Liquid Anti-Strip Technology
&
Best Practices

NCAUPG

Overland Park, KS

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ArrMaz Custom Chemicals

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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?

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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 H20

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

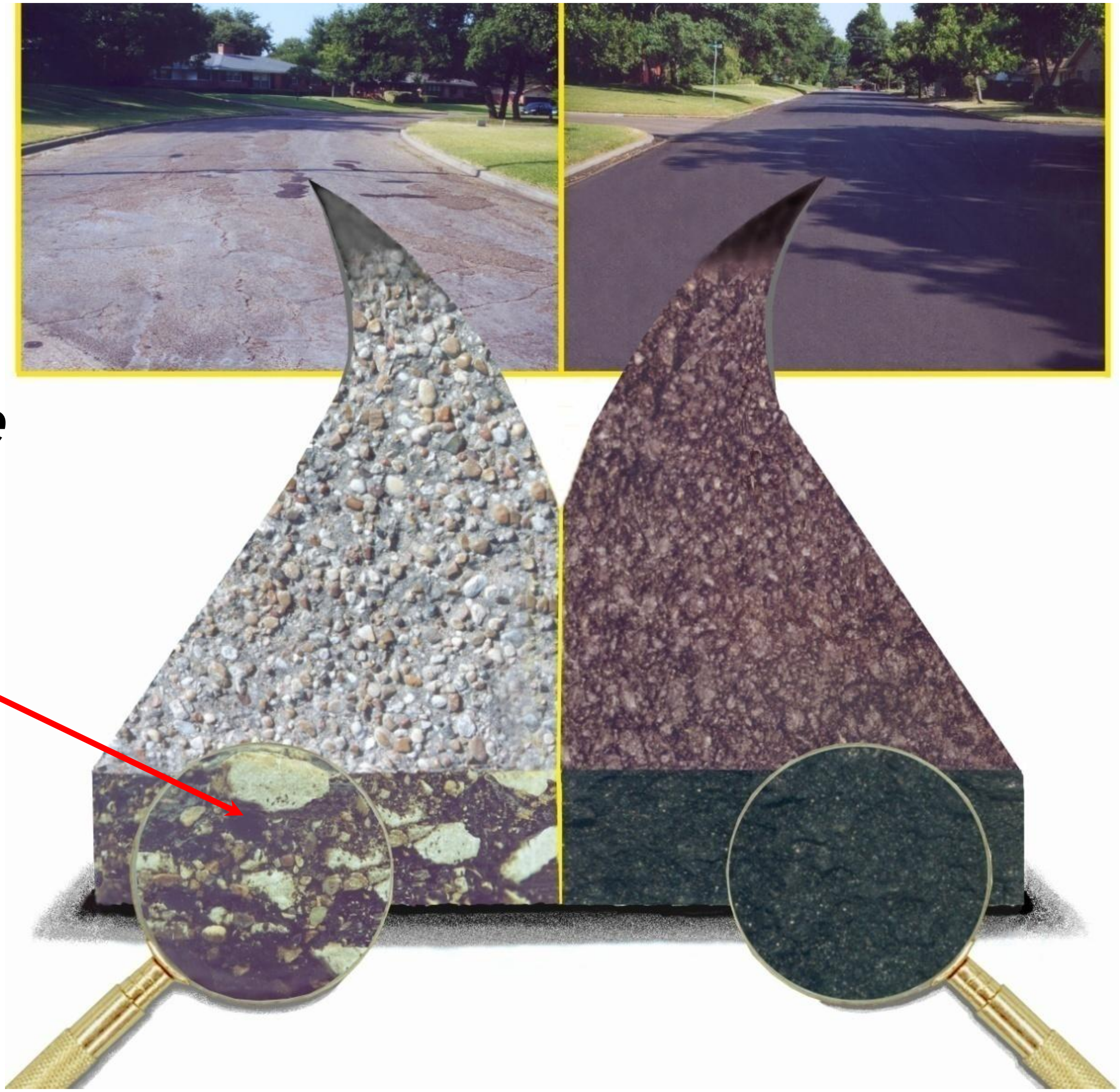
Mitigate Stripping → Significantly prolong pavement life-cycle and quality of roadway network

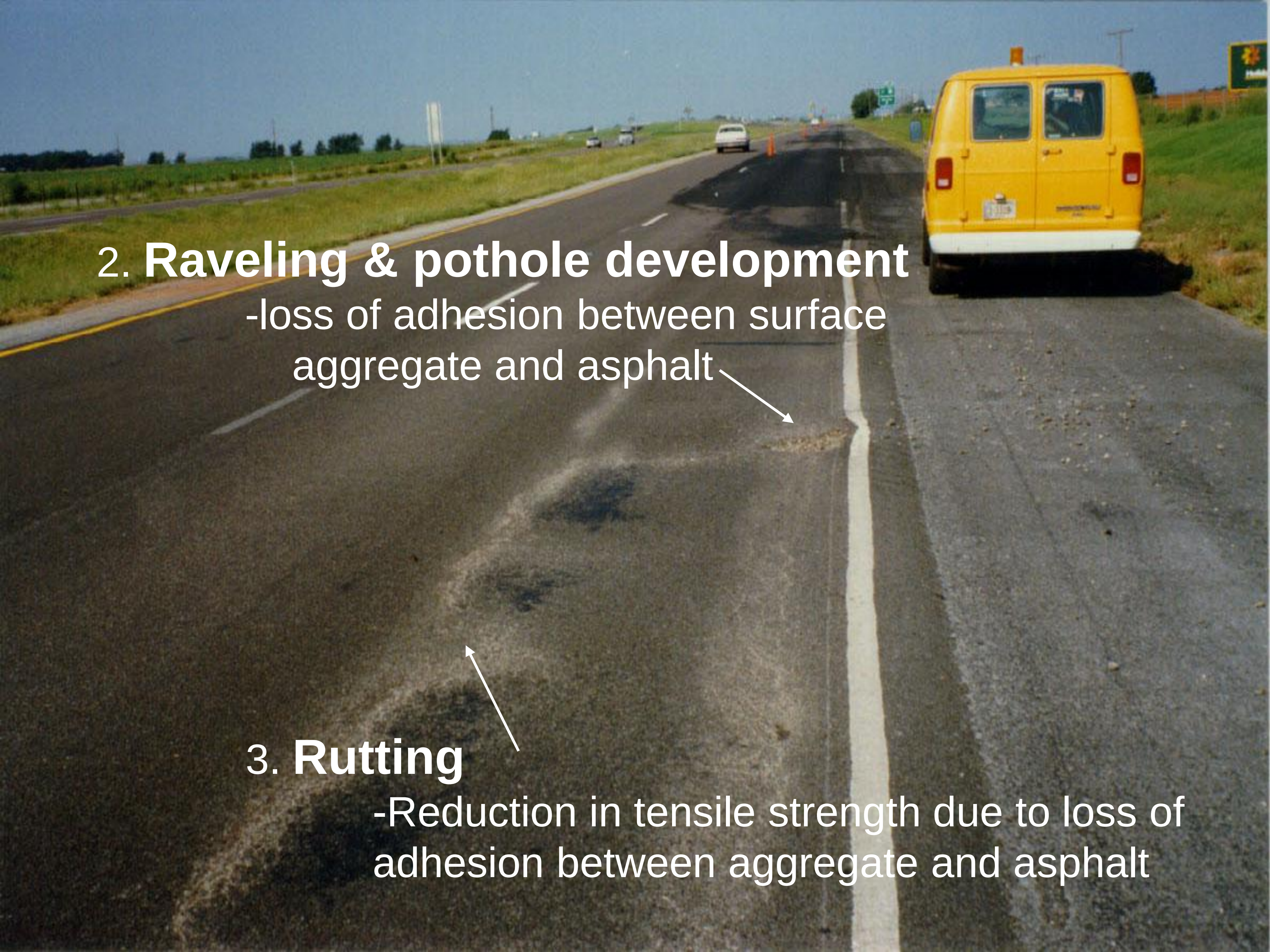
Stripping in Field = Moisture Damage

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

Liquid Anti-Strip Additive Chemistry

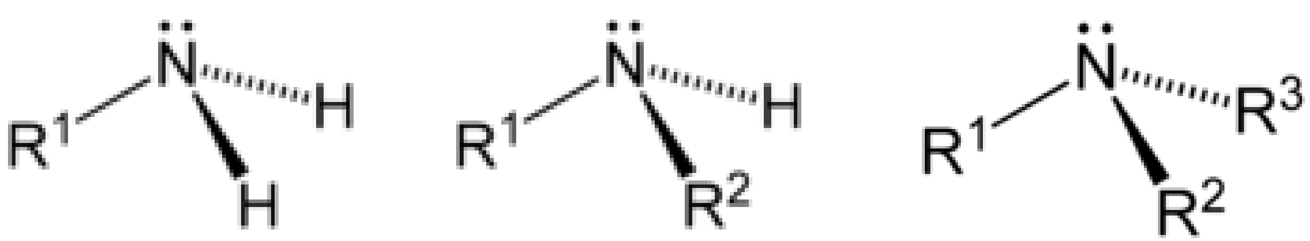
Ethylene Amine-Based Chemistry

- 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 hydrophillic (water-loving, polar)

Amine Functional Groups

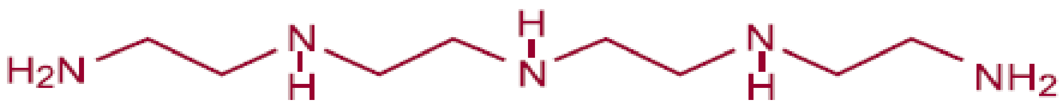


R= hydrocarbon chain

Types of Amines in Liquid Anti-Strip Chemistry

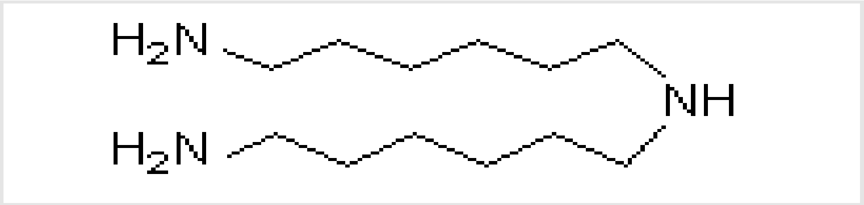
- ***Polyamines***– compound with 2 or amine functional groups
  - Heavies –5 or more functional groups per molecule, large molecules, vary in size
  - Many different types of polyamines, differ in number & types of amine functional groups, size of hydrocarbon chain
  - Highly effective, lower odor

Tetraethylenepentamine (**TEPA**)



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

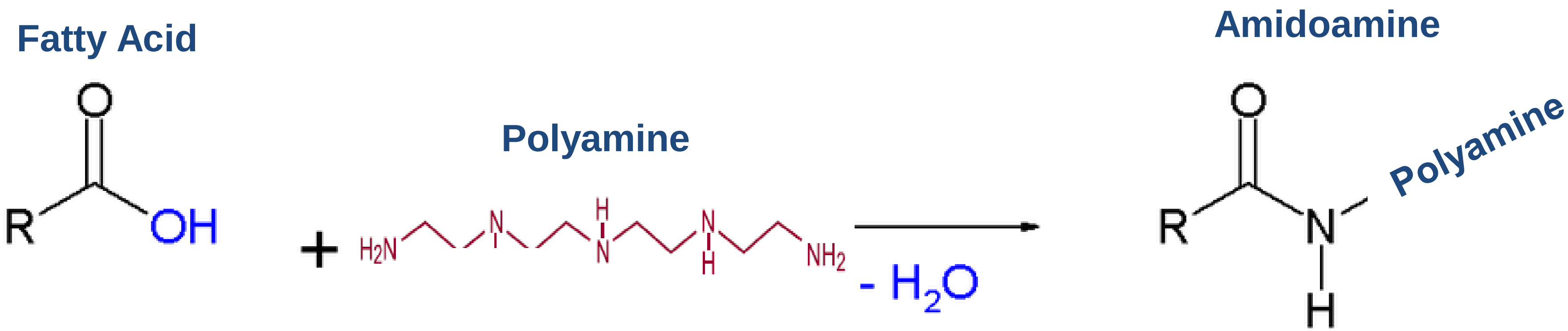
Bishexamethylenetriamine (**BHMT**)



- ***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



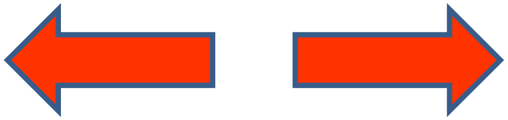
Other types of Anti-Strip Chemistry

- ***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 $H_2$0 Induced Stripping?

