1,2,3,4-butanetetracarbonic acid amide

Reaction products from multifunctional isocyanates and propylenimine

This reaction is based upon the reactivity of the propylenimine ring and the N=C=O-groups.

Trimethylhexamethylendipropylenurea

Another example for such a propylenimine group containing compound is:

1,6-Hexamethylendipropylenurea (HMPU)
A pressure sensitive adhesive being prepared from 65 parts 2-ethylhexylacrylate, 30 parts methylacrylate and 5 parts acrylic acid was taken to find out the efficiency of  N,N’-bis-propylenadipinic acid amide (BPA) and 1,6-hexamethyldipropylenurea (HMPU) as crosslinkers.

<table>
<thead>
<tr>
<th>Propylenimine crosslinker [wt.-%]</th>
<th>Coat weight [g/m²]</th>
<th>Tack [N]</th>
<th>Peel resistance [N]</th>
<th>Shear strength [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA 0.1 HMPU 0.1</td>
<td>60</td>
<td>22</td>
<td>21 pCF</td>
<td>16 pCF</td>
</tr>
<tr>
<td>- 0.1</td>
<td>59</td>
<td>20</td>
<td>18</td>
<td>15 pCF</td>
</tr>
<tr>
<td>0.2 -</td>
<td>61</td>
<td>20.5</td>
<td>18.5</td>
<td>10.5</td>
</tr>
<tr>
<td>- 0.2</td>
<td>58</td>
<td>18.5</td>
<td>17.0</td>
<td>7.5</td>
</tr>
<tr>
<td>0.3 -</td>
<td>60</td>
<td>18.5</td>
<td>14.5</td>
<td>8.0</td>
</tr>
<tr>
<td>- 0.3</td>
<td>60</td>
<td>17.0</td>
<td>11.0</td>
<td>6.5</td>
</tr>
<tr>
<td>0.4 -</td>
<td>59</td>
<td>15.0</td>
<td>9.0</td>
<td>7.0</td>
</tr>
<tr>
<td>- 0.4</td>
<td>60</td>
<td>14.5</td>
<td>7.5</td>
<td>5.5</td>
</tr>
<tr>
<td>0.5 -</td>
<td>60</td>
<td>10.0</td>
<td>7.5</td>
<td>5.5</td>
</tr>
<tr>
<td>- 0.5</td>
<td>61</td>
<td>6.5</td>
<td>5.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

PCF: partly cohesive failure

**Reaction products from multifunctional acrylates and propylenimine**

Propylenimine reacts with the double bond of the acryloyl group:

\[
\begin{align*}
R-\overset{\text{O}}{\text{O}}-\overset{\text{C}}{\text{C}}-\overset{\text{CH=CH}_2}{\text{CH}} & \quad + \quad \overset{\text{N}}{\text{CH}_3} \\
\rightarrow & \quad R-\overset{\text{O}}{\text{O}}-\overset{\text{C}}{\text{C}}-\overset{\text{CH}_2}{\text{CH}_2}-\overset{\text{N}}{\text{CH}_3}
\end{align*}
\]

Some classical compounds of this section are shown in [12] including:

\[
\text{CH}_3\text{CH}_2\left(\overset{\text{CH}_2\overset{\text{O}_2\text{C}}{\text{C}}-\overset{\text{CH}_2}{\text{CH}_2}-\overset{\text{N}}{\text{CH}_2}}{\text{CH}_3}\right)_3
\]

Trimethylolpropane-tris-(N-methylaziridinyl)-propionate

That crosslinker is manufactured by Zeneca Resins or Polyvinyl Chemical available under the trade mark CX-100.

**Aromatic Propylenimine Derivatives**

The synthesis of the aromatic propylenimine group containing crosslinking agents is based upon the reaction of aromatic multifunctional isocyanates with propylenimine
or upon the reaction of propylenimine with the corresponding halogene or amide compounds.

**Reaction products from propylenimine and isocyanates**

The synthesis of such crosslinkers is quite simple since it is a mere addition reaction.

