

Polyphosphoric Acid in Asphalt Modification

by

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and

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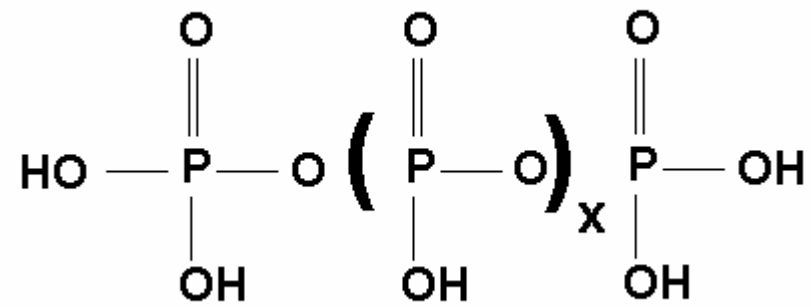
**Symposium – Additives Used in Asphalt Pavements
Cheyenne, WY June 24, 2004**

**Astaris- Manufacturer of
phosphorus based chemicals-
joint venture of FMC Corp and
Solutia(Monsanto)**

**PRI Asphalt Technologies, Inc.-
Consultants to the asphalt
industry in both paving and
roofing .**

Introduction

- Objective: Discuss what polyphosphoric acid is , it's affinity for organic systems and how it helps to improve the properties of asphalt cement.



What does the term “P₂O₅ Content” mean?



- It is a way to assess how much phosphorus is in any compound.
- It does not mean that the entity “P₂O₅” actually exists in the compound.
- For example Na H₂PO₄, monosodium phosphate has a P₂O₅ content of 59.1%

Now for the acid :

- Orthophosphoric acid, H_3PO_4 , has a P_2O_5 content of 72.4%.
- There is an analytical procedure to determine P_2O_5 content.
- Now—How do you get anything greater than 100%? It is a relative measure. You set up a ratio.
- **$100\% \text{ acid} / 72.4\% \text{ P}_2\text{O}_5 = X / 83.2\% \text{ P}_2\text{O}_5$**
 $X = 115\% \text{ Polyphosphoric Acid}$

Literature References:

- Arnold Hoiberg, US Pat # 2,450,756—10/5/1948, assigned to Lion Oil Division, Monsanto Company
- W. Shearon and Arnold J. Hoiberg, Catalytic Asphalt, *Industrial and Engineering Chemistry*, 45(10), 2122 - 2312(1953).
- Monsanto Document- The use of polyphosphoric acid in asphalt. 5/14/1965

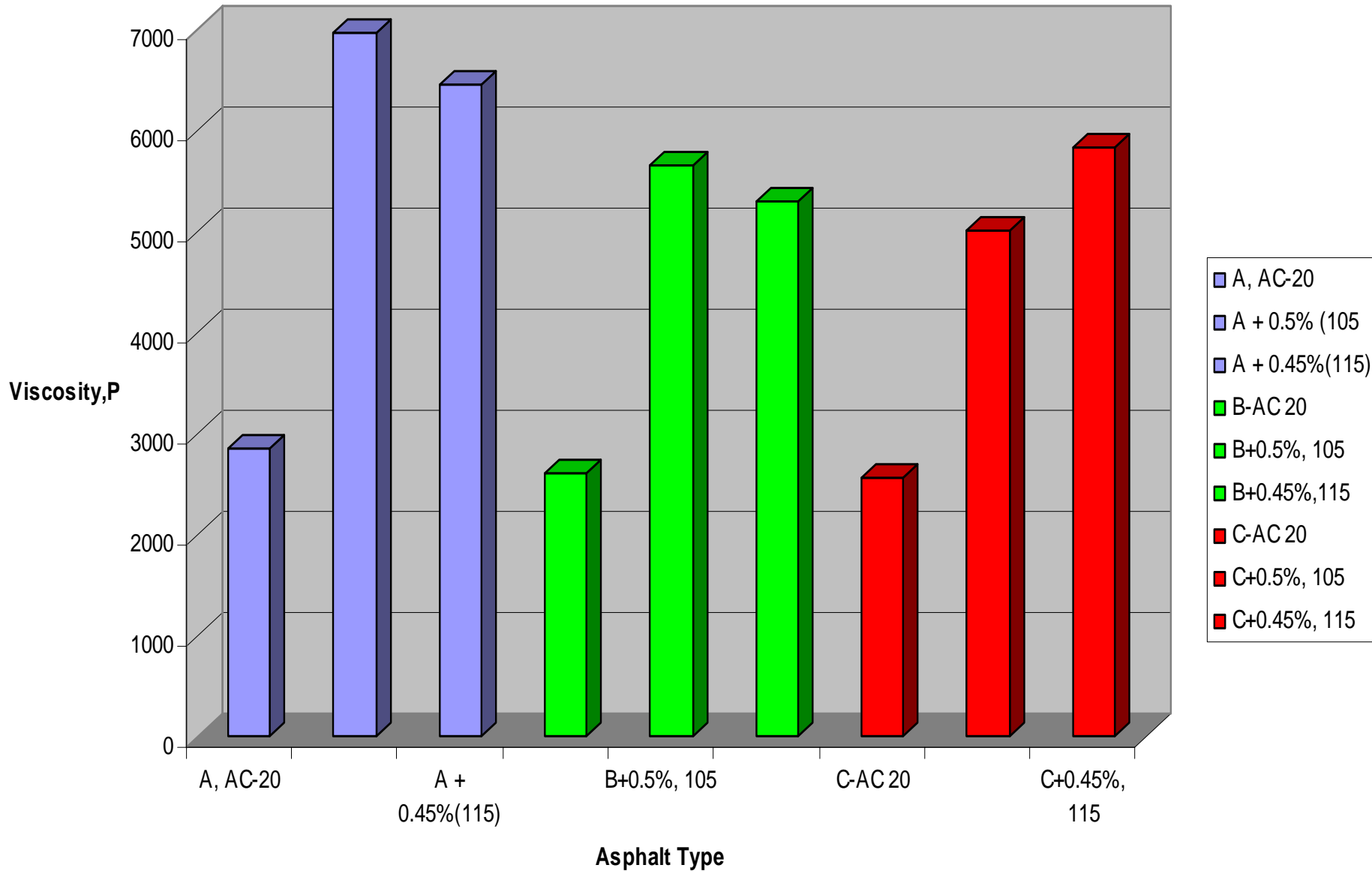


History of reactivity in organic systems, including rearrangements, polymerizations, dehydration, nitration, bromination and cyclization reactions.

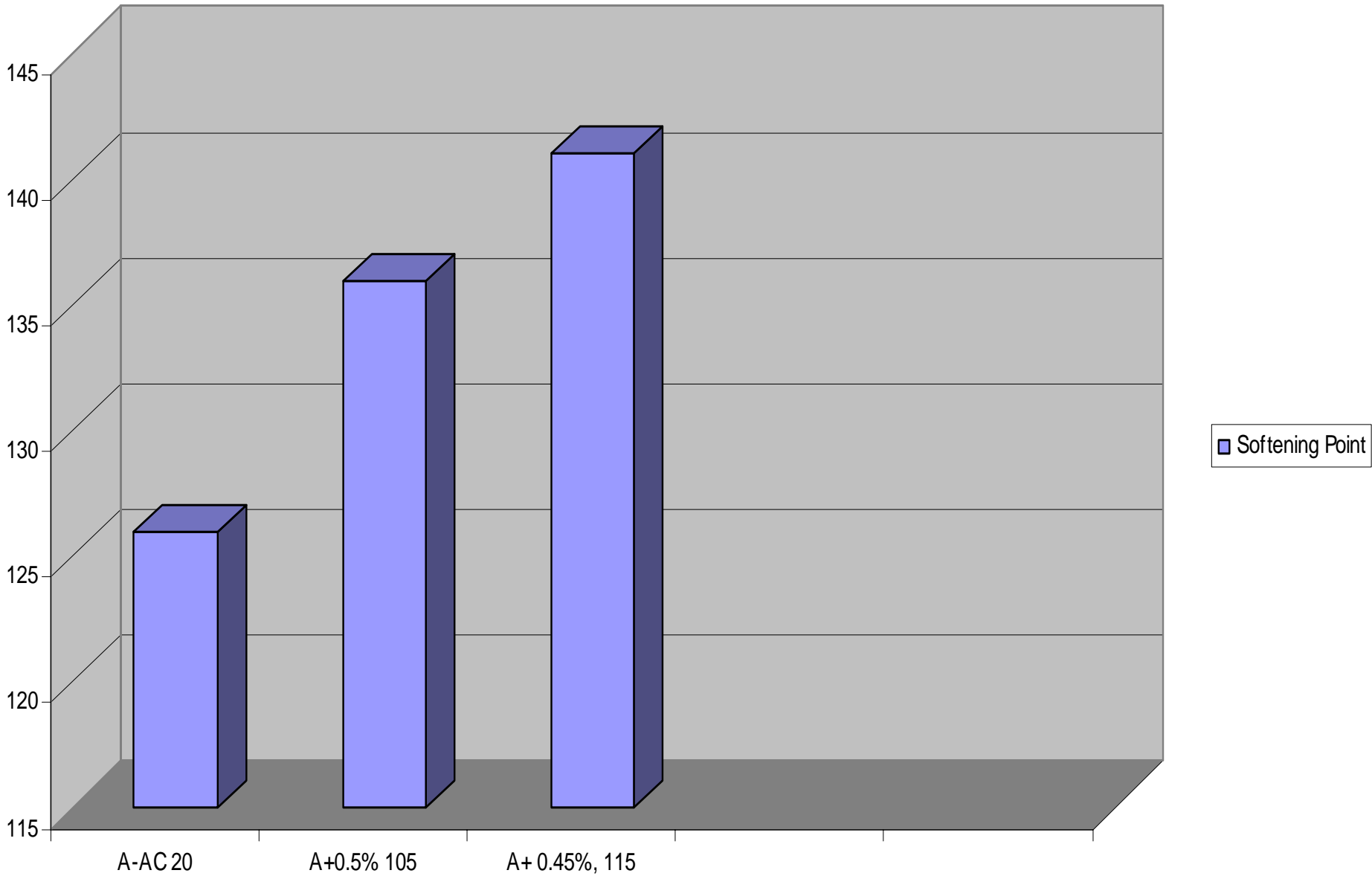
Topics of Discussion

- Conventional Properties
- Superpave Parameters
- Potential for Corrosion
- Stability in Storage
- Moisture Sensitivity
- Improvement in Adherence
- Lottman Tests and Hamburg Wheel Tests