- $H_2$0 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**

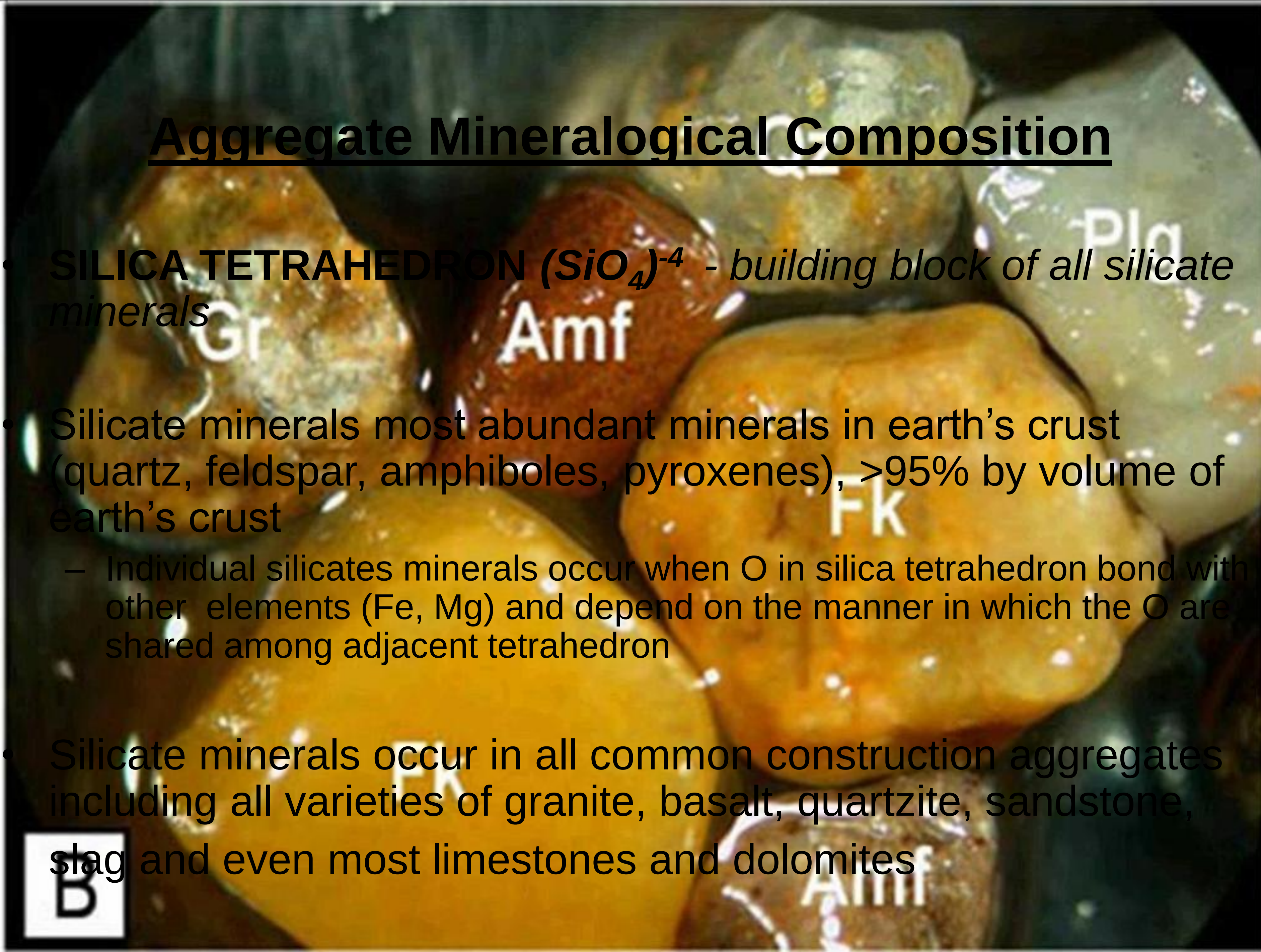


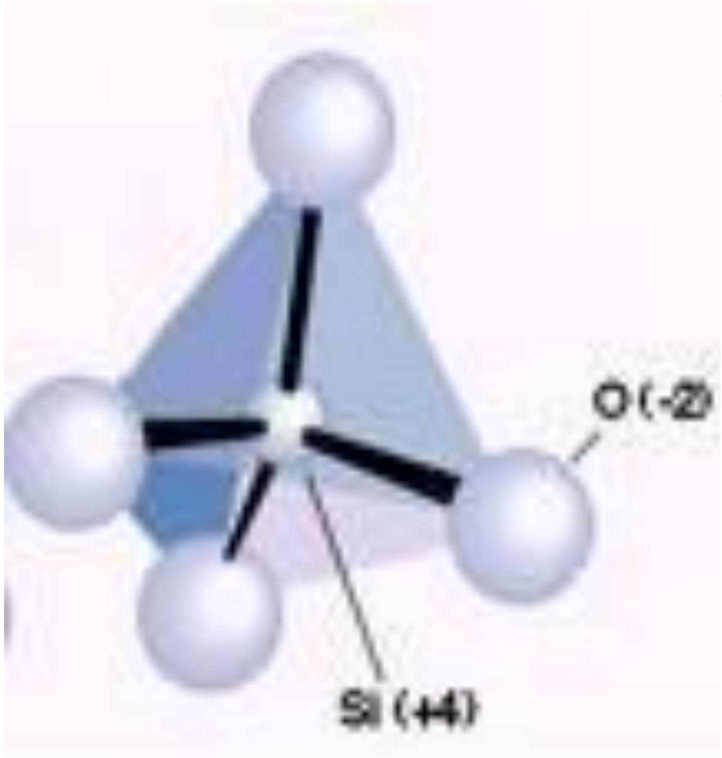
  - asphalt “detaches or strips from aggregate”

- To understand how **REPULSION FORCE** develops, we must understand basic aggregate and asphalt chemistry

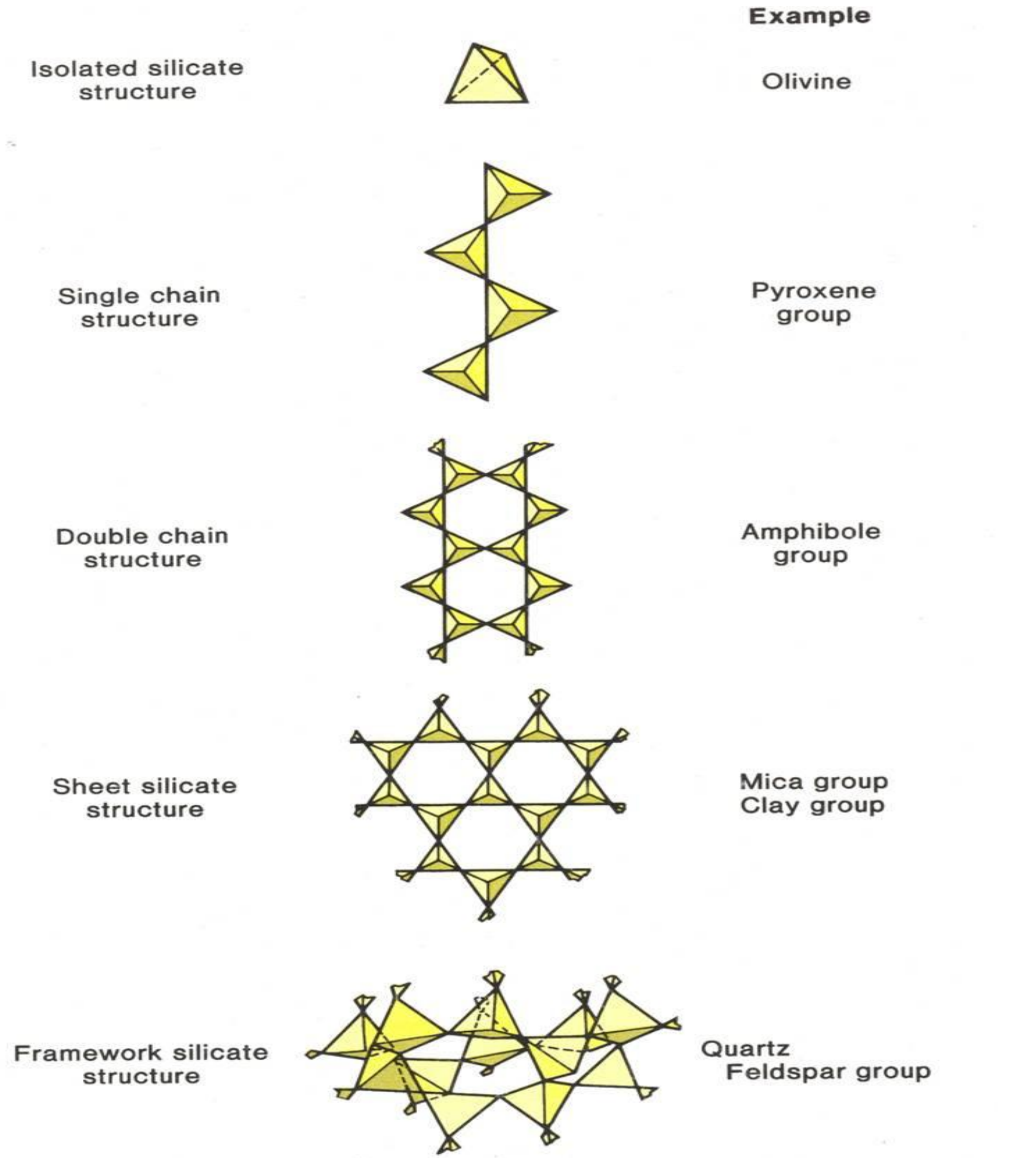
Aggregate Mineralogical Composition

- **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 $(SiO_4)^{-4}$



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 H_20 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 H20 along asphalt-aggregate interface, a reaction occurs yielding a negative charge on aggregate**