![Reaction products from propylenimine and isocyanates](image)

**Reaction products from acid derivatives and propylenimine**

A typical candidate is isophthaloyl-bis(propylenimine known as BPI [15]:

![Reaction products from acid derivatives and propylenimine](image)

**BPI also named 1,1'-(1,3-Phenyldicarbonyl)-bis-[2-methylaziridine] can be synthesized in the following way:**
Only reaction 2 has been favoured in practice because of its simple realization.

There are further aromatic propylenimine crosslinkers like

\[
\text{N,N',N''-Tris-propylenbenzene-1,3,5-tricarbonic acid amide}
\]

**Aromatic naphthol ring based propylenimine derivatives**

\[
\text{N,N',N''-Tetra-propylen-1,4,5,8-naphthalenetetra-}
\]
N,N'-Bis-propylen-1,1'-dinaphthyl-8,8'-dicarboxylic acid amide

However, the naphtholring based propylenimine crosslinkers are almost insoluble in common organic solvents.

Carefully evaluated was N,N'-bis-propylenimine isophthalic acid amide (BPI) as shown in the following table:

<table>
<thead>
<tr>
<th>BPI [wt.-%]</th>
<th>Coat weight [g/m²]</th>
<th>Tack [N]</th>
<th>Peel resistance [N] at 20 °C</th>
<th>Peel resistance [N] at 70 °C</th>
<th>Shear strength [N] at 20 °C</th>
<th>Shear strength [N] at 70 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>60</td>
<td>12.5</td>
<td>15.0</td>
<td>25 pCF</td>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>0.10</td>
<td>60</td>
<td>11.5</td>
<td>14.5</td>
<td>21 pCF</td>
<td>90</td>
<td>25</td>
</tr>
<tr>
<td>0.15</td>
<td>60</td>
<td>11.0</td>
<td>14.0</td>
<td>13.0</td>
<td>&gt;90</td>
<td>30</td>
</tr>
<tr>
<td>0.20</td>
<td>60</td>
<td>10.0</td>
<td>13.5</td>
<td>11.5</td>
<td>&gt;90</td>
<td>35</td>
</tr>
<tr>
<td>0.25</td>
<td>60</td>
<td>8.5</td>
<td>12.5</td>
<td>10.0</td>
<td>&gt;90</td>
<td>40</td>
</tr>
</tbody>
</table>

pCF = partly cohesive failure

As shown BPI provides high quality crosslinked polyacrylic PSAs.

We also followed up the shelf life of an acrylic PSA (35 % solids) crosslinked with 0.1, 0.15 and 0.20 weight-% BPI. As can be seen in the graph the adhesive masses are still processable even after more than two months storage time.
Cycloaliphatic Propylenimine Derivatives

To this section belong products prepared from propylenimine and cycloaliphatic acid chlorides or multifunctional cycloaliphatic isocyanates.

Cycloaliphatic Bisamide Crosslinkers

\[ \text{N,N'}-\text{Bis-propylene-1,3-cyclohexanedicarboxylic acid amide} \]

\[ \text{N,N'}-\text{Bis-propylene-1,4-cyclohexanedicarboxylic acid amide (PCHA)} \]

Reaction products from propylenimine and multifunctional isocyanates

\[ \text{Isophoronedipropyleneurea} \]

\[ \text{Dicyclohexylmethane-bis-4,4'}-\text{dipropyleneurea} \]
Propylenimines based on s-Triazine

As a result of the reaction between propylenimine and cyanuric acid chloride or tris-(2-carboxyethyl)isocyanurate we find the following crosslinker:

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{CH}_3 & \quad \text{N} \quad \text{N} \quad \text{N} \\
\end{align*}
\]

2,4,6-Tris(1-methylaziridinyl)-1,3,5- triazine (tripropylenemelamine)

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{O} \\
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{O} \\
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{O} \\
\end{align*}
\]

2,4,6-Tris(propylenepropionic acid amide)-1,3,5-triazine

Propylenimines With Central Heteroatoms

Mainly phosphorus and sulfur serve as heteroatoms.