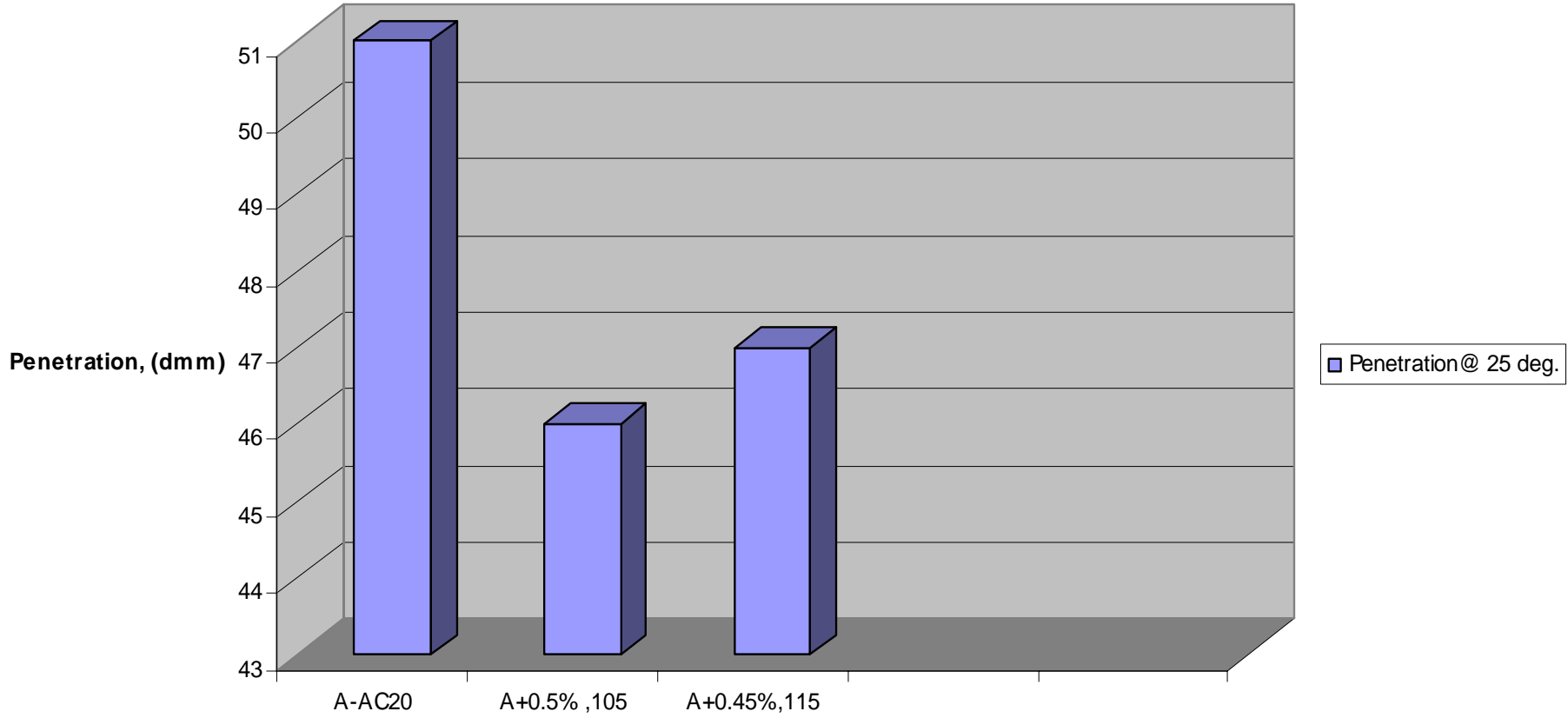
Viscosity Improvements: Asphalts A, B, and C