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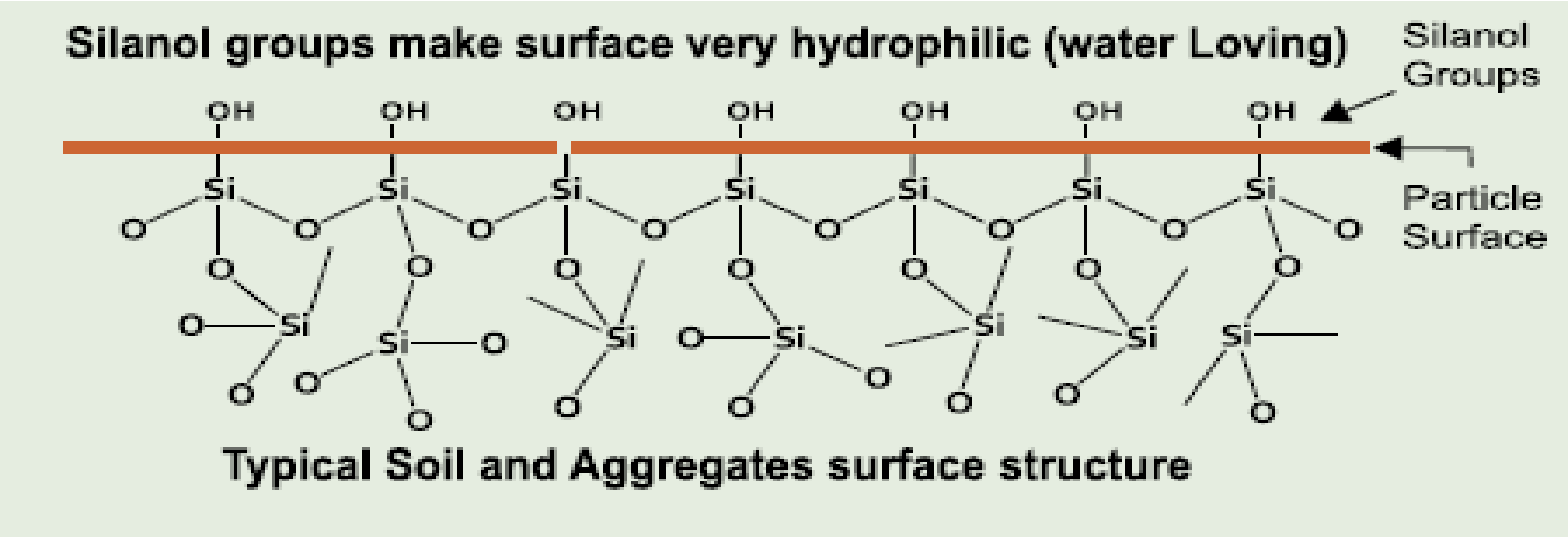
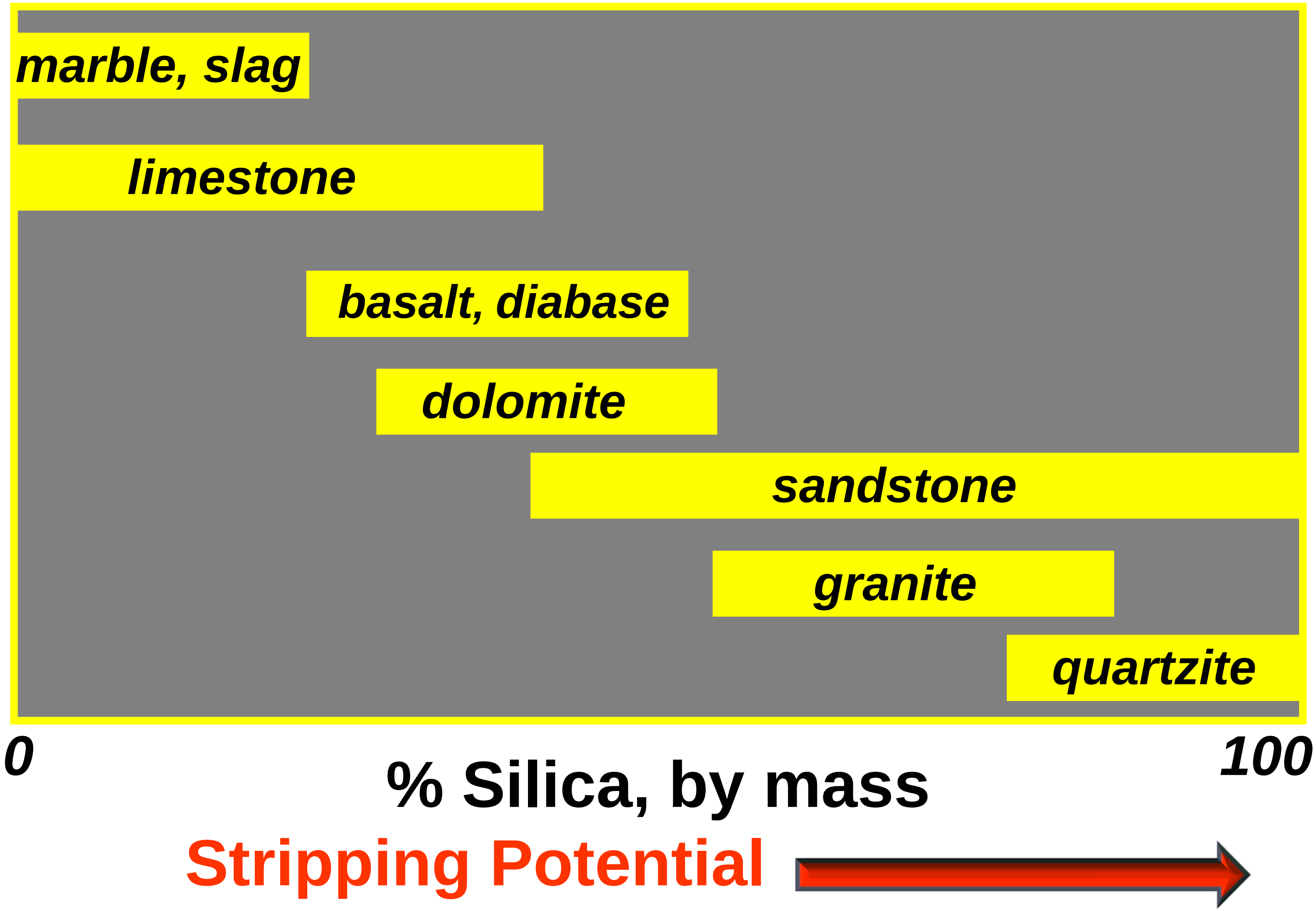
Si-OH + H2O » Si-O$^-$ + H3O$^+$



- Silanol reacts with H_20, 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



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Asphalt Chemical Composition

