Liquid Anti-Strip Technology & Best Practices

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ArrMaz Custom Chemicals
C. Ivann Harnish
Technical Manager - Asphalt Additives
Topics

- Liquid anti-strip chemistry
- Mechanisms of Stripping
- Mechanism(s) of how liquid anti-strip additives enhance asphalt-aggregate adhesion
- Considerations in choosing proper liquid anti-strip additive for mix designs
- Aspects to consider in agency specification of liquid anti-strip additives
- Questions from audience?
**Liquid Anti-Strip** – liquid additive added to asphalt to increase the occurrence and strength of asphalt-aggregate adhesion

**Adhesion** – process of creating chemical bonds between the asphalt film and aggregate surface

**Stripping** - deterioration of asphalt-aggregate bond in the presence of H2O

- Stripping contributes to pavement distresses – raveling, potholes, rutting

Mitigate Stripping ➔ Significantly prolong pavement life-cycle and quality of roadway network
Stripping in Field = Moisture Damage

Pavement Distresses

1. Loss of fine aggregate
lack and deterioration of chemical bonding between asphalt and aggregate (poor adhesion)
2. Raveling & pothole development
   - loss of adhesion between surface aggregate and asphalt

3. Rutting
   - Reduction in tensile strength due to loss of adhesion between aggregate and asphalt
Ethylene Amine-Based Chemistry

- Ethylene amines part of everyday life
  - Common products made of ethylene amines include paints, adhesives, fabric softeners, pharmaceuticals
  - Ethylene amine production involves reacting ammonia with ethylene oxide under high temperature and pressure with hydrogen gas and a catalyst

Amine - organic compound whose functional group containing a N atom with a lone pair of e- and at least one H atom replaced with an alkyl or aryl group (hydrocarbons)

- Hydrocarbon tail is lipophilic (oil-loving, non-polar), functional group head is hydrophilic (water-loving, polar)

Amine Functional Groups

\[ R^1 \text{H} \quad R^1 \text{H} \quad R^1 \text{R}^2 \text{R}^3 \]

R= hydrocarbon chain
**Types of Amines in Liquid Anti-Strip Chemistry**

- **Polyamines**– compound with 2 or amine functional groups
  - Heavies –5 or more functional groups per molecule, large molecules, vary in size
  - Many different types of polyamines, differ in number & types of amine functional groups, size of hydrocarbon chain
  - Highly effective, lower odor

  Tetraethylenepentamine (TEPA)

- **Bishexamethylenetetramine (BHMT)**– polyamine, produced during nylon production
  - Commonly used compound in anti-strip in the past
  - Effective, but acrid odor

- **Fatty (tallow) amines**– derived from processing fatty deposits of animals
  - Tallow diamine, tallow triamine
  - Older type of amine anti-strip, engineered to have long chain hydrocarbon
  - Generally less affective compared to newer liquid anti-strip technologies
**Types of Amines in Liquid Anti-Strip Chemistry**

- **Amidoamines** – created by reacting polyamines with fatty acids (carboxylic acid with hydrocarbon tail)
  - Fatty acids derived from natural oils (coconut oil, tall oil)
  - Creates much larger molecule and substantially lengthens hydrocarbon chain of amine molecule
  - In some cases, performance equal to better than polyamines
  - Larger molecule = enhanced heat stability
  - Different combinations of polyamines and fatty acids under varying reaction conditions yield amidoamines with different anti-strip performance characteristics

![Chemical Reaction Diagram](image)
Other types of Anti-Strip Chemistry

- **Phosphate Esters** – liquid additive product of reaction between phosphoric acid and alcohol
- **Hydrated Lime** – Ca(OH)$_2$, product of lime (CaO) slaked with water
  - Not a liquid additive - typically applied to aggregate as a slurry or dry added to wetted aggregate
Mechanism of H₂O Induced Stripping?

• H₂O seeps into pavement and migrates between the asphalt-aggregate interface (through various mechanisms), causing negative charge to develop on both aggregate and asphalt surface over time.