Tris(methylaziridinyl)phosphinoxide, known as MAPO, is described in [16]:

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{P} \quad \text{O} \\
\text{CH}_3 & \quad \text{N} \quad \text{P} \quad \text{O} \\
\text{CH}_3 & \quad \text{N} \quad \text{P} \quad \text{O} \\
\end{align*}
\]

The reaction with MAPO leads in case of carboxyl group containing PSAs to these bondings:

\[
\begin{align*}
\text{O} & \quad \text{P} \quad \text{N} \quad \text{CH}_2 \quad \text{C} \quad \text{O} \quad \text{C} \\
\end{align*}
\]
Further examples of propylenimine crosslinkers with central heteroatoms are shown below:

Tris-1-(2-methyl)aziridinylphosphinesulfide

N,N'-Bis-propanephosphonic acid diamide

Dipropyleniminepropanephosphonic acid

2,2'-(N,N'-propylenethiodiacetic acid amid)

**Propyleniminesilanes**

Here we have an interesting bundle of crosslinking agents synthesized from propylenimine and the corresponding multifunctional chlorosilanes [7]:

Vinyltripropyleniminesilane
Propylenimineborane [4]

Prepared from boranetricloride and aziridinylithium:

\[ \text{BCl}_3 + 3 \text{Li} - \text{N} - \text{CH}_3 \rightarrow B\left(\text{N} - \text{CH}_3\right)_3 + 3 \text{LiCl} \]

These compounds have not been accepted as crosslinking agents.

Other Propylenimines

The variety of organic chemistry allows the synthesis of even more exotic crosslinking agents containing propylenimine groups:

**Fluorinated propylenimines**

\[ \text{CH}_3\text{N} - \text{C} - \text{(CF}_2\text{)}_4 - \text{C} - \text{N} - \text{CH}_3 \]

**N,N'-Bis-propylenoctafluoro adipic acid amide**

\[ \text{CH}_3\text{N} - \text{C} - \text{C} - \text{F}_4 - \text{C} - \text{N} - \text{CH}_3 \]

**N,N'-Bis-propylenetetrafluoro isophthalic acid amide**
Propylenimineformiate

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{(CH}_2\text{)}_4 \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

Butandiol-bis-propylenimineformiate

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{(CH}_2\text{)}_6 \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

Hexandiol-bis-propylenimineformiate

Heterocyclic propylenimines

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{N, C, H} \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

Pyridine-2,5-(N,N'-bis-propylenedicarbonic acid amide)

\[
\begin{align*}
\text{CH}_3 & \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

5-Dimethylmaleinimidyl-N,N'-bis-propylenisophthalic acid amide

TEST RESULTS

Some selected propylenimine crosslinkers have been evaluated how they influence the thermal resistance of a polyacrylate PSA measured as shear strength at 70°C. A copolymer served as standard adhesive consisting of 65 parts 2-ethylhexyl-acrylate, 30 parts methylacrylate and 5 parts acrylic acid.
All these crosslinkers improve the cohesion of the adhesive mass significantly. The best results were achieved by using butandiol-bis-propylenimineformiate. In comparison to metal chelates propylenimines seem to be more efficient at the same dosage.

Despite outstanding crosslinking results like not-existing afterreactions, aggressive tack without sacrificing the thermal resistance of the pressure sensitive adhesive layer only a few propylenimine crosslinkers are commercially available.

The table below comprises the characteristics of propylenimine crosslinkers being offered in the market.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Neocryl CX-100</th>
<th>Trazidin VN</th>
<th>MAPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Name</td>
<td>Trismethylolpropane-tris-(N-methylaziridinyl)propionate</td>
<td>Polyfunctional Propylenimine derivative</td>
<td>Tris-[1-(2-methylaziridinyl)]phosphinoxide</td>
</tr>
<tr>
<td>Molecular Mass [Dalton]</td>
<td>467</td>
<td>475</td>
<td>215</td>
</tr>
<tr>
<td>PH</td>
<td>10.5</td>
<td>8 ... 9</td>
<td>8.5 ... 9.5</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear, yellowish liquid</td>
<td>Light liquid</td>
<td>Light liquid</td>
</tr>
<tr>
<td>Viscosity @ 25 °C [mPa·s]</td>
<td>200</td>
<td>220</td>
<td>180</td>
</tr>
<tr>
<td>Solubility</td>
<td>in a basic environment in water otherwise in ethylacetate, alcohol and in aromates. Limited solubility in aliphates.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These three crosslinkers have been compared by using a polyacrylate PSA at a coating weight of 60 g/m².
The figures in this table show that the crosslinker Neocryl CX-100 and Trazidin VN have presumably the same chemical composition and that they contribute to a somewhat better thermal resistance of the PSA than the crosslinker MAPO.