***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”

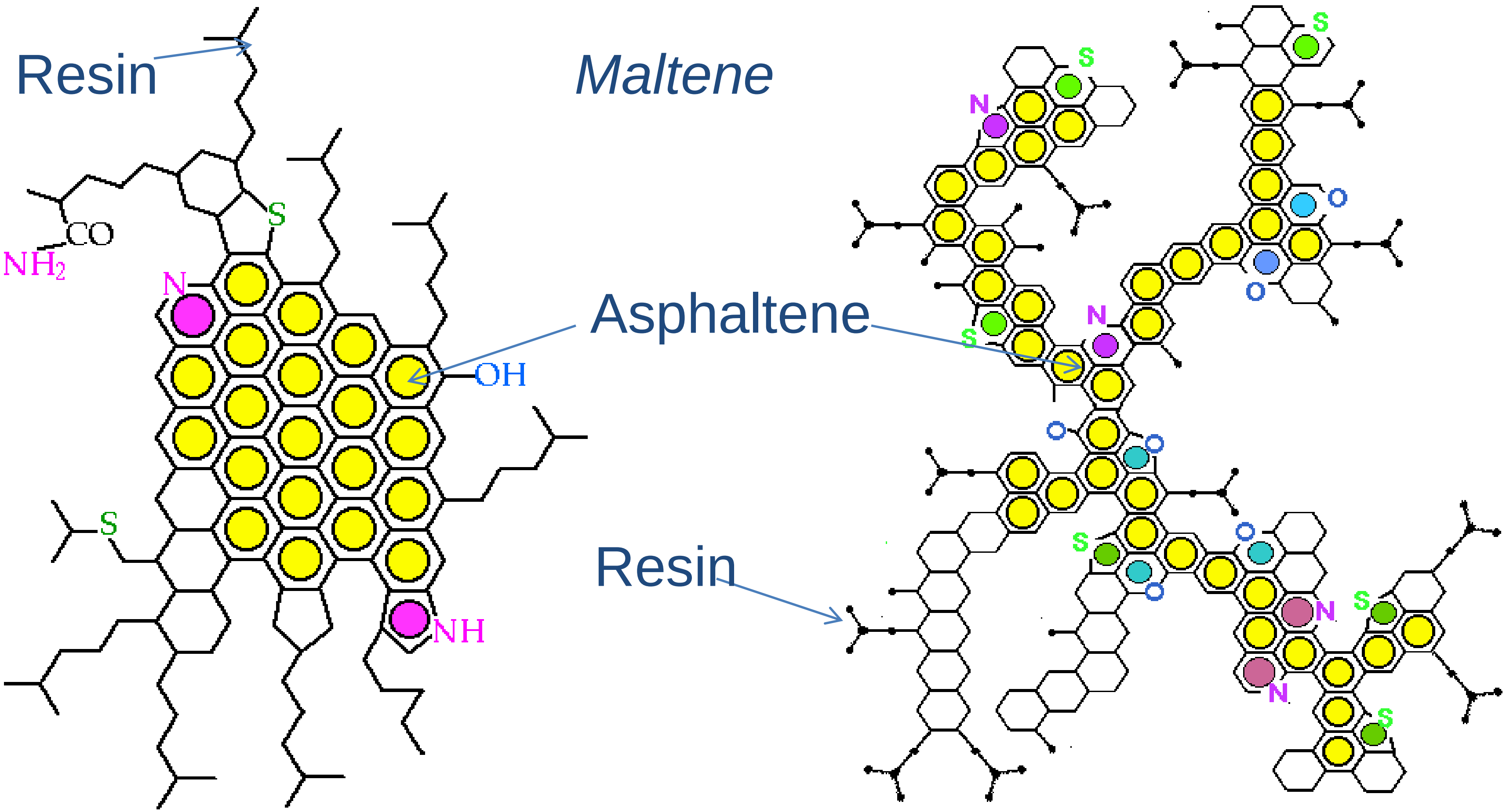
Asphalt Chemical Composition

***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

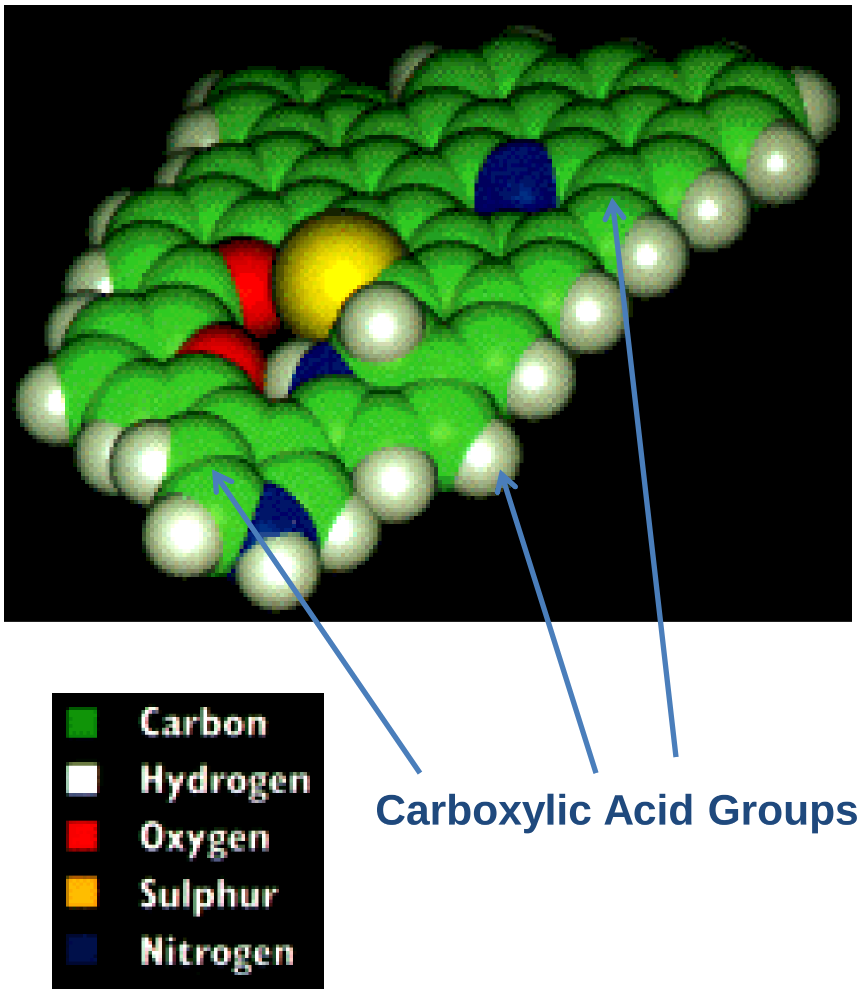
***Asphaltenes and Resins are the components of asphalt that provide the adhesive properties of asphalt**

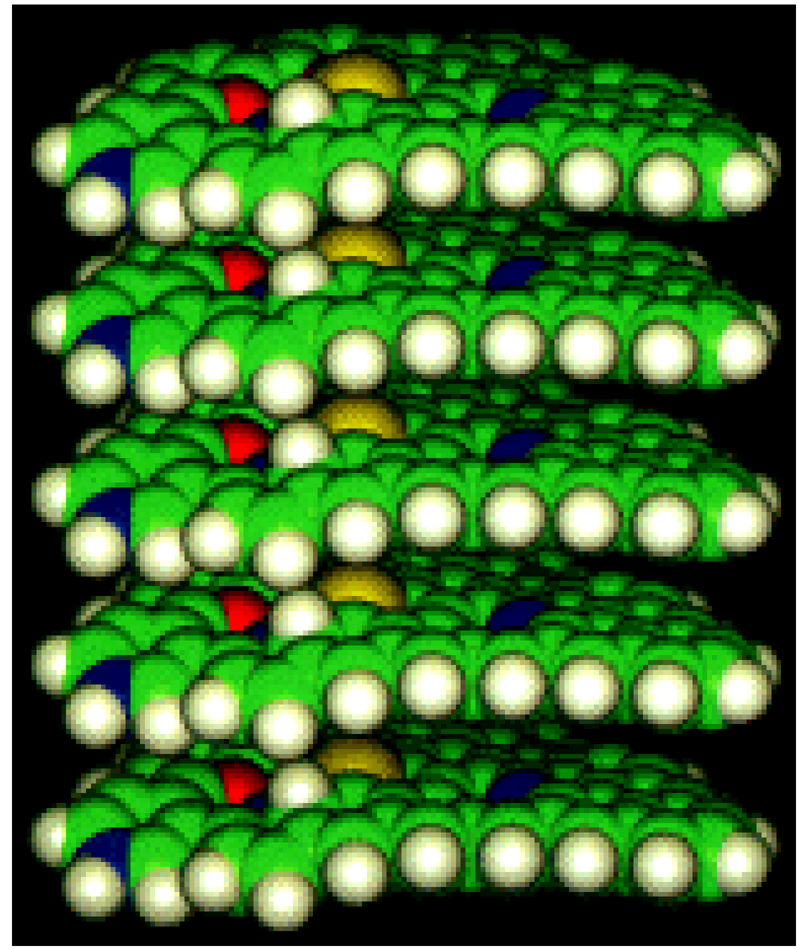
Maltenes- non-polar fraction of asphalt, consist mainly of naphthenic (aromatic) and parrafinic waxes and oils



Mexican asphalt **Venezuelan asphalt**

Asphaltene


Carbon
Hydrogen
Oxygen
Sulphur
Nitrogen
Carboxylic Acid Groups



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Negative Charge Development in Asphalt

When carboxylic acid groups of asphalt at asphalt-aggregate interface come into contact with $H_2$0 a reaction occurs yielding a negative charge on asphalt

NEGATIVELY Charged Asphalt
at Asphalt-Aggregate Interface

-COOH + H2O » -COO$^-$ + H3O$^+$

Acid group at Asphalt –
Aggregate Interface

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

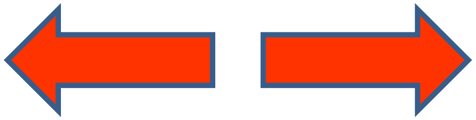
Negative Charge in Asphalt

+

Negative Charge Along Aggregate Perimeter

=

REPULSION FORCE



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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

$$Ca(OH)_2 \text{ in water}_{(pH > 11)} \gg CaOH^+ + OH^-$$

- $CaOH^+$ 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

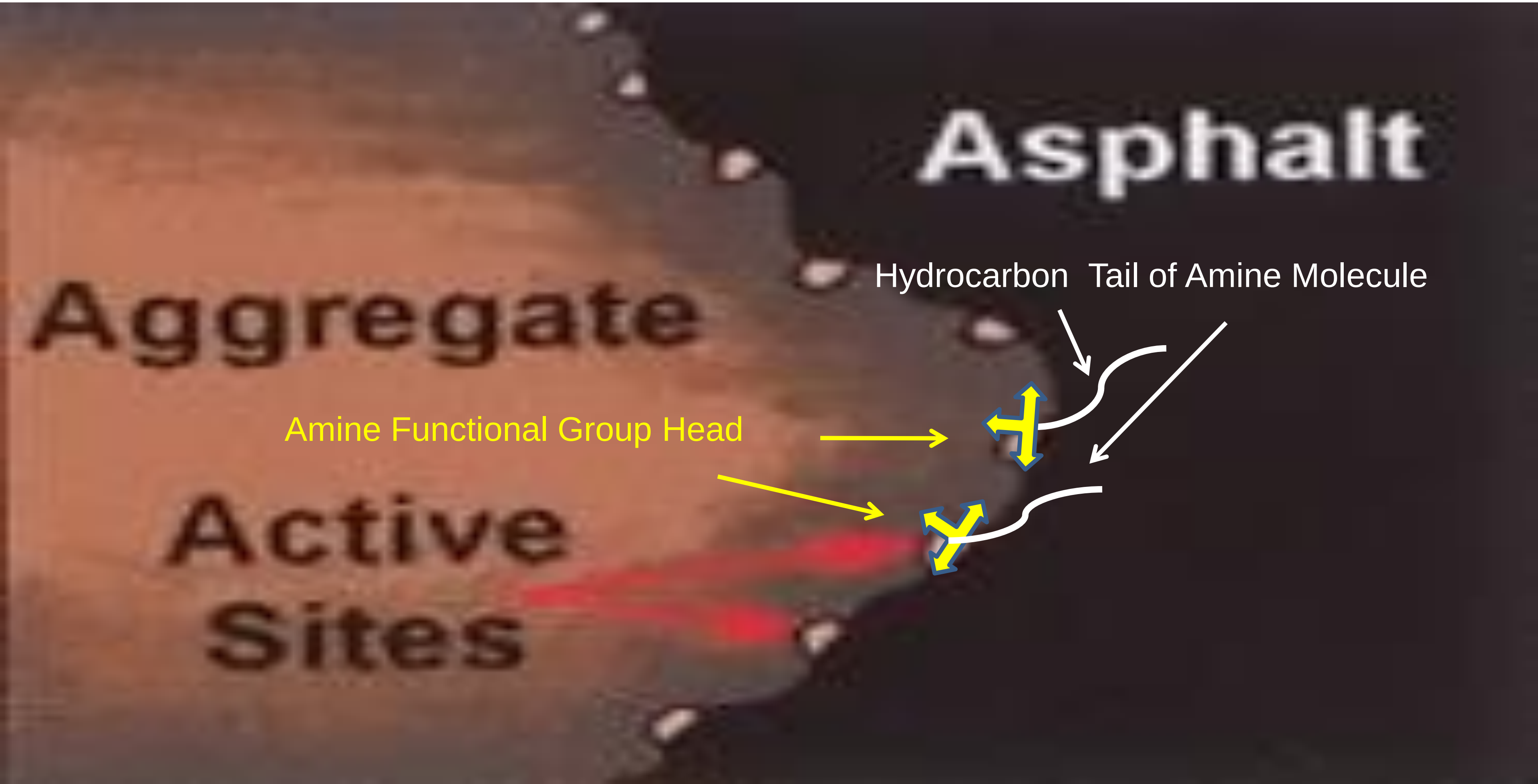
How Amine Anti-Strips Reduce Stripping

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.