• Creates a REPULSION FORCE
  - asphalt “detaches or strips from aggregate”

• To understand how REPULSION FORCE develops, we must understand basic aggregate and asphalt chemistry.
Aggregate Mineralogical Composition

- **SILICA TETRAHEDRON** \( (SiO_4)^4^- \) - building block of all silicate minerals

- Silicate minerals most abundant minerals in earth’s crust (quartz, feldspar, amphiboles, pyroxenes), >95% by volume of earth’s crust
  - Individual silicates minerals occur when O in silica tetrahedron bond with other elements (Fe, Mg) and depend on the manner in which the O are shared among adjacent tetrahedron

- Silicate minerals occur in all common construction aggregates including all varieties of granite, basalt, quartzite, sandstone, slag and even most limestones and dolomites
Silica Tetrahedron ($\text{SiO}_4^{-4}$)
Charge Development Along Aggregate Perimeter

- Polar silanol (Si-OH) groups form along silicate mineral perimeter surfaces where Si-O bond is broken.
- OH (derived from H₂O vapor in air) bonds with Silicon atom and is ever present, even at typical hot-mix asphalt mixing temperatures.
- When silanol comes into contact with H₂O along asphalt-aggregate interface, a reaction occurs yielding a negative charge on aggregate.
Si-OH + H2O → Si-O⁻ + H3O⁺

- Silanol reacts with H₂O, liberates H⁺, surface now NEGATIVELY charged
- This reaction is why granites and other rocks rich in silicates are termed “acidic”
Aggregates Rich in Silica Have More Propensity to Strip

- marble, slag
- limestone
- basalt, diabase
- dolomite
- sandstone
- granite
- quartzite

Stripping Potential

% Silica, by mass
Asphalt

Asphalt - complex hydrocarbon consisting of a colloidal dispersion of asphaltenes in maltenes, stabilized by resins

Asphaltenes - most polar, highest molecular weight, solid compound

• arranged in sheet-like structures of condensed aromatic rings with C side chains, carboxylic acid groups
• asphaltenes “cluster” or aggregate together due to polarity
• other atoms present – S, N, O, metals – Ni, Fe
  • presence varies among different asphalt crude sources
    Sulphur 0.3-10.8%, Nitrogen 0.5-3.3%, Oxygen 0.3-6.6%
• these atoms along with aromatic rings contribute to polarity of asphaltenes
• polarity enables adhesive properties of asphaltenes
  • “Cholesterol of crude oil”
Asphalt Chemical Composition

Resins- similar to asphaltenes but lower molecular weight version

- Resin molecules have lipophilic and hydrophilic (polar) ends
  - Resins surround asphaltene clusters and allow clusters to be dispersed in maltene

*Asphaltenes and Resins are the components of asphalt that provide the adhesive properties of asphalt

Maltenes- non-polar fraction of asphalt, consist mainly of naphthenic (aromatic) and parrafinic waxes and oils
Maltene

Mexican asphalt

Venezuelan asphalt

Resin

Asphaltene

Resin
Asphaltene

Carboxylic Acid Groups
Negative Charge Development in Asphalt

When carboxylic acid groups of asphalt at asphalt-aggregate interface come into contact with H\textsubscript{2}O a reaction occurs yielding a negative charge on asphalt.
Asphalt-Aggregate Interaction

Asphaltenes and Resins are the components of asphalt that provide adhesive properties – HOWEVER…………

Arrangement of molecules not conducive to bonding with polar aggregate surface – asphaltenes sheltered by hydrophobic layer of resins

• Thermodynamics, HMA mixing

• Predominate asphalt-aggregate bonding is Van der Waals (intermolecular, weak electrostatic bond) between asphalt and aggregate
  • Leads to stripping
Asphalt Chemical Composition is Variable

• Asphalt chemistry is complex and varies significantly among crude sources
  • Chemical composition, configuration of asphaltenes and resin molecules variable in asphalt of different crude slates
  • Can expect varying adhesion performance characteristics among asphalts even with the same aggregate
  • Some asphalts have such poor chemical composition (high acidity, low asphaltene content) that poor adhesion performance characteristic can be expected even with aggregates of low silica percentages

– Variance in chemical characteristics of different asphalts evident in emulsification properties
Negative Charge in Asphalt
+ Negative Charge Along Aggregate Perimeter
= REPULSION FORCE
= STRIPPING
TSR 40

H20 Conditioned Specimens

Unconditioned Specimens
What Determines Severity of STRIPPING Potential in Pavements?