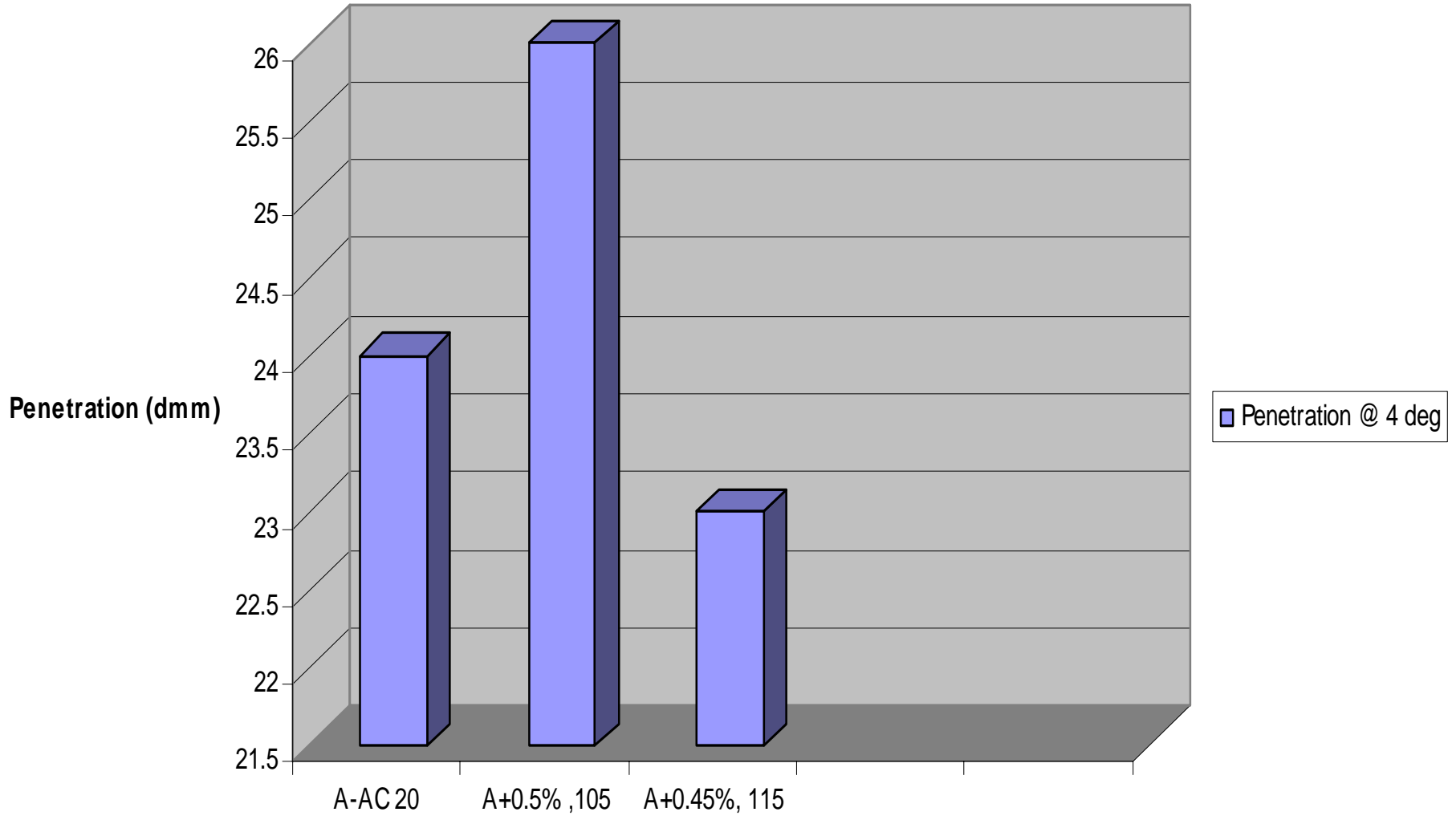
Softening Point, deg F



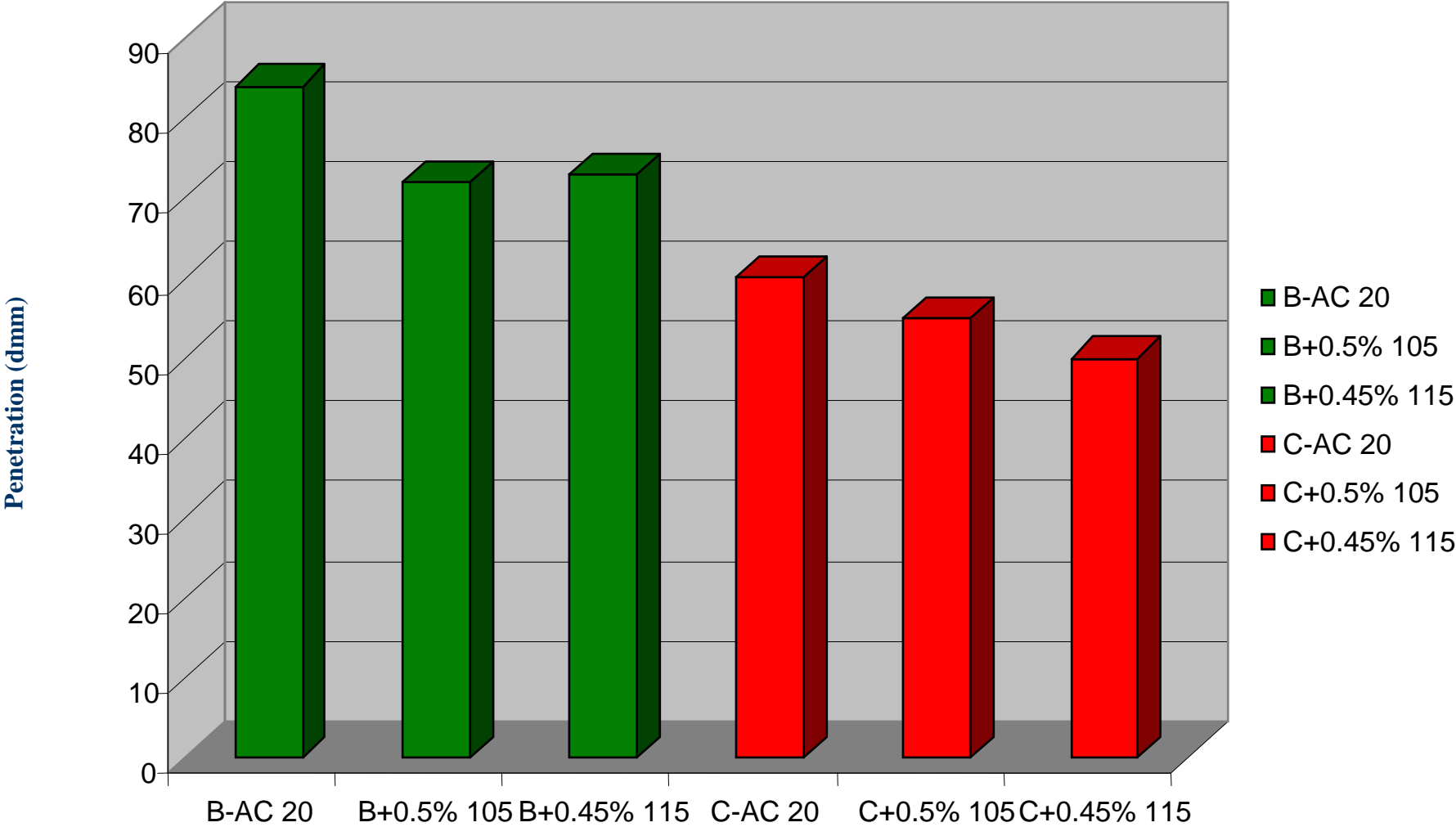
Penetration @ 25 deg C



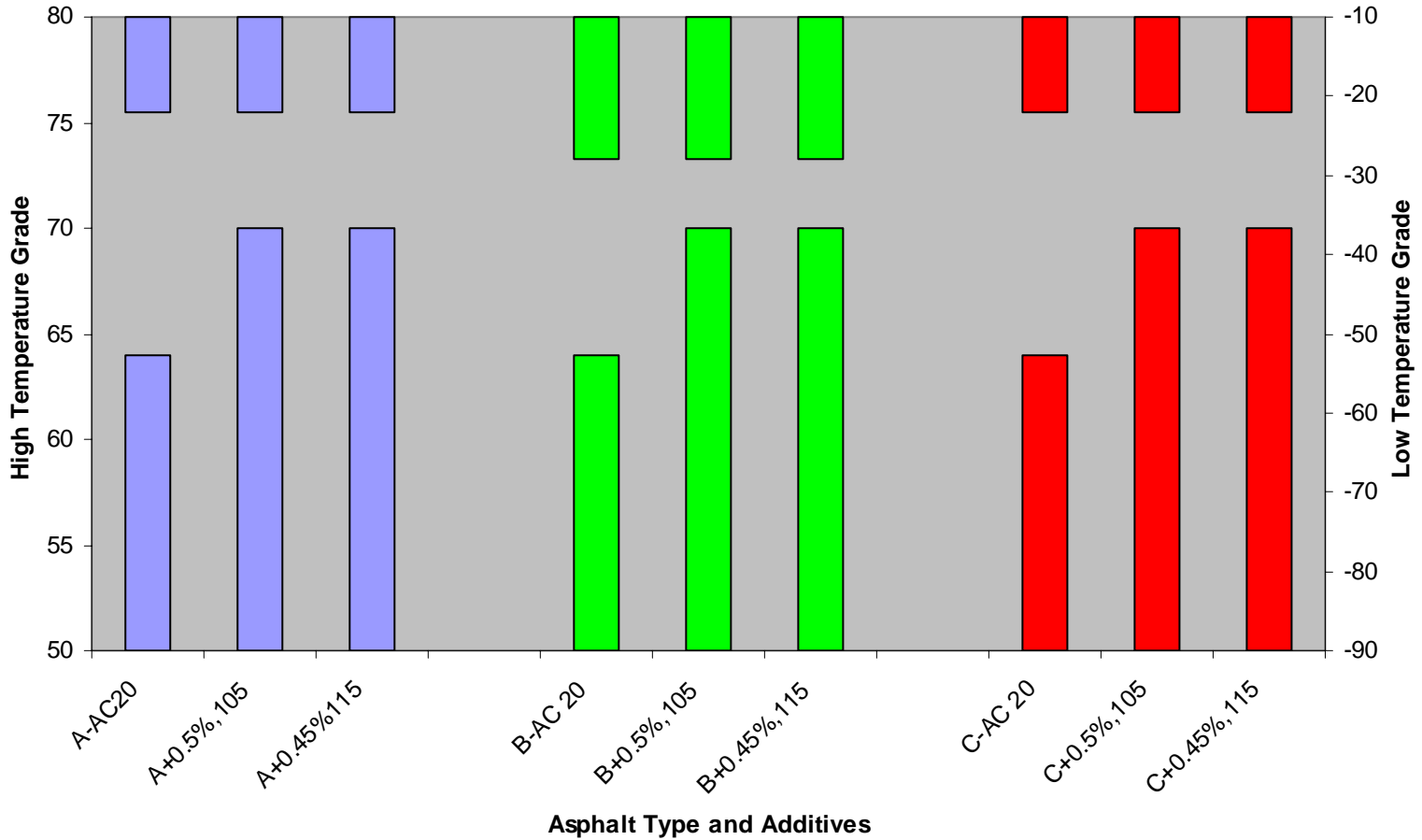
Penetration @ 4 deg C



Penetration @ 25 deg



Asphalt Performance Grades



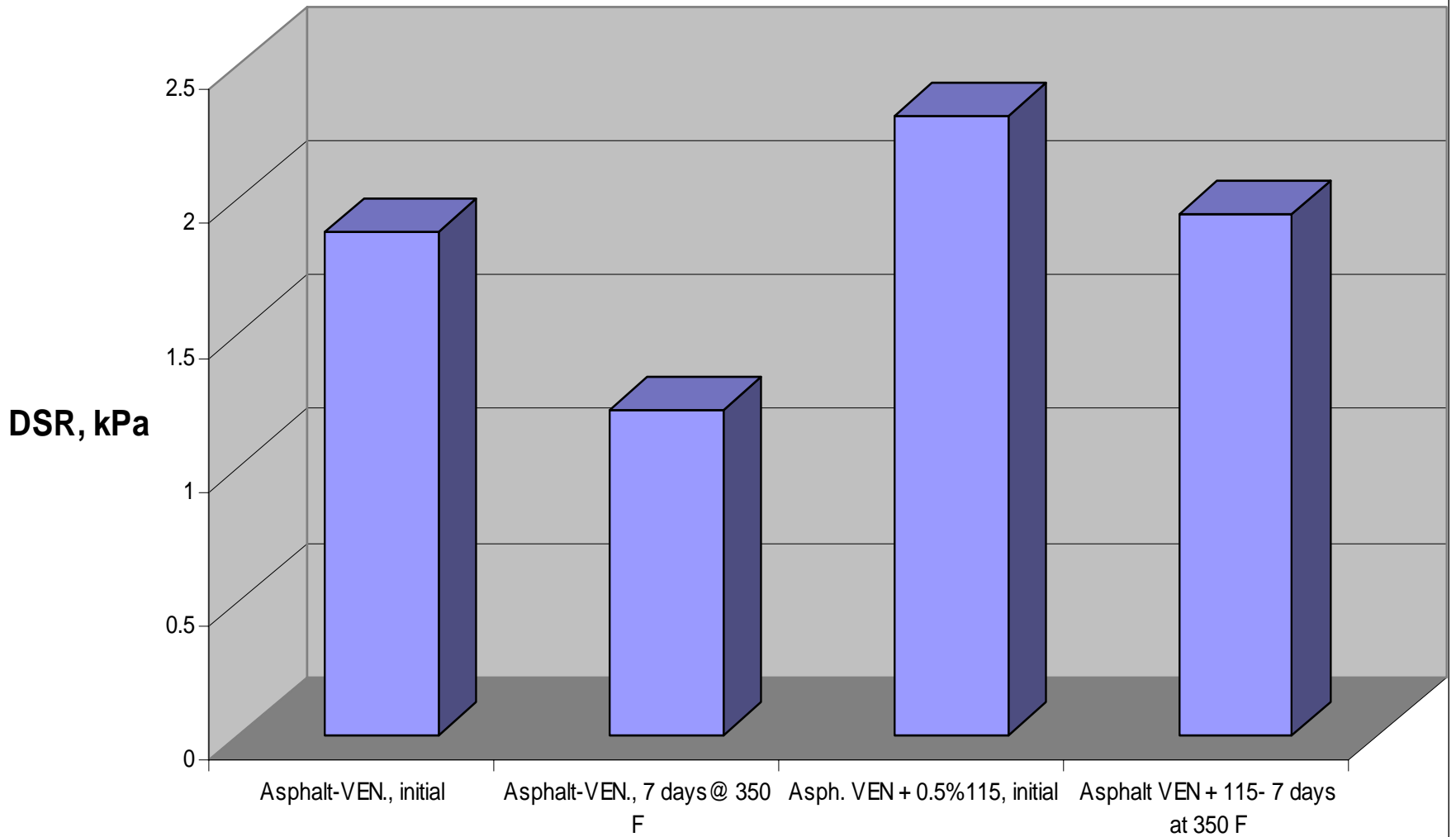
Corrosion Study

- Both mild steel and aluminum coupons exposed to liquid and vapor state for 3 weeks at 150 deg C. Comparison of three neat asphalts to samples with polyphosphoric acid.
- No corrosion vs. Neat asphalt samples

Terminal Storage Stability

- 7 days storage of both neat and modified asphalt at 350 deg F -- Properties assessed before and after simulated field storage.
- In addition to exhibiting PG stability, also slightly improved PAV cold temperature properties.