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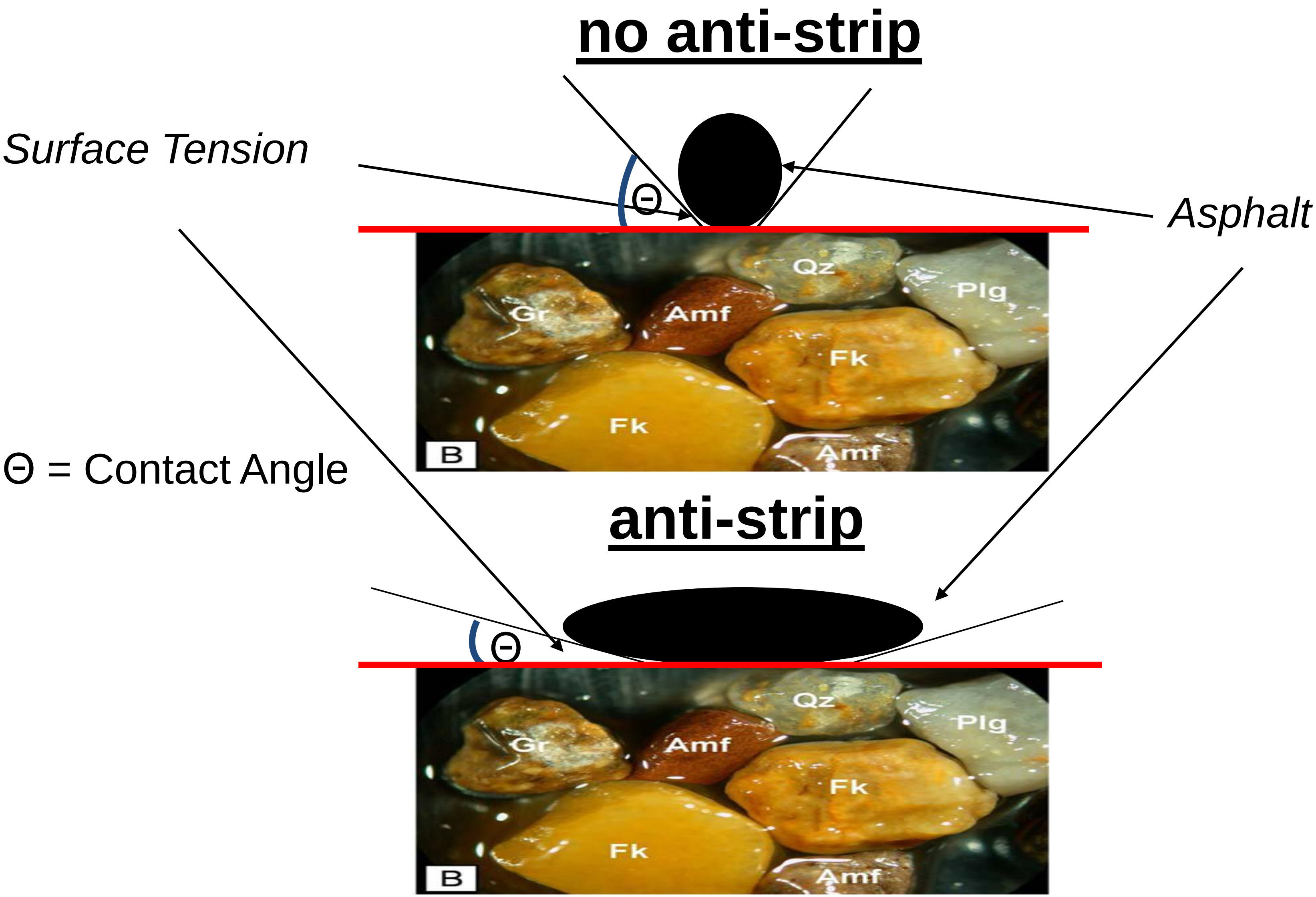
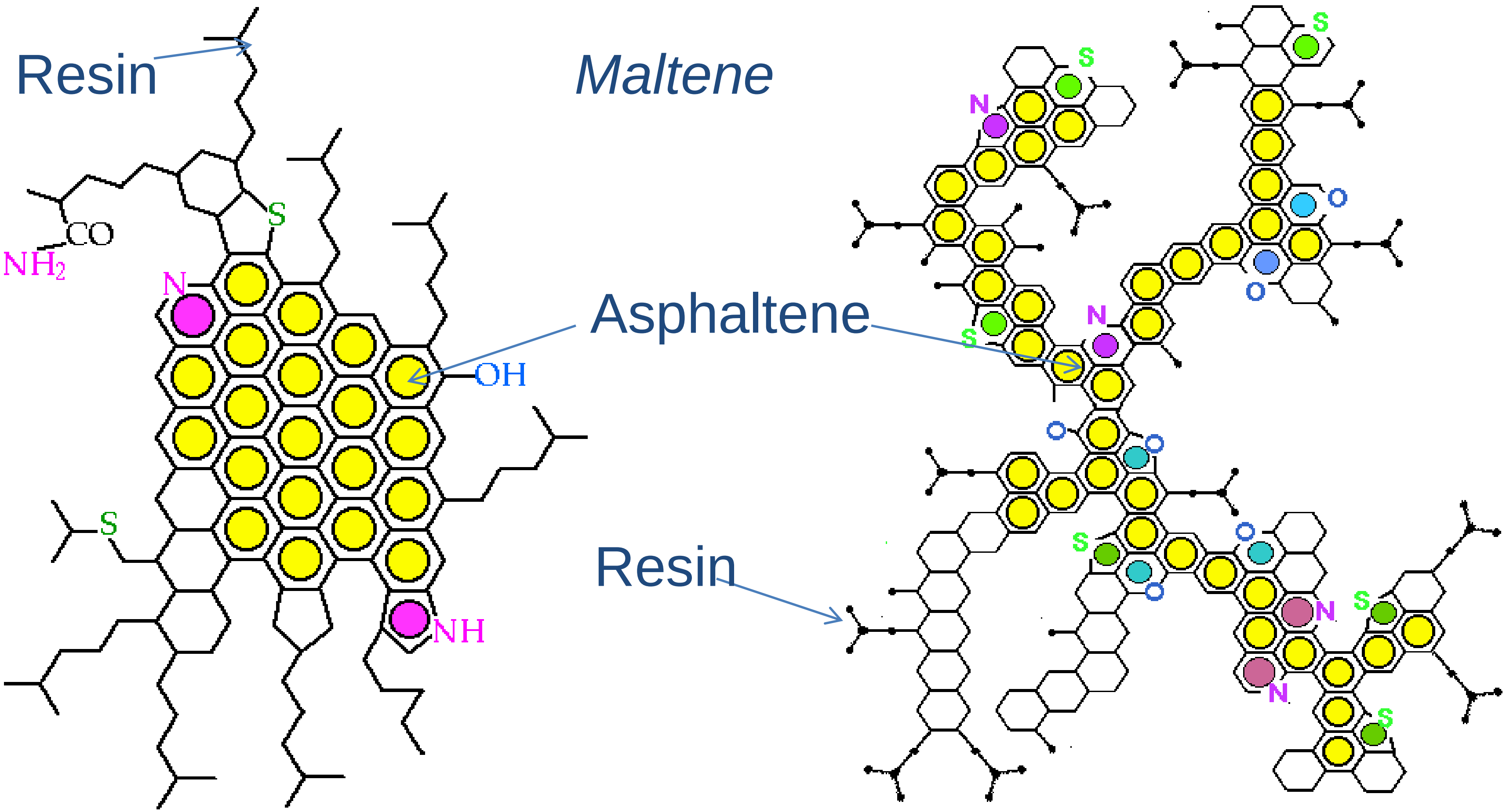


How Amine Anti-Strips Reduce Stripping

Other Theories

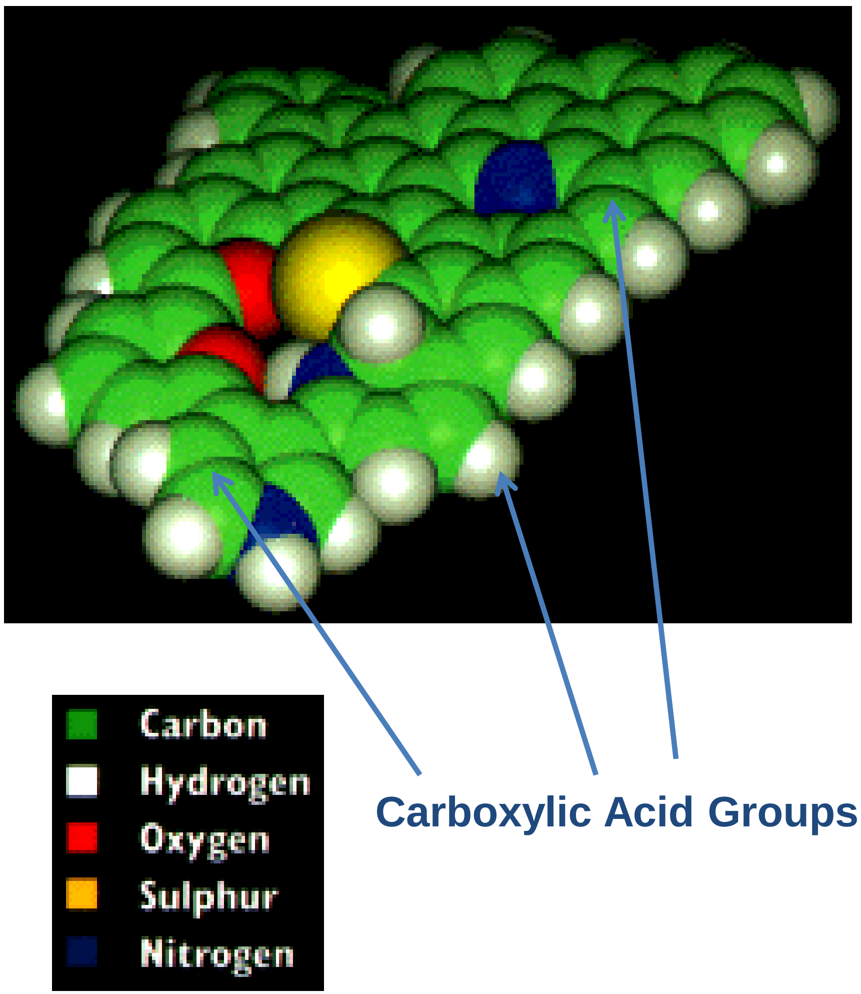
- Explain increased asphalt-aggregate adhesion by mechanism other than as surfactant

1. Dispersion Theory – amines react with acid groups of asphaltenes 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