Factors

1. Aggregate mineralogical composition
2. Asphalt chemical characteristics
3. Aggregate Cleanliness
4. Mix Design ($P_{be}$)
5. Construction quality ($V_{a}$)
6. Pavement drainage conditions, climatic conditions
How Then, Do We Reduce Stripping?

Two options….
1. Increase Adhesion Force
2. Reduce Detachment Force
How Hydrated Lime Reduces Stripping

• Reduces Detachment Force

\[
Ca(OH)\_2 \text{ in water}_{(pH > 11)} \Rightarrow CaOH^+ + OH^- 
\]

• CaOH\(^+\) strongly adsorbed by aggregate at pH 11-13
  • Charge along aggregate surface reversed from negative to positive
  • Eliminates repulsion force between aggregate and asphalt
  • Other multivalent ions work similarly but at different pH ranges
    • Fe, Cu, Al
How Amine Anti-Strips Reduce Stripping

- Increase Adhesion Force
- Handful of proposed mechanisms and theories
How Amine Anti-Strips Reduce Stripping

Classic Theories

• Amines of anti-strip are surfactants at asphalt-aggregate interface

1. **Bridge Theory**- lone pair of N electrons of amine functional group chemically bonds (covalent, hydrogen) with positively charged and electron deficient sites (Ca, Fe, Na, K cations) along surface of aggregate, long hydrocarbon tail miscible in & attached to asphalt
Bridge Theory
How Amine Anti-Strips Reduce Stripping

Classic Theories

2. **Wetting Agent**- anti-strip improves asphalt-aggregate adhesion by reducing the surface tension.
Asphalt

Surface Tension

no anti-strip

\[ \theta = \text{Contact Angle} \]

anti-strip
How Amine Anti-Strips Reduce Stripping

Other Theories

• Explain increased asphalt-aggregate adhesion by mechanism other than as surfactant

1. Dispersion Theory – amines react with acid groups of asphaltene and resins and disperse the clusters
   • Liberated e- rich and polar components can now be easily adsorbed by aggregate surface
   • Adhesive forces greatly increased through the chemical bond formation
     • Hydrogen, covalent, pi bonds with aggregate – much stronger than Van der Waals bonds
   • Resultant bonding is stronger & can resist detachment forces
   • Ropes, Swedish bikini team, TV analogy
Maltene

Asphaltene

Resin

Mexican asphalt

Venezuelan asphalt
Asphaltene

Carboxylic Acid Groups
Evaluating Liquid Anti-Strip Additive in Mix Designs

In most cases, the properly selected additive and dosage rate can mitigate stripping and increase conditioned tensile strength

- Additive added to asphalt, typically at rate of 0.25-1.00% by weight of asphalt

- Additives are diverse, most will perform differently with different combinations of asphalt and aggregate types
  
  - Variation in amine, amidoamine molecules of anti-strip brands/types (hydrocarbon chain length, type and occurrence of amine functional groups) = performance varies
  
  - Lower-grade products may have low quality amines, low percentage of amine molecules
Evaluating Liquid Anti-Strip Additive in Mix Designs

Additive compatibility and performance must be evaluated for each mix design for Optimum Performance

- GOAL – Increase TSR & CONDITIONED SUBSET TENSILE STRENGTH, w/o significant affect to Unconditioned Subset Tensile Strength
- Recommend evaluating control specimens and specimens with additives at varying dosage levels (TSR, Hamburg)
  - Review data – performance, value
- Examples
IDOT D7 Surface Mix Design