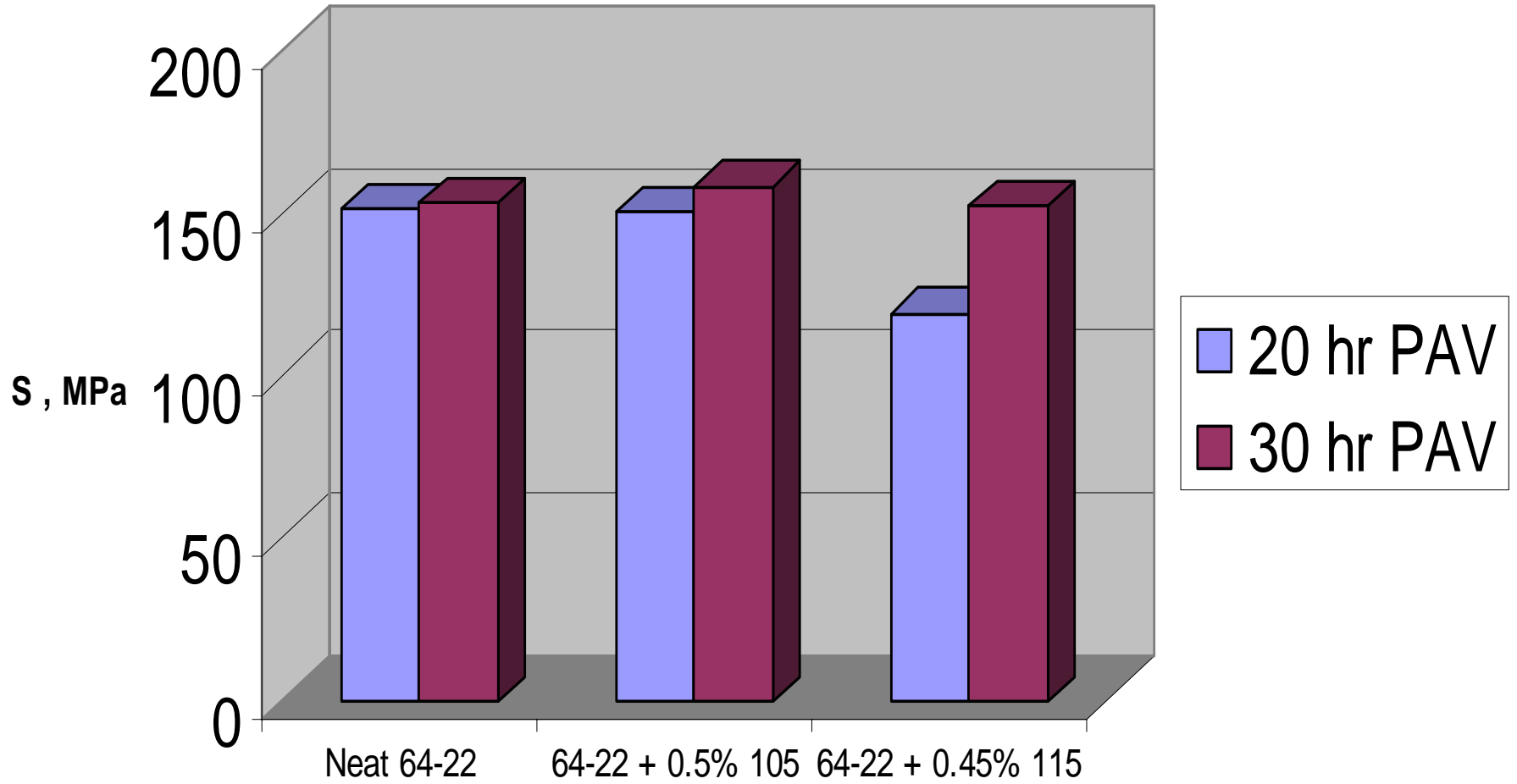
DSR @ 70 deg C, (storage)



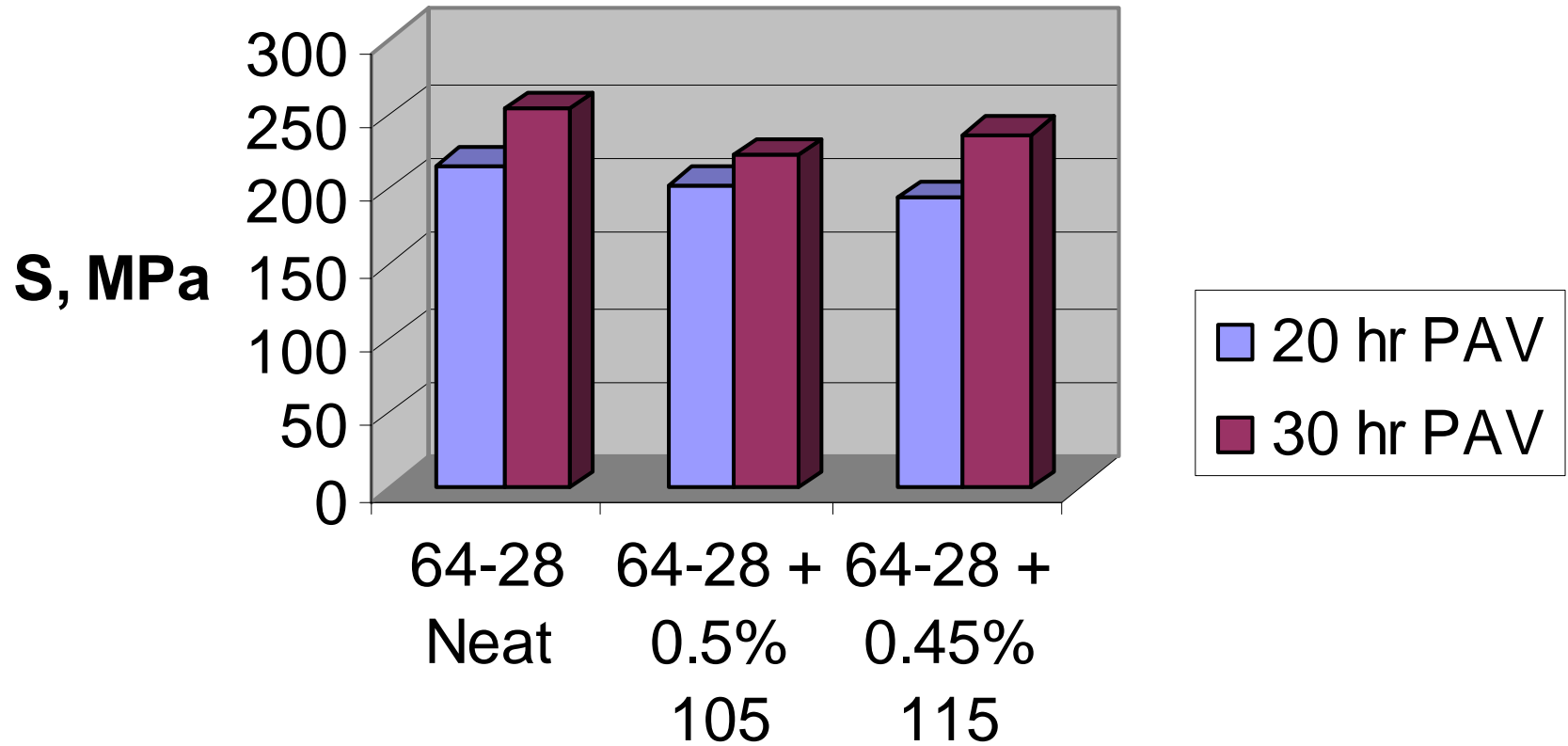
No Adverse Effects on Overheating

- Original DSR 1.30
- Conditioned : Reheated to 450 deg F for 8 hrs
- Ambient for 16 hrs
- Reheat to 325 deg F
- DSR– 1.24