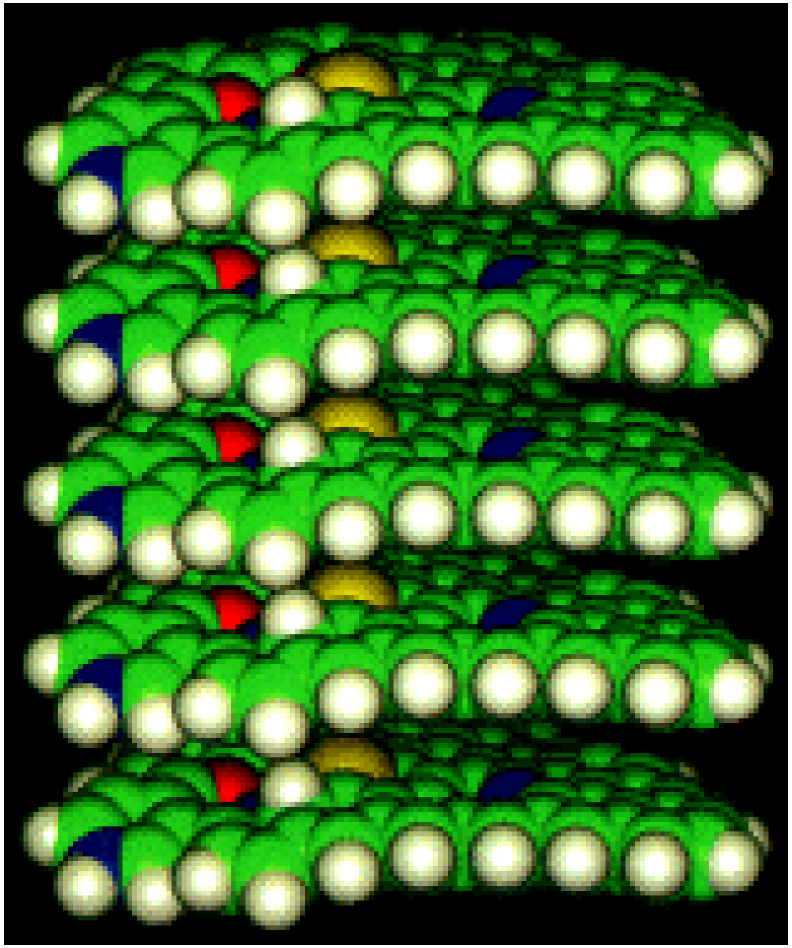


Mexican asphalt **Venezuelan asphalt**

Asphaltene



Carbon
Hydrogen
Oxygen
Sulphur
Nitrogen
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*

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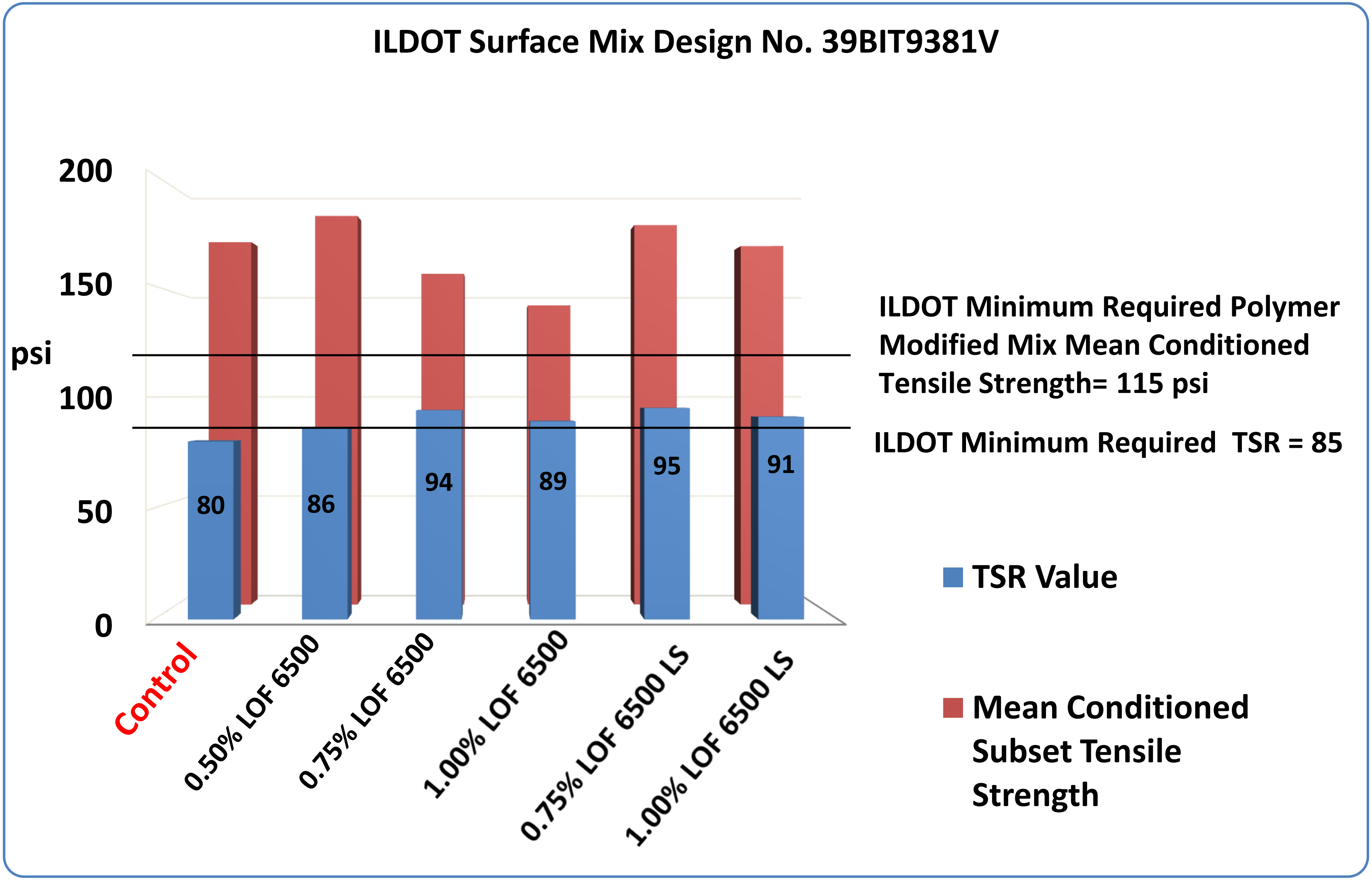

Which is Option is Best?

- 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**

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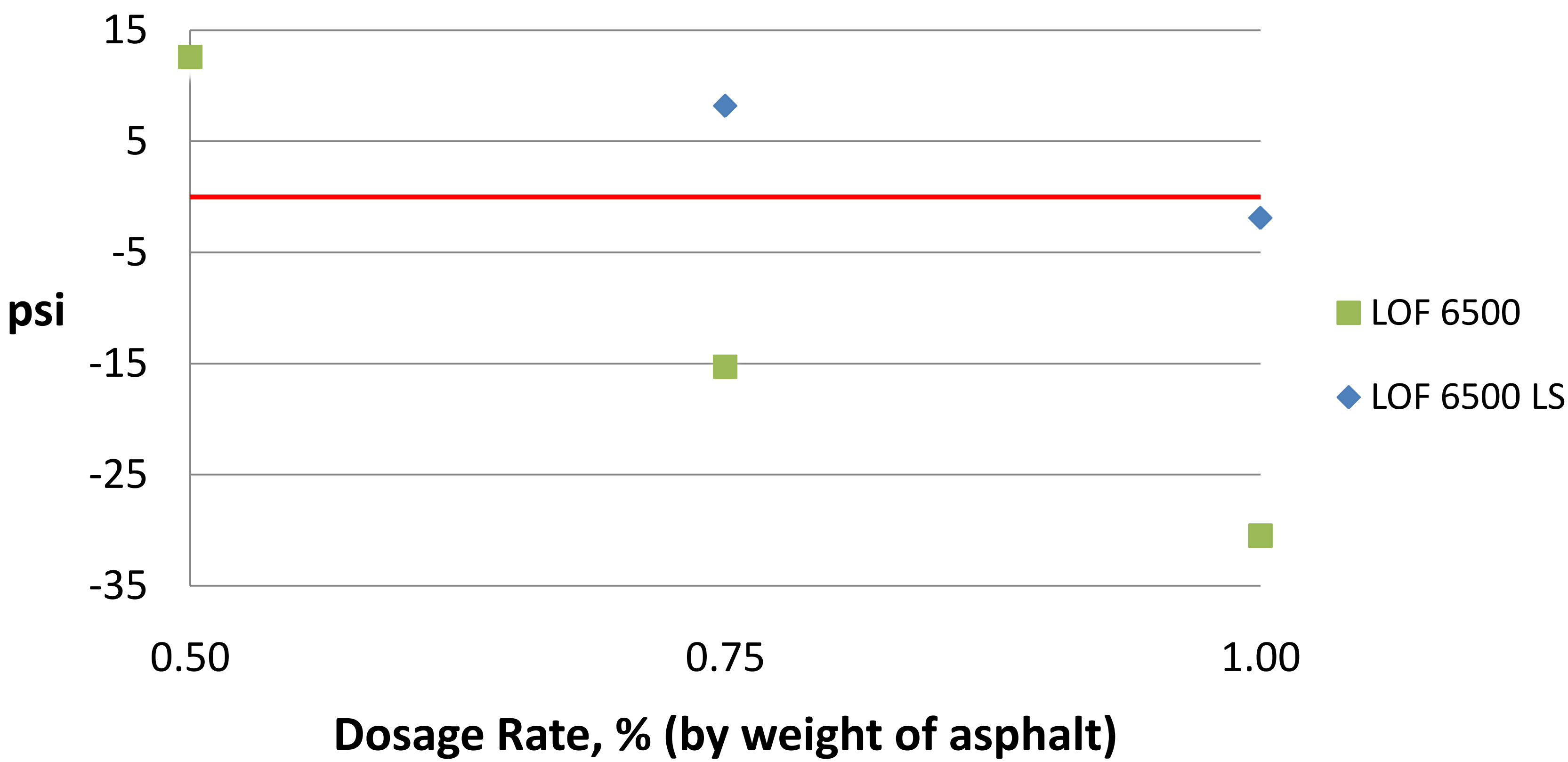
Change in Mean Conditioned Subset Tensile Strength From Control Specimens – ILDOT Surface Mix Design No. 39BIT9381V



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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”*

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ILDOT - Design No. 39BIT9381V
Control Specimens

ILDOT Design No. 39BIT9381V
0.75% AD-here LOF 6500 LS

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*

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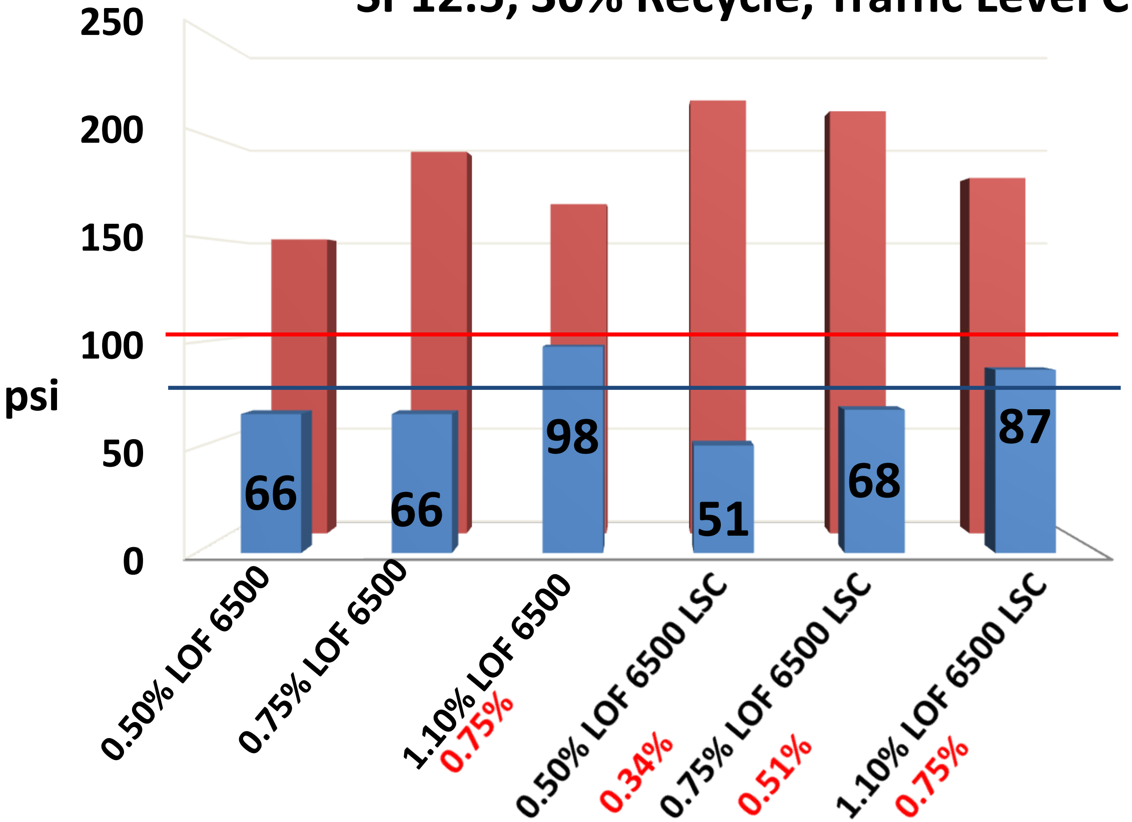
FDOT Structural Design No. 081909-1
SP12.5, 30% Recycle, Traffic Level C