- SP 12.5mm, $N_{des}$ 105 gyrations, Traffic Level E, surface mix
- PG 76-22 SBS, 70% limestone, 26.5% sandstone with carbonitic cement, 3.5% natural sand, no RAP
- Evaluate controls and 2 different amidoamine additives
  - AD-‐here® LOF 6500
  - AD-‐here® LOF 6500 LS
ILDOT Surface Mix Design No. 39BIT9381V

ILDOT Minimum Required Polymer Modified Mix Mean Conditioned Tensile Strength = 115 psi
ILDOT Minimum Required TSR = 85

Control
0.50% LOF 6500
0.75% LOF 6500
1.00% LOF 6500
0.75% LOF 6500 LS
1.00% LOF 6500 LS

TSR Value
Mean Conditioned Subset Tensile Strength
Which is Option is Best?

• 0.75% LOF 6500 LS provides highest TSR
  – TSR from 80 to 95 (19%) and mean conditioned tensile strength increased approximately 8 psi from control with no additive
    • Mean unconditioned strength = 193.3psi
    • Control mean unconditioned strength = 219.0psi
• 0.50% LOF 6500 provides lesser degree of TSR Increase
  – TSR from 80 to 86 (8%) and BUT mean conditioned tensile strength increased approximately 13 psi from control with no additive
    • Mean unconditioned strength = 218.6psi
    • Control mean unconditioned strength = 219.0psi
  – Economics = 33% less additive used
  – Best Option
Change in Mean Conditioned Subset Tensile Strength From Control Specimens – ILDOT Surface Mix Design No. 39BIT9381V

Dosage Rate, % (by weight of asphalt)
Which is Option is Best?

- Consideration should always be given 1st to effect anti-strip has on mean conditioned tensile strength
  - TSR increase could be attributed to dry and/or conditioned subset strength decrease
    - Higher dosage levels of anti-strip increase adhesion but may impart effect of softening mix and decreasing cohesive strength

- Cohesion vs. Adhesion
  - “More is not always better”
FDOT D1 Structural Mix Design

- SP 12.5mm, $N_{des}$ 75 gyrations, Traffic Level C, structural mix
- PG 64-22, 65% GA granite, 30% RAP, 5% natural sand
- Evaluate controls and 2 different amidoamine additives
  - AD-here® LOF 6500
  - AD-here® LOF 6500 LSC
FDOT Structural Design No. 081909-1
SP12.5, 30% Recycle, Traffic Level C

Control TSR = 49
Uncond. Subset Tensile Strength = 194 psi

FDOT Minimum Required Mean Unconditioned Subset Tensile Strength = 100 psi
Traffic Levels C Through E

FDOT Minimum Required TSR = 80

Anti-Strip Additive Dosage Rate, % by Weight of Virgin Asphalt
Anti-Strip Additive Dosage Rate, % by Weight of Total Asphalt
Conditioned Subset Tensile Strength vs. Additive Dosage Rate

Anti-Strip Additive Dosage Rate, % by Weight of Virgin Asphalt

Anti-Strip Additive Dosage Rate, % by Weight of Total Asphalt

CONTROL

0.50  0.75  1.00  1.10  1.25

0.34  0.51  0.75  0.75

LOF 6500
LOF 6500 LSC
Which is Option is Best?

- 0.75% (by weight total asphalt) LOF 6500 provides highest TSR
  - TSR from 49 to 98 (100%) and mean conditioned tensile strength increased approximately 70 psi (74%) from control with no additive
    - Mean unconditioned strength = 168.9 psi
    - Control mean unconditioned strength = 194 psi
    - Best Option
IDOT D1 Surface Mix Design

- SP 9.5mm, $N_{des}$ 90 gyrations, Traffic Level F, surface mix
- PG 70-22 SBS, 70.5% dolomite, 27.5%, 2.5% mineral filler, no RAP
- Evaluate controls and an amidoamine additive
  - AD-herer® LOF 6500
TSR Performance - ILDOT Design No. 19536 HMA N90F SURF

ILDOT Minimum Required Mean Conditioned Subset Tensile Strength = 115 psi (Polymer Modified Mix)

ILDOT Minimum Required TSR = 85

Anti-Strip Additive Dosage Rate, % by Weight of Total Asphalt

Control
0.25% LOF 6500
0.50% LOF 6500
0.75% LOF 6500

TSR Value
Conditioned Subset Mean Tensile Strength, psi
Overall Increase in Subset Tensile Strength

- **Unconditioned**
  - Subset Mean Tensile Strength, psi

- **Conditioned**
  - Subset Mean Tensile Strength, psi

AD-hered LOF 6500 Dosage Rate, % by Weight of Total Asphalt
Which is Option is Best?