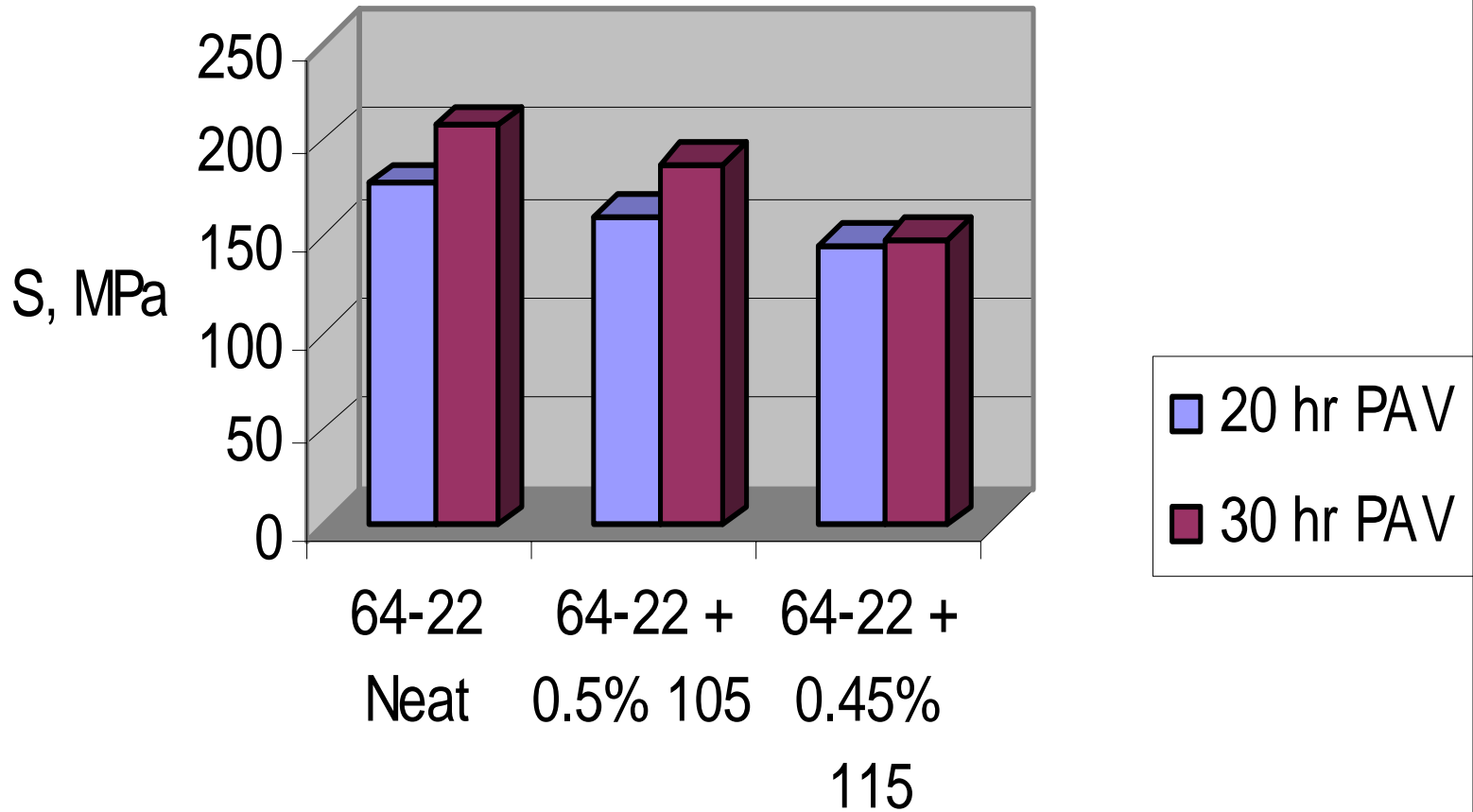
Extended Oxidative Aging - Asphalt A



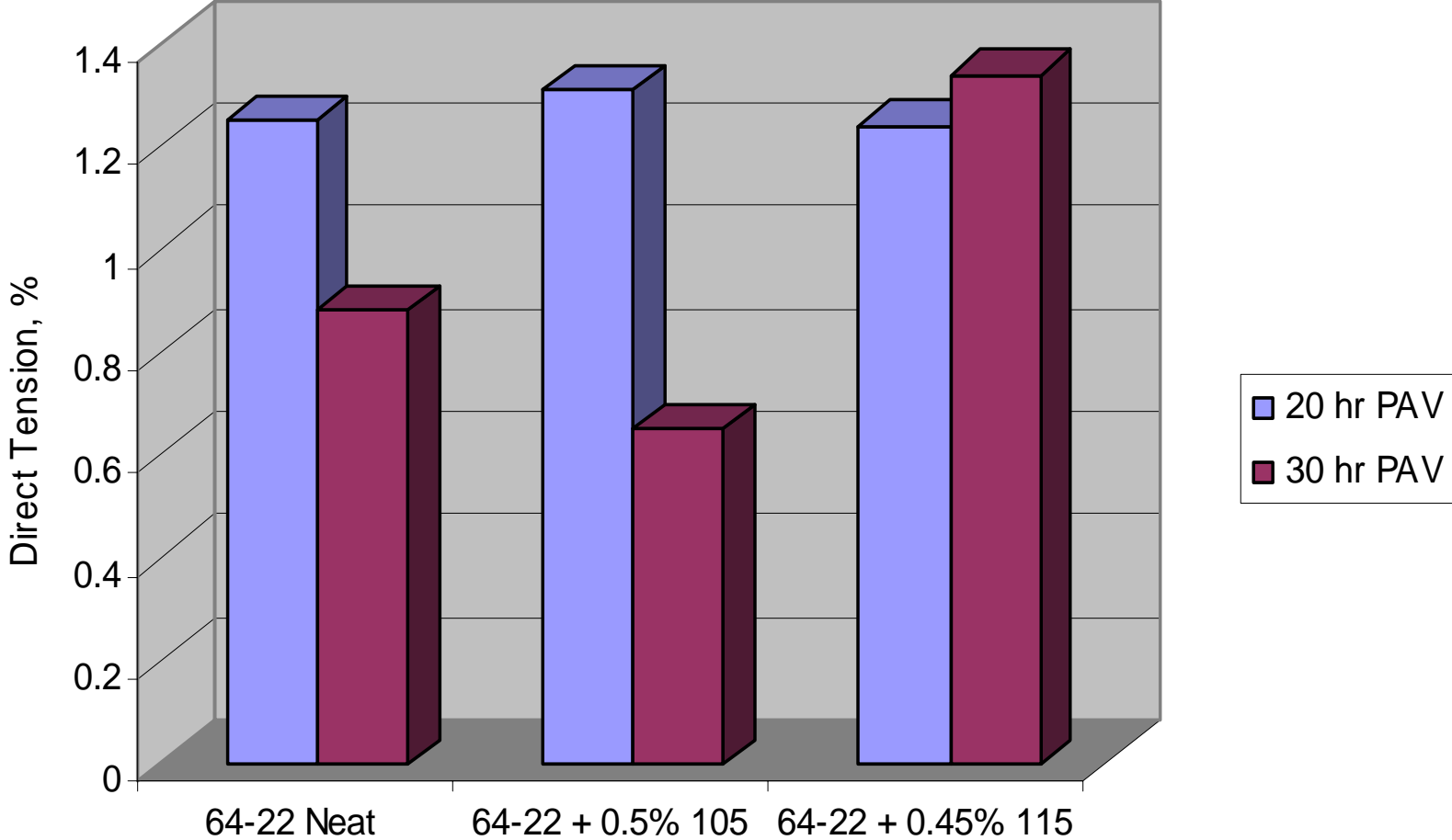
Extended Oxidative Aging - Asphalt B



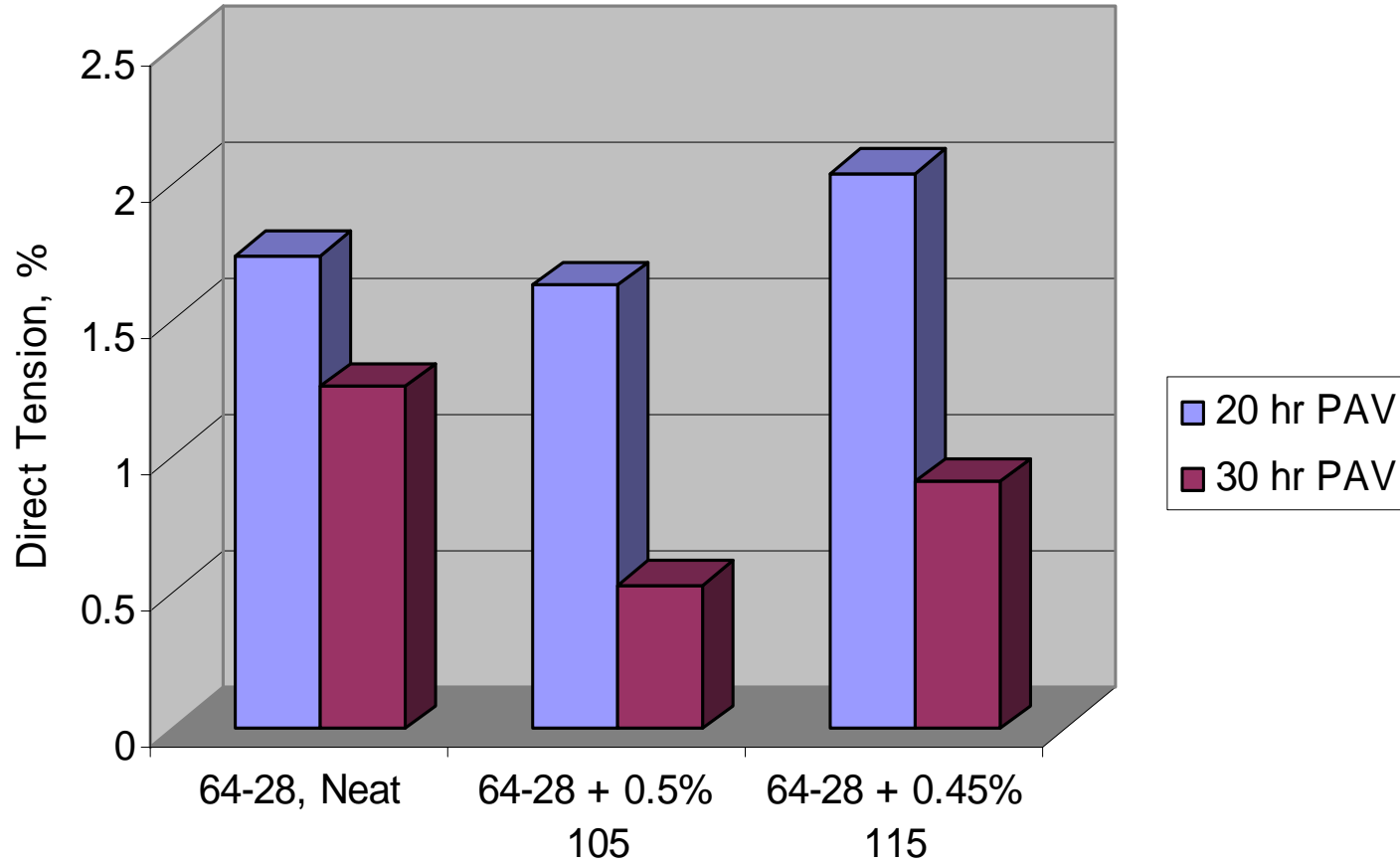
Extended Oxidative Aging - Asphalt C



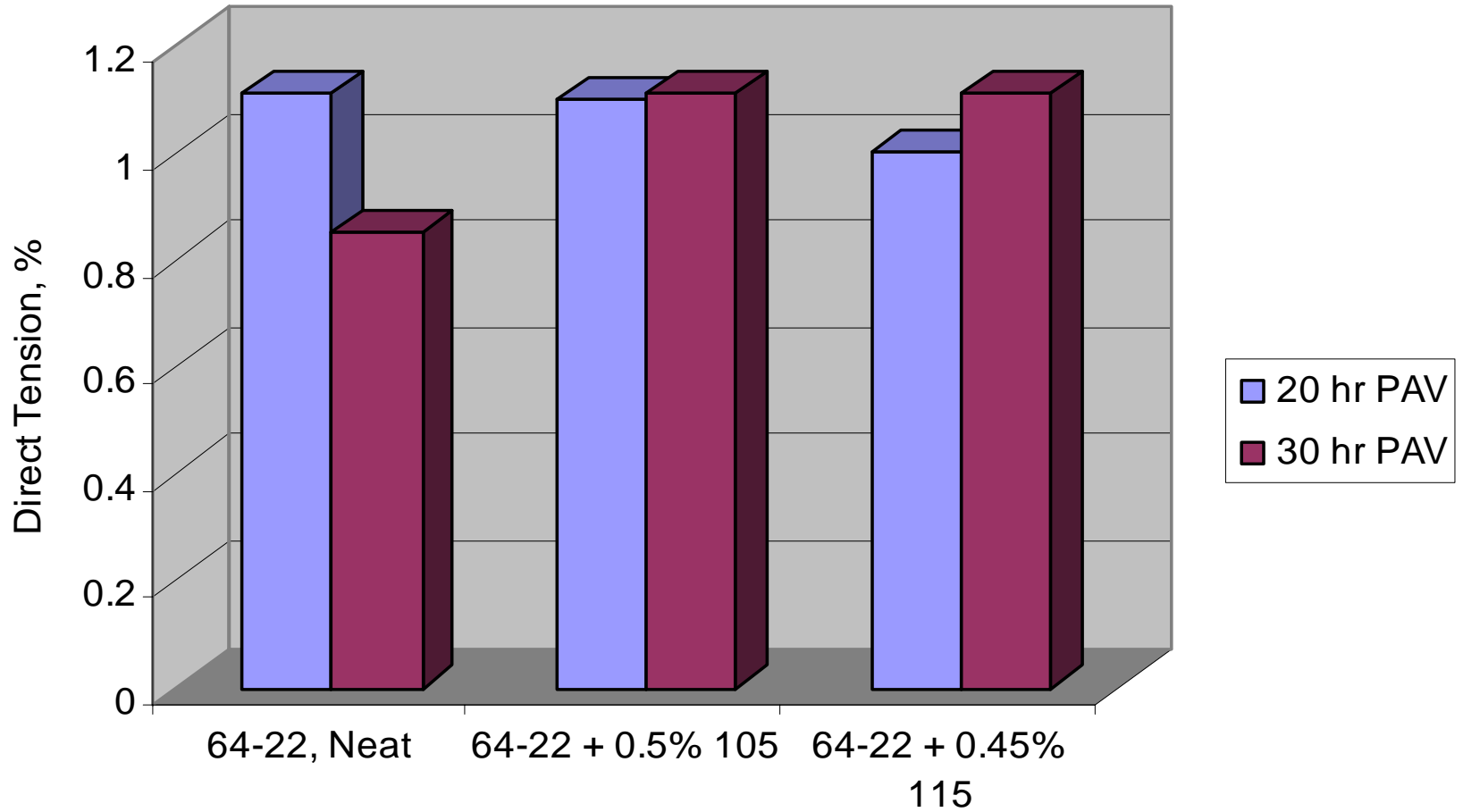
Extended Oxidative Aging - Asphalt A - DTT



Extended Oxidative Aging - Asphalt B - DTT



Extended Oxidative Aging - Asphalt C - DTT



Evaluate migration of polyphosphoric acid in the presence of water

- Even in the presence of boiling water, the phosphorus remains in the asphalt phase. (98+%).