Then we evaluated the increase of adhesion in case of a PSA crosslinked with 0.2 weight-% Neocryl CX-100 being modified with various resins:

<table>
<thead>
<tr>
<th>Crossl. [wt-%]</th>
<th>Tack [N]</th>
<th>Peel resistance [N]</th>
<th>Shear strength [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 °C</td>
<td>70 °C</td>
</tr>
<tr>
<td>Neocryl CX-100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>23.0</td>
<td>19.0</td>
<td>13.0</td>
</tr>
<tr>
<td>0.15</td>
<td>21.5</td>
<td>18.0</td>
<td>11.5</td>
</tr>
<tr>
<td>0.20</td>
<td>19.0</td>
<td>16.5</td>
<td>10.0</td>
</tr>
<tr>
<td>Trazidin VN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>22.5</td>
<td>18.5</td>
<td>12.0</td>
</tr>
<tr>
<td>0.15</td>
<td>20.5</td>
<td>17.0</td>
<td>11.0</td>
</tr>
<tr>
<td>0.20</td>
<td>18.5</td>
<td>16.0</td>
<td>9.5</td>
</tr>
<tr>
<td>MAPO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>19.0</td>
<td>24.0</td>
<td>18.0</td>
</tr>
<tr>
<td>0.15</td>
<td>17.5</td>
<td>20.0</td>
<td>10.0</td>
</tr>
<tr>
<td>0.20</td>
<td>15.0</td>
<td>18.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Only the resin Tertac 30 improved the peel resistance.

We also tested the thermal resistance (shear strength @ 70 °C) of the PSA resin modified with Tertac 30 (table ).
Neocryl CX-100 gave the highest thermal resistance making it so predestined for further laboratory tests in the concentration range of 0.1 ... 1.0 weight-%:

<table>
<thead>
<tr>
<th>Neocryl CX-100 [wt.-%]</th>
<th>Coating weight [g/m²]</th>
<th>Tack [N]</th>
<th>Peel resistance [N]</th>
<th>Shear strength [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>20 °C</td>
<td>70 °C</td>
</tr>
<tr>
<td>0.10</td>
<td>60</td>
<td>10.0</td>
<td>15.5</td>
<td>14.5</td>
</tr>
<tr>
<td>0.15</td>
<td>60</td>
<td>10.5</td>
<td>14.0</td>
<td>14.0</td>
</tr>
<tr>
<td>0.20</td>
<td>61</td>
<td>10.5</td>
<td>13.5</td>
<td>13.3</td>
</tr>
<tr>
<td>0.40</td>
<td>62</td>
<td>9.0</td>
<td>12.5</td>
<td>9.5</td>
</tr>
<tr>
<td>0.60</td>
<td>60</td>
<td>8.5</td>
<td>11.5</td>
<td>8.0</td>
</tr>
<tr>
<td>0.80</td>
<td>63</td>
<td>7.5</td>
<td>10.5</td>
<td>7.0</td>
</tr>
<tr>
<td>1.00</td>
<td>60</td>
<td>5.5</td>
<td>8.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Even at low crosslinker concentrations the shear stability is extremely high and other adhesive properties like tack and peel strength should be drawn attention to:
In contrast to the commonly used metal chelates just 0.1 ... 0.2 weight-% Neocryl CX-100 are sufficient in order to achieve excellent shear strength, high tack and peel strength values. In practice a concentration of 0.15 weight-% Neocryl CX-100 makes sense.