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

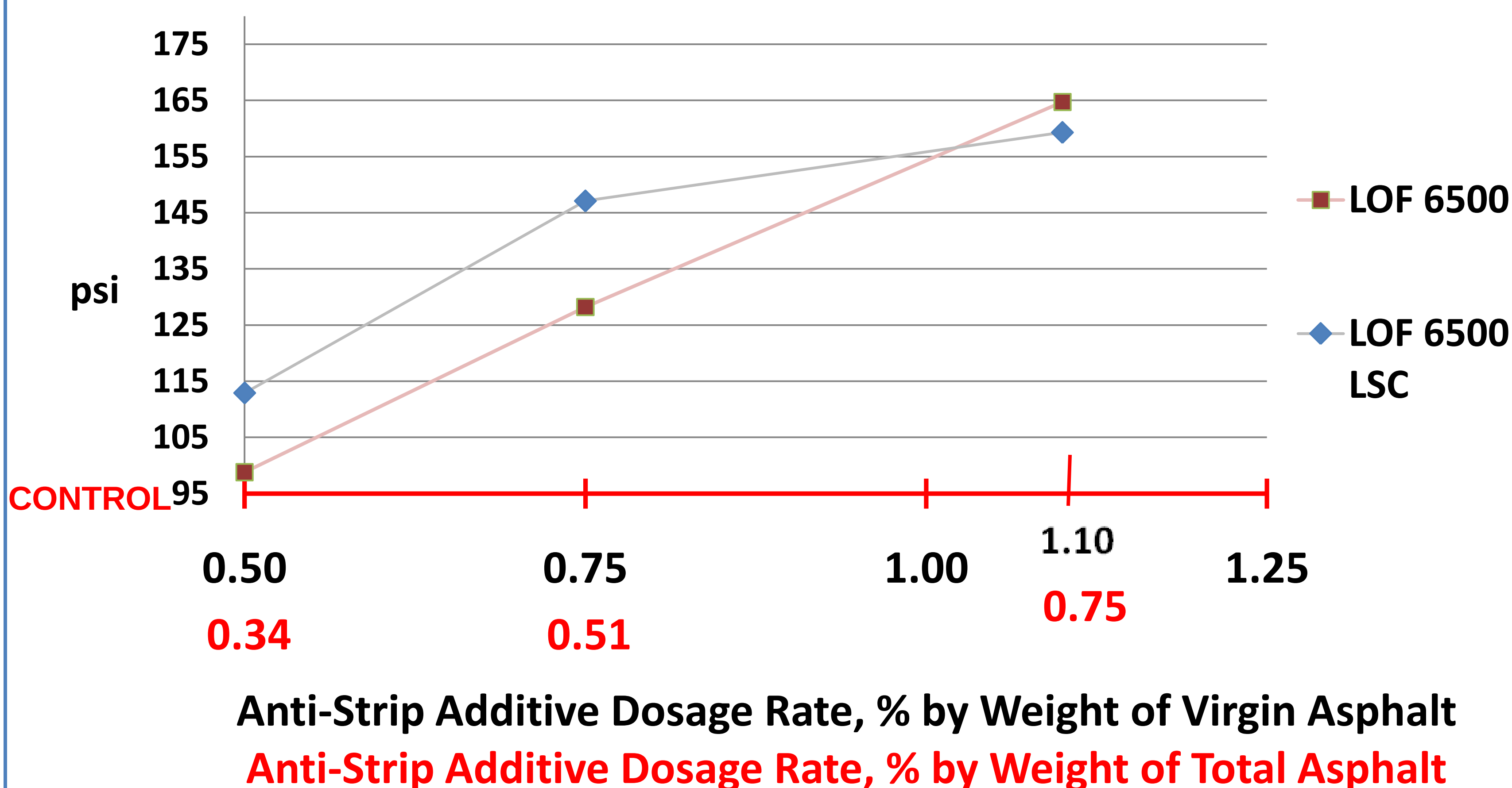
■ TSR Value

■ Mean Unconditioned Subset Tensile Strength

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



Which is Option is Best?

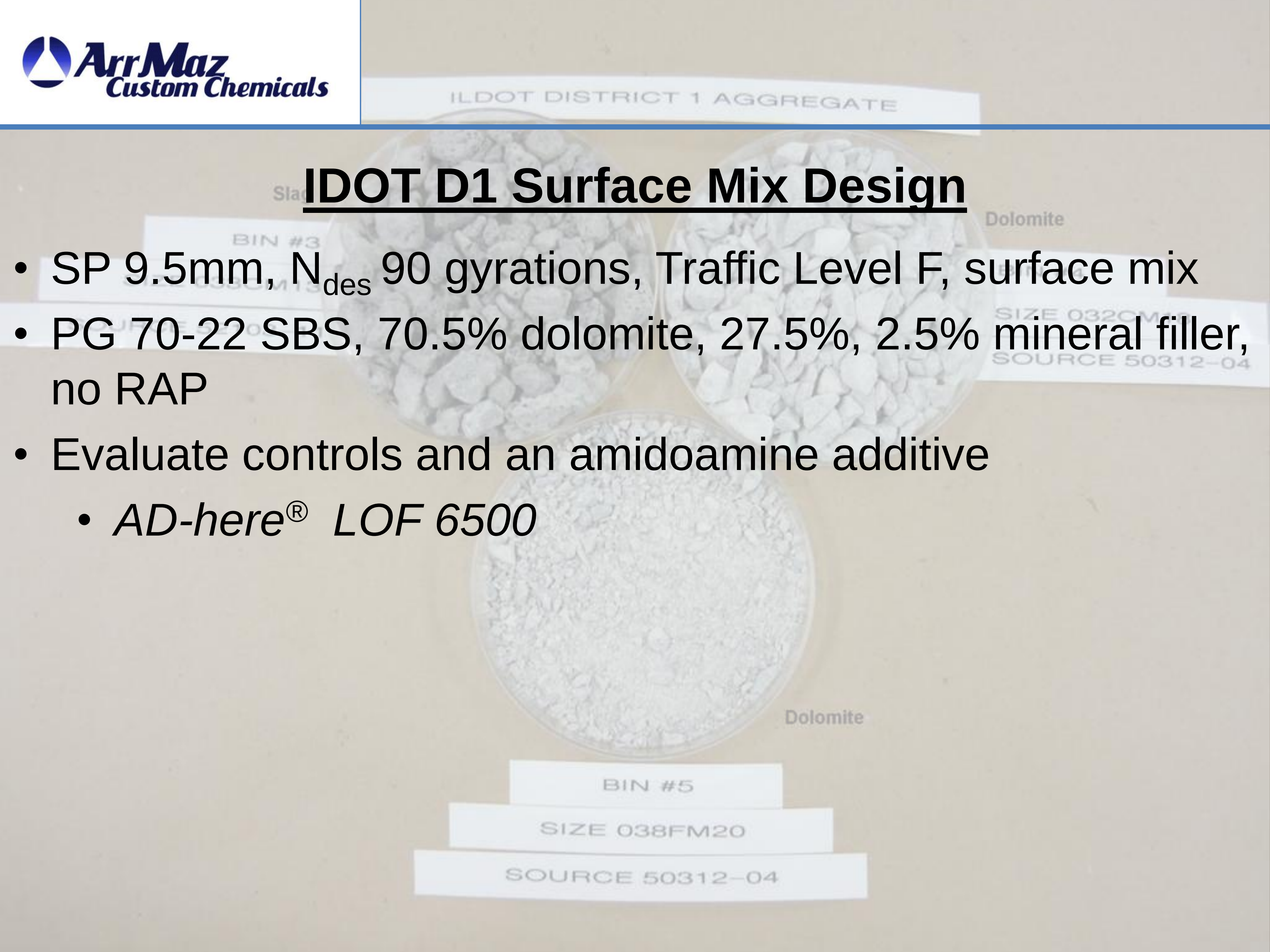
- 0.75% (by weight total asphalt) LOF 6500 provides highest TSR
  - TSR from 49 to 98 (100%) and mean conditioned tensile strength increased approximately 70 psi (74%) from control with no additive
    - Mean unconditioned strength = 168.9 psi
    - Control mean unconditioned strength = 194 psi
    -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