- Once mixed in, at reasonable level, it will not migrate.

Catalyst or Reactant?

- A. Hoiberg found that it was not possible to extract the phosphorus from an organic layer with boiling water.
- So, in a sense, it's not a catalyst, since it is not recovered.

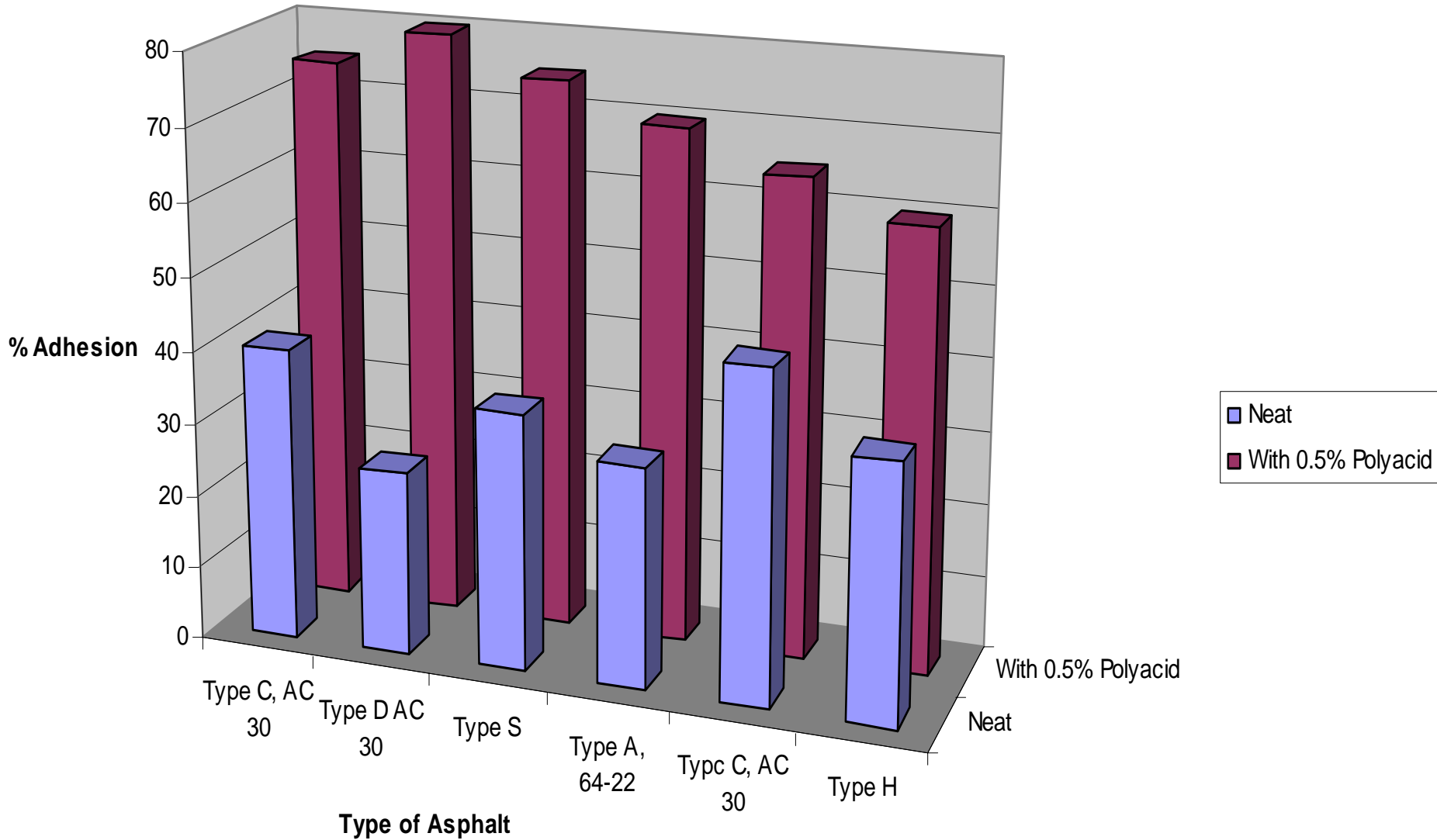
Moisture Sensitivity

- Texas Boil Tests
- Lottman T-283 Tests
- Hamburg Loaded Wheel Test

Texas Boil Tests

- Adhesion of six asphalts to aggregate all increased with the addition of 0.5% polyphosphoric acid to the binder
- Aggregate- Lithonia Granite , sensitive to moisture