Yet even this outstanding crosslinker Neocryl CX-100 does not protect the adhesive mass against an adhesion decline at elevated temperatures:

A drastic break-down of peel strength is to be noticed within the temperature range of 70 and 120°C, while beyond 120°C adhesion failure versus the carrier occurs.

Unexpectedly the application of Neocryl CX-100 improves the specific adhesion on various, particularly on low energetic substrates:
Other Multifunctional Alkylethyleneimines

Other alkylaziridine group containing compounds have been proven to be chemically quite attractive and effective as crosslinkers as well:

![Chemical structure of 1,3,5-Tris(2-ethyl-1-aziridinyl)carbonylbenzene](attachment:image1.png)

1,3,5-Tris(2-ethyl-1-aziridinyl)carbonylbenzene [17]

![Chemical structure of 1,1'-Trimethyladipoyl-bis(2-ethylaziridine)](attachment:image2.png)

1,1'-Trimethyladipoyl-bis(2-ethylaziridine) [17]

![Chemical structure of 2,4,6-Tris(2-ethyl-1-aziridinyl)-1,3,5-triazine](attachment:image3.png)

2,4,6-Tris(2-ethyl-1-aziridinyl)-1,3,5-triazine [18]

Further multifunctional alkylethyleneimine derivatives like:

- Tri(2,3-dimethyl-1-aziridinyl)phosphinoxide
- Tri(2-isopropyl-1-aziridinyl)phosphinoxide
- Tri(2-methyl-3-ethyl-1-aziridinyl)phosphinoxide
- Tri(2-methyl-3-n-butyl-1-aziridinyl)phosphinoxide
- Tri(2-hexyl-1-aziridinyl)phosphinoxide
- Tri(2,3-diheptyl-1-aziridinyl)phosphinoxide
- Tri(2-methyl-3-octyl-1-aziridinyl)phosphinoxide
- Tri(2-ethyl-3-decyl-1-aziridinyl)phosphinoxide
- Tri(2-dodecyl-1-aziridinyl)phosphinoxide or
- Tri(2-methyl-3-tridecyl-1-aziridinyl)phosphinoxide

are mentioned in [16].
POTLIFE OF PSAS CROSSLINKED WITH CROSSLINKERS CONTAINING PROPYLENIMINE GROUPS

A marginal disadvantage of the propylenimine crosslinking systems is their potlife which is limited to several hours only.

Because of the potential risk of gelation it is quite difficult to convert propylenimine containing adhesives. The normal routine - mixing the PSA with crosslinker, transfer to the coating plant, using the adhesive for coating – seems not being viable. Also the in situ mixing of crosslinker with PSA just before it enters the coating head may be not the best solution of the problem because of quality variations.

Facing the high reactivity of aziridinyl crosslinkers the addition of alcohol does not provide the same stabilizing effect as it is the case for the conventional metal acetyl acetonates. But there is a way out: the prolongation of potlife up to several days or even weeks is achieved by adding volatile aminoorganic stabilizers to the propylenimine crosslinker containing polyacrylate PSA [19]. The concentration of such stabilizers ranges from 1 to 4 weight-%. The next table shows some of those:

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>Boiling point $B_b$ [°C]</th>
<th>Vapor pressure [°C/mbar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tert.-Butylamine</td>
<td>45</td>
<td>20/532</td>
</tr>
<tr>
<td>n-Propylamine</td>
<td>49</td>
<td>20/330</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>55</td>
<td>20/250</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>78</td>
<td>20/760</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>88</td>
<td>20/62</td>
</tr>
<tr>
<td>4-Amino-1-butanol</td>
<td>98</td>
<td>20/135</td>
</tr>
<tr>
<td>Piperidine</td>
<td>105</td>
<td>20/33</td>
</tr>
<tr>
<td>Dipropropylamine</td>
<td>108</td>
<td>20/42</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>116</td>
<td>20/12</td>
</tr>
<tr>
<td>1,2-Diaminopropane</td>
<td>119</td>
<td>20/3,6</td>
</tr>
</tbody>
</table>