- 0.25% LOF 6500 provides TSR of 87
  - TSR from 86 to 87 (1%) and mean conditioned tensile strength increased approximately 17 psi (12%) from control with no additive
    - Mean unconditioned strength = 178.6 psi
    - Control mean unconditioned strength = 160.2 psi
- 0.50% LOF 6500 provides highest TSR of 91
  - But note mean conditioned tensile strength decreased approximately 3 psi (2%) from 0.25% specimens?
  - But note mean unconditioned tensile strength decreased approximately 12 psi (7%) from 0.25% specimens?
- ASTM D4867 Within-laboratory Precision
  - laboratory mixed specimens, single operator, 1SD = 8 psi
  - d2S limit = 23 psi
Which is Option is Best?

• 0.75% LOF 6500 provides TSR of 87
  – TSR from 86 to 87 (1%) and mean conditioned *tensile strength increased approximately 33 psi (24%)* from control with no additive
    • Mean unconditioned strength = 195.8 psi
    • Control mean unconditioned strength = 160.2 psi
    • 22% increase in unconditioned strength !
    • Best bet
Dioritic Aggregate - 55-60% Silica, 0.50% XL9000

TSR 40

TSR 91
TSR 95
Rhyolitic Aggregate
70-75% Silica
1.00% XL9000
Evaluating Liquid Anti-Strip Additive in Mix Designs

• Thorough evaluation of anti-strip additive for every individual design is key to maximizing performance and value
  – Anti-strip products should not be substituted in any design unless proper evaluation has been performed
    • Could be a detriment to mix design performance
    • Not all are created equal
Specification of Liquid Anti-Strip Additive

• Initially Qualify Each Anti-Strip Additive for QPL inclusion
  – Ensure performance by having evaluation conducted using a few reference designs that are prone to stripping around the state.
  – Passing TSRs with an increase in conditioned tensile strengths from controls in dosage range of 0.25 to 1.00% would provide DOT with confidence that additive will perform well.
  – If DOT cannot achieve satisfactory results, contractors cannot
  – Empirical coating tests not recommended
    – Do not indicate how anti-strip may affect cohesion
    – Performance tests better option
Specification of Liquid Anti-Strip Additive

- **Periodic Infrared (IR) Scans of Approved Additives**
  - Measures the additives % absorption of different infrared wavelengths of light, provides product fingerprint
  - Check to verify originally qualified additive formulation has not changed

- **Minimum Total Amine Value (TAV) (ASTM D2074)**
  - Eliminate evaluation and use of low quality additives that do not contain an effective amount of amine
  - CalTrans, MODOT, KDOT have specified minimums
  - Higher TAV does not always mean better performance
    - Primary amine vs. tertiary amine
Specification of Liquid Anti-Strip Additive

Design Phase

- **Evaluate control specimens and specimens with additives at varying dosage levels**
  - Determine optimum dosage level

TSR and Subset Tensile Strength Criteria

- Specifying minimum TSR alone will not always yield optimum quality and value
  - Specification of a minimum % or psi increase in conditioned tensile strength assures enhanced pavement moisture resistance performance
  - Specification of a minimum psi or maximum % reduction in unconditioned tensile strength assures pavement strength undiminished
    - Eliminates “false TSR” or TSR increase due to drop in unconditioned strength divisor of TSR calculation
Questions?

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C. Ivann Harnish
Technical Manager- Asphalt Additives
iharnish@am-cc.com
863.669.8765

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