%Adhesion-Texas Boil Test, Lithonia Granite

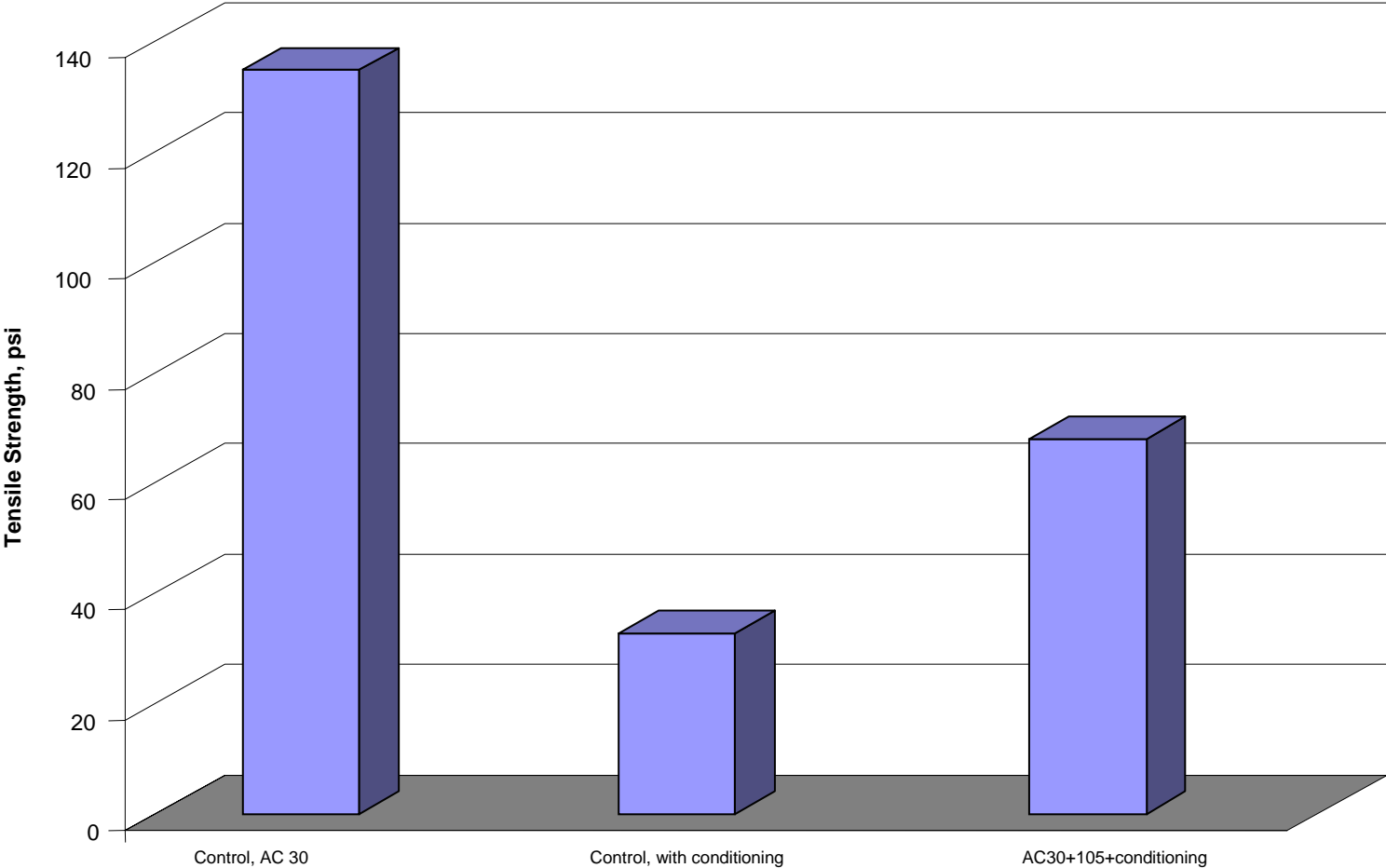


Tensile Strength Ratios/Lottman Tests

- Experimental Design:
 - Lithonia Granite
 - Limestone Aggregate
 - Selected asphalt D, based upon 30% neat and 80% adhesion with 0.5% polyphosphoric

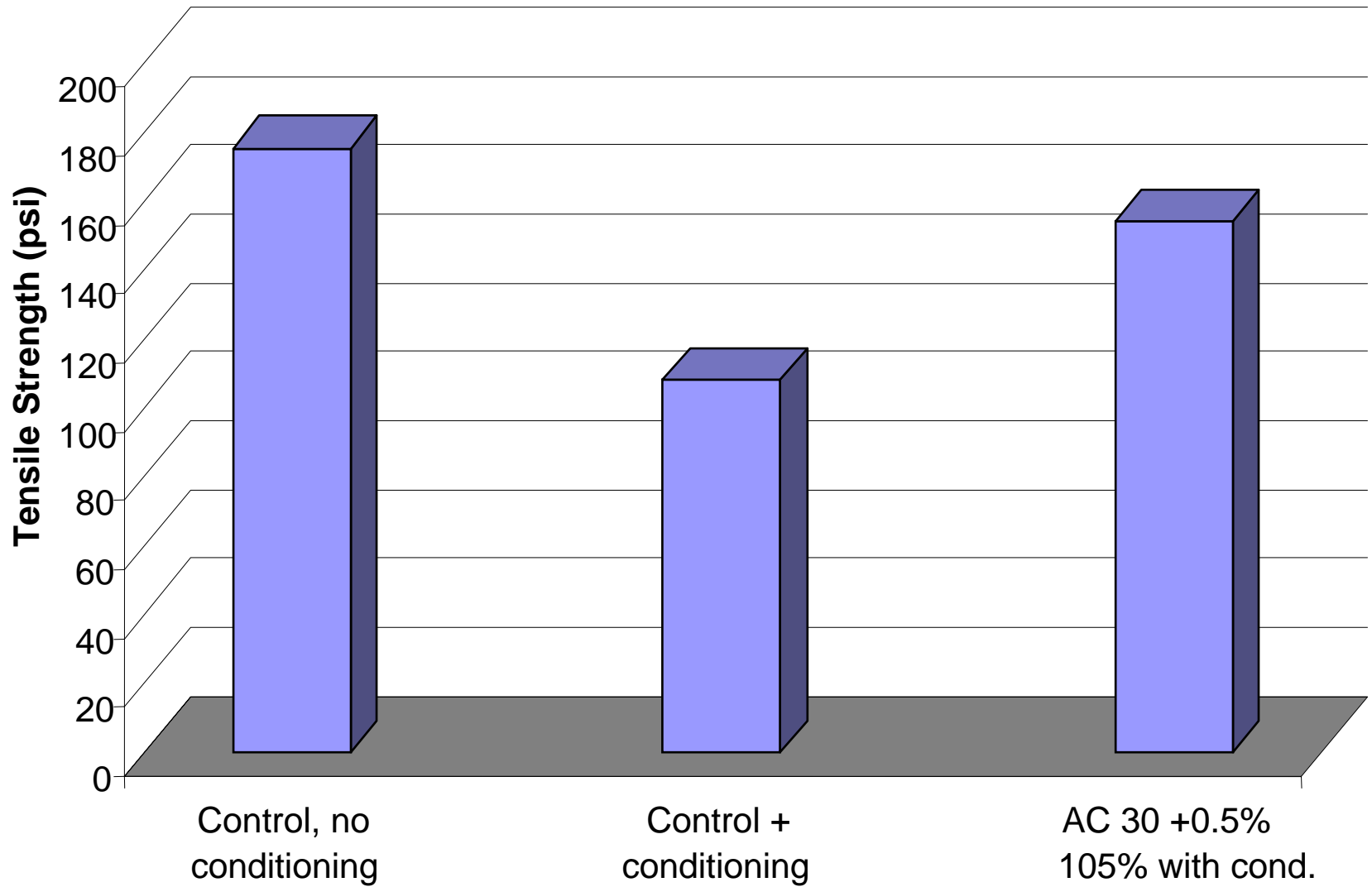
Tensile Strength, Lithonia Granite

Asphalt D



Type of Treatment

Tensile Strength, Limestone Aggregate Asphalt D



Tensile Strength Ratios

- Lithonia Granite. – TSR % for neat asphalt was increased by ~ 25% when 0.5% polyphosphoric acid was used
- Limestone Aggregate- TSR % for neat asphalt was increased by ~ 30% when 0.5% of polyphosphoric acid was used

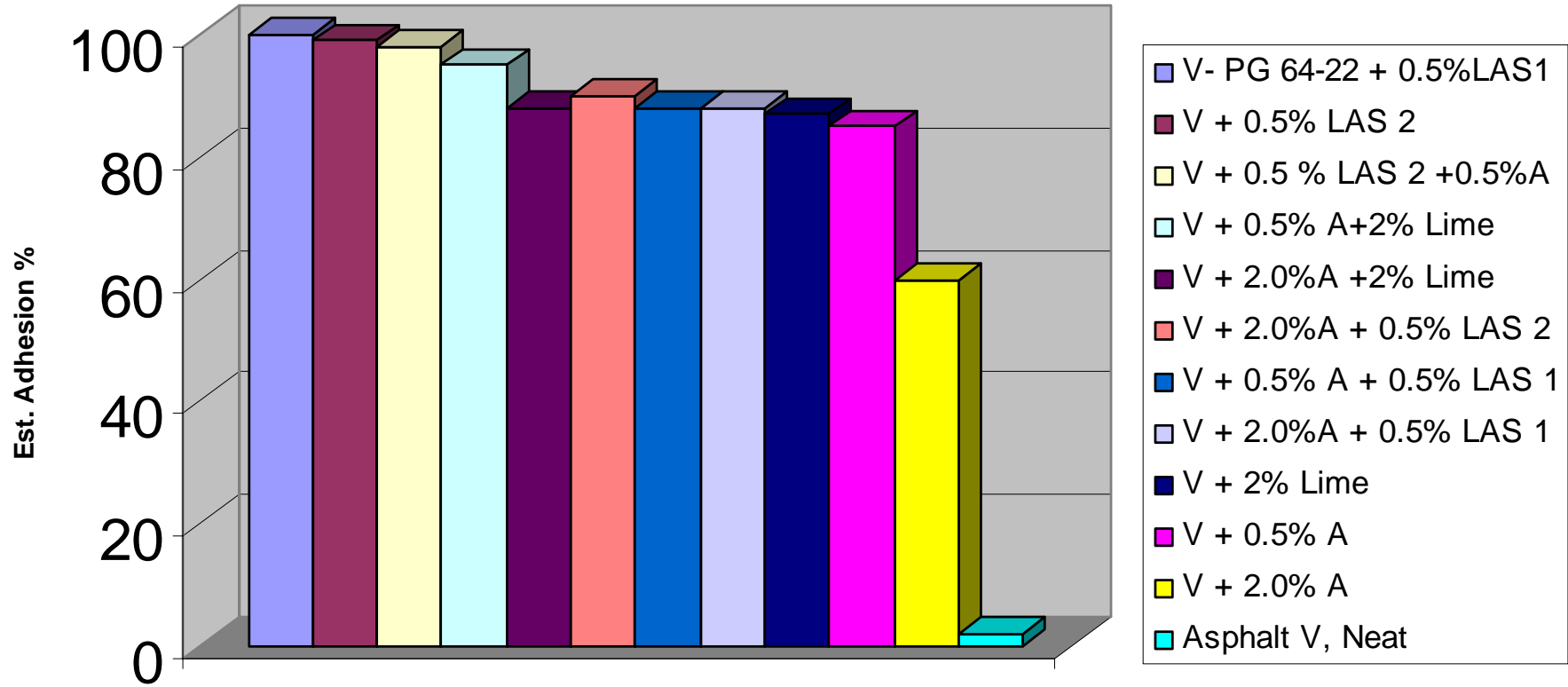
Moisture Sensitivity in Presence of Anti-strip Additives

- Literature reports about potential for interaction (Ludo Zanzutto and G. King)
- Some used orthophosphoric acid rather than polyphosphoric acid and some used too much polyphosphoric acid
- Study to assess adhesion in presence of such agents

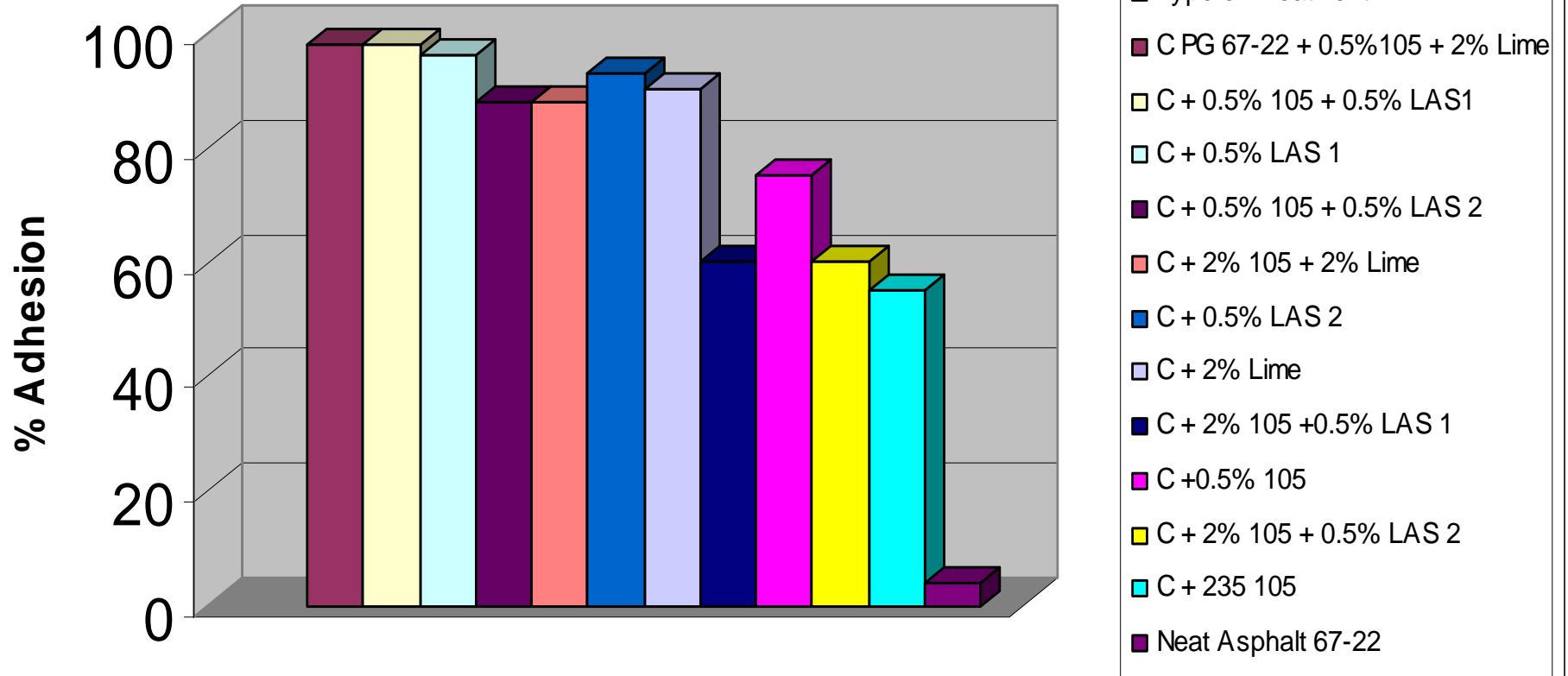
Three asphalts/one stripping aggregate/Texas Boil Tests

- Asphalts: PG 64-22, PG 67-22 and PG 58-22
- Additives: Polyphosphoric acid(0.5% and 2%)
- Liquid ASA 1, liquid ASA 2 and lime 2%
- Estimated Adhesion (Aged at 120 deg F –one week)

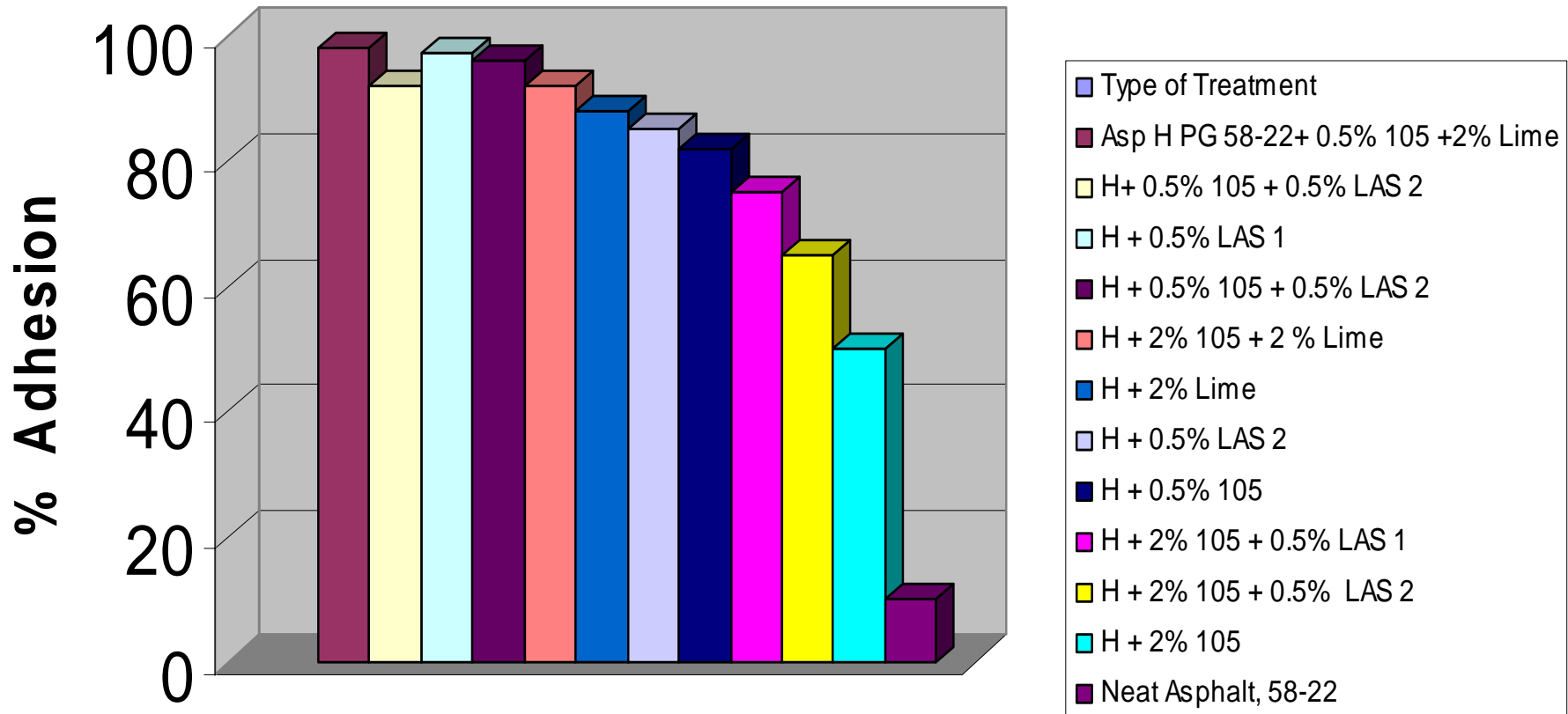
Estimated % Adhesion - Asphalt V



Est. % Adhesion - Asphalt C