The following graph shows how triethylamin (TEA) influences the change of viscosity of a MAPO containing polyacrylate PSA:
Triethylamine does not deteriorate pressure sensitive adhesive properties like dynamic shear strength or peel resistance:

<table>
<thead>
<tr>
<th>TEA [%]</th>
<th>Dynamic shear strength [N]</th>
<th>Peel resistance [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80 °C</td>
<td>120 °C</td>
</tr>
<tr>
<td>0</td>
<td>450</td>
<td>310</td>
</tr>
<tr>
<td>0.5</td>
<td>438</td>
<td>305</td>
</tr>
<tr>
<td>1.0</td>
<td>440</td>
<td>300</td>
</tr>
<tr>
<td>2.0</td>
<td>455</td>
<td>315</td>
</tr>
<tr>
<td>4.0</td>
<td>430</td>
<td>308</td>
</tr>
</tbody>
</table>

Dynamic shear strength: measured on cardboard after laminating with 50 N pressure (bonding area 400 mm²)

The test results underline that triethylamine is a good choice when used as a stabilizer for propylenimine containing PSAs.

Nevertheless the potlife of such adhesive systems can also be extended by adding special amino resins offered by Cyanamid. This was evaluated for a Cymel resin in combination with TEA and a Neocryl CX-100 containing polyacrylate PSA.
In general the following nitrogen atom containing organic derivatives may be used for the stabilization of PSAs containing propylenimine crosslinkers:

1. Ammonia  (used for PSA dispersions and hydrophilic PSAs)

2. Aliphatic Amines:
   - Primary
     - n-Butylamine \( B_p = 78 \, ^\circ \text{C} \)
     - n-Propylamine \( B_p = 49 \, ^\circ \text{C} \)
     - i-Butylamine \( B_p = 78 \, ^\circ \text{C} \)
   - Secondary
     - Diethylamine \( B_p = 55 \, ^\circ \text{C} \)
     - Dipropylamine \( B_p = 108 \, ^\circ \text{C} \)
   - Tertiary
     - Triethylamine \( B_p = 88 \, ^\circ \text{C} \)
     - Tripropylamine \( B_p = 156 \, ^\circ \text{C} \)

3. Diamines
   - Diaminopropane \( B_p = 136 \, ^\circ \text{C} \)
   - Ethylenediamin \( B_p = 116 \, ^\circ \text{C} \)

4. Cyclic Amines
   - Piperidine \( B_p = 105 \, ^\circ \text{C} \)
   - Cyclohexylamine \( B_p = 135 \, ^\circ \text{C} \)

5. Aromatic Amines
   - Primary
     - Aniline \( B_p = 184 \, ^\circ \text{C} \)
     - o-Toluidine \( B_p = 194 \, ^\circ \text{C} \)
   - Secondary
     - Methylaniline \( B_p = 196 \, ^\circ \text{C} \)
   - Tertiary
     - Dimethylanil!ne \( B_p = 194 \, ^\circ \text{C} \)

6. Heterocyclic Amines
   - Pyridine \( B_p = 115 \, ^\circ \text{C} \)
   - Pyrrol \( B_p = 130 \, ^\circ \text{C} \)

7. Melamine-Formaldehyde-Resins
   - Cymel 303
   - Cymel 323
   - Cymel 370
   - Cymel 1158

8. Ureaderivatives
   - Urea

9. Aminoalcohol/-phenols
   - 4-Amino-1-butanol \( B_p = 98 \, ^\circ \text{C} \)
   - 4-Aminophenol

10. Acrylamides, Amides und Aminoacids
LITERATURE

1. Patent DE 1470358
2. Patent DE 1908264
4. U.S. Patent 3,393,184
5. U.S. Patent 3,539,547
7. U.S. Patent 3,711,466
10. DDR-Patent 143917
11. CAN Patent 767118
12. U.S. Patent 4,490,505
14. U.S. Patent 5,208,092
15. U.S. Patent 5,296,277
17. Patent EP 0 206 669
19. Patent DE 44 33 007