APAC-CENTRAL
FDOT SP12.5 RECYCLE
1.1% ADHERE LOF 6500
12/18/09

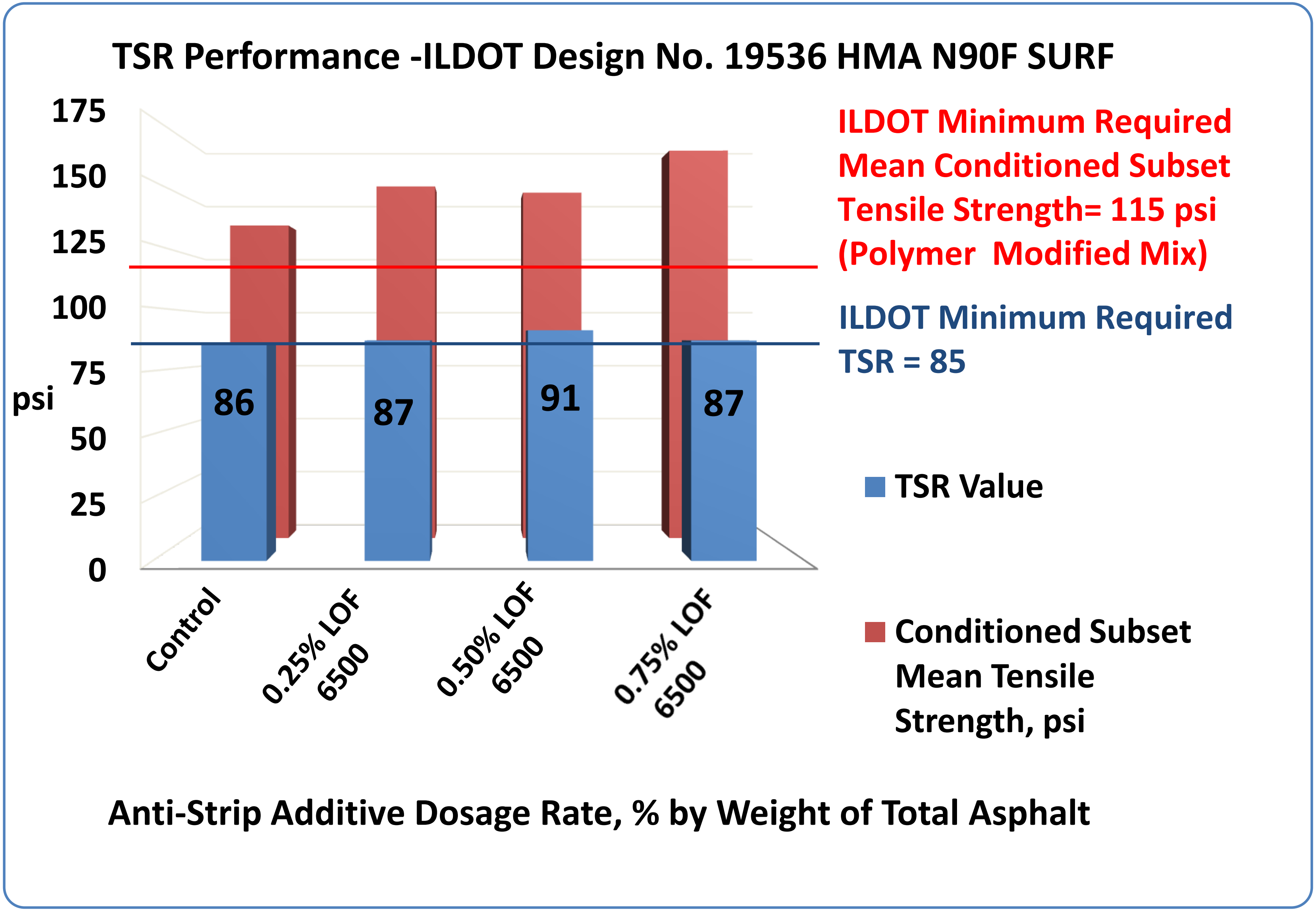

APAC-CENTRAL
FDOT SP12.5 RECYCLE
.50% LOF 6500 LSC
12/18/09

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-here® LOF 6500*

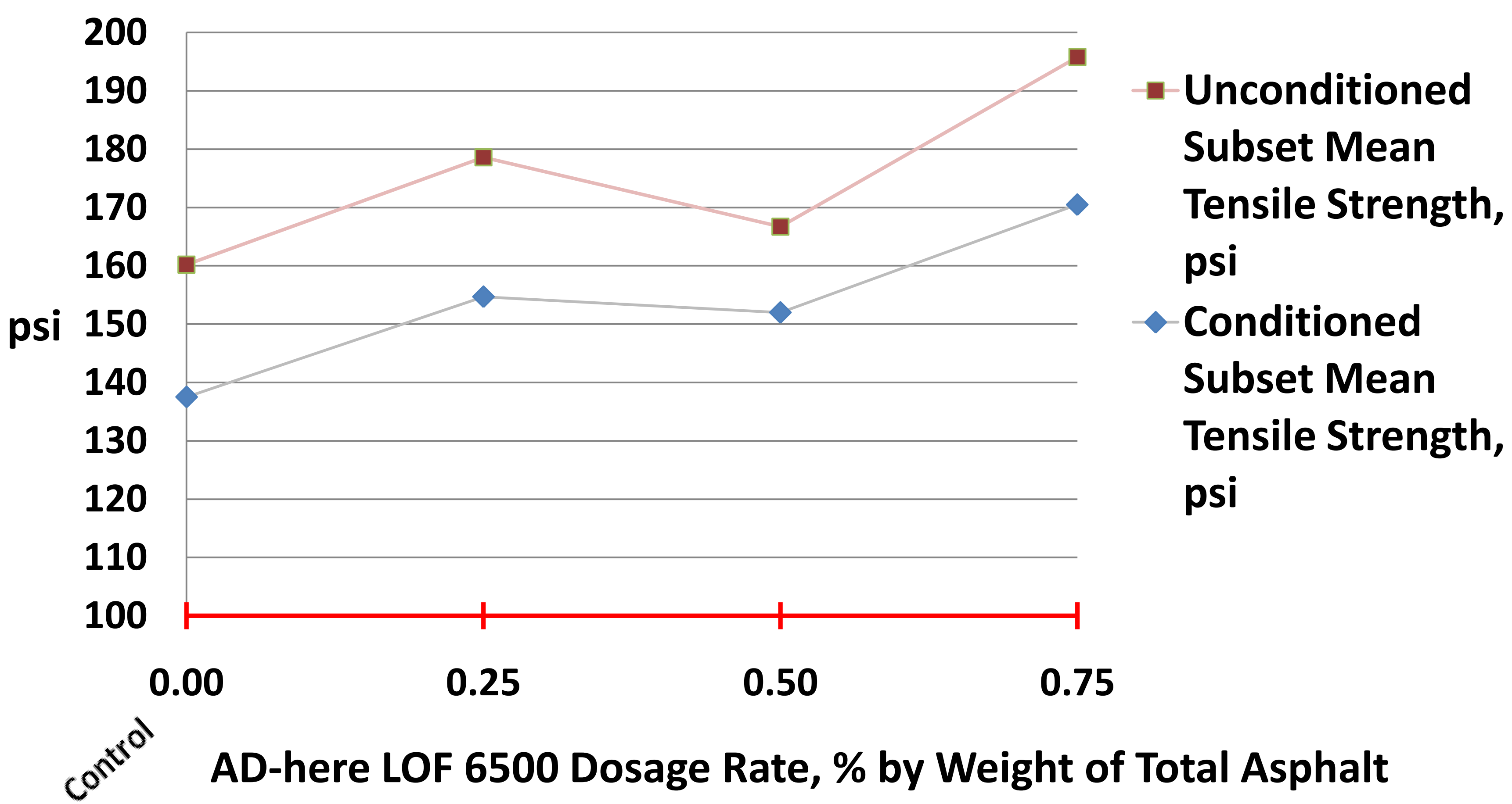


ILDOT DISTRICT 1 AGGREGATE
Slag
BIN #3
SIZE 033CM13
SOURCE 52103-11
Dolomite
BIN #4
SIZE 032CM18
SOURCE 50312-04
Dolomite
BIN #5
SIZE 038FM20
SOURCE 50312-04



TSR Performance -ILDOT Design No. 19536 HMA N90F SURF
175
150
125
100
75
50
25
0
psi
86
87
91
87
Control
0.25% LOF 6500
0.50% LOF 6500
0.75% LOF 6500
ILDOT Minimum Required Mean Conditioned Subset Tensile Strength= 115 psi (Polymer Modified Mix)
ILDOT Minimum Required TSR = 85
TSR Value
Conditioned Subset Mean Tensile Strength, psi
Anti-Strip Additive Dosage Rate, % by Weight of Total Asphalt

Overall Increase in Subset Tensile Strength



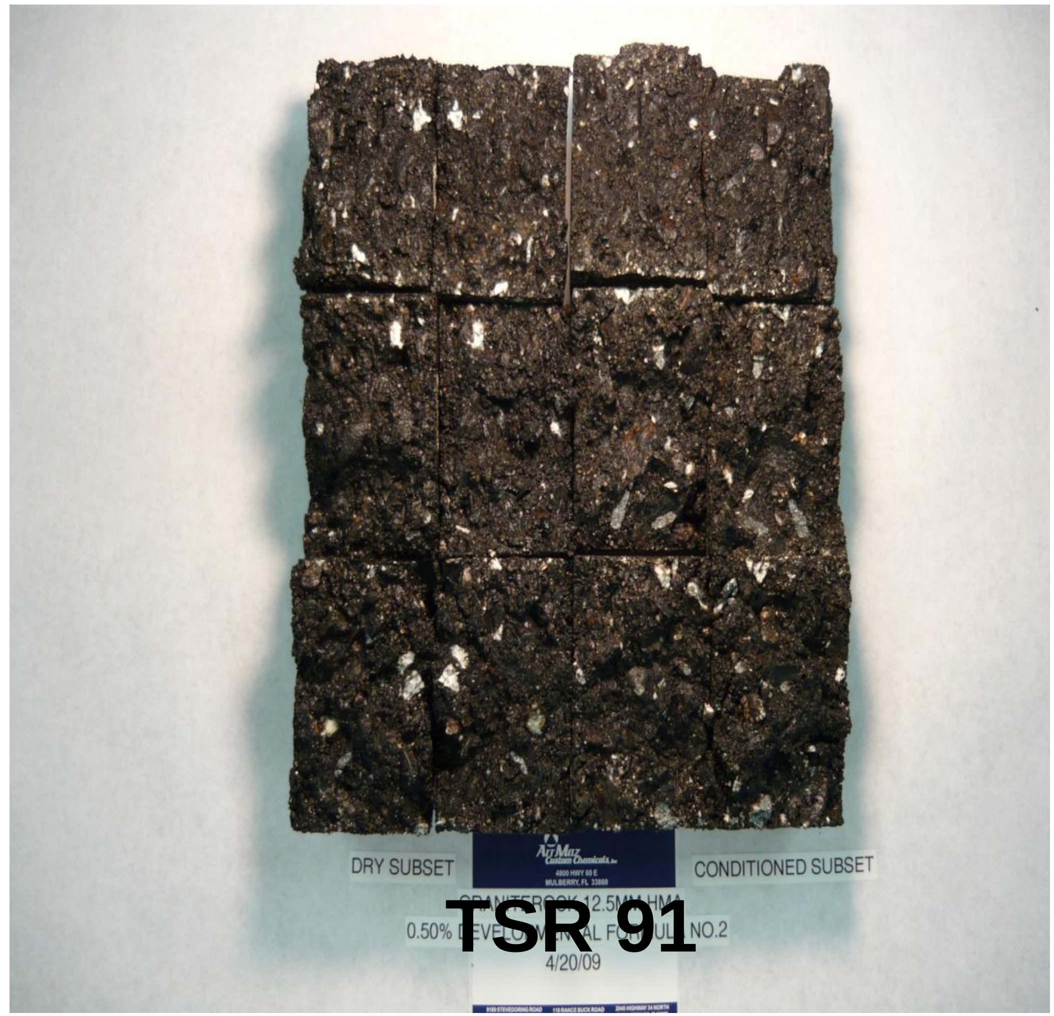
Which is Option is Best?

- 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 = 8psi
      - 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 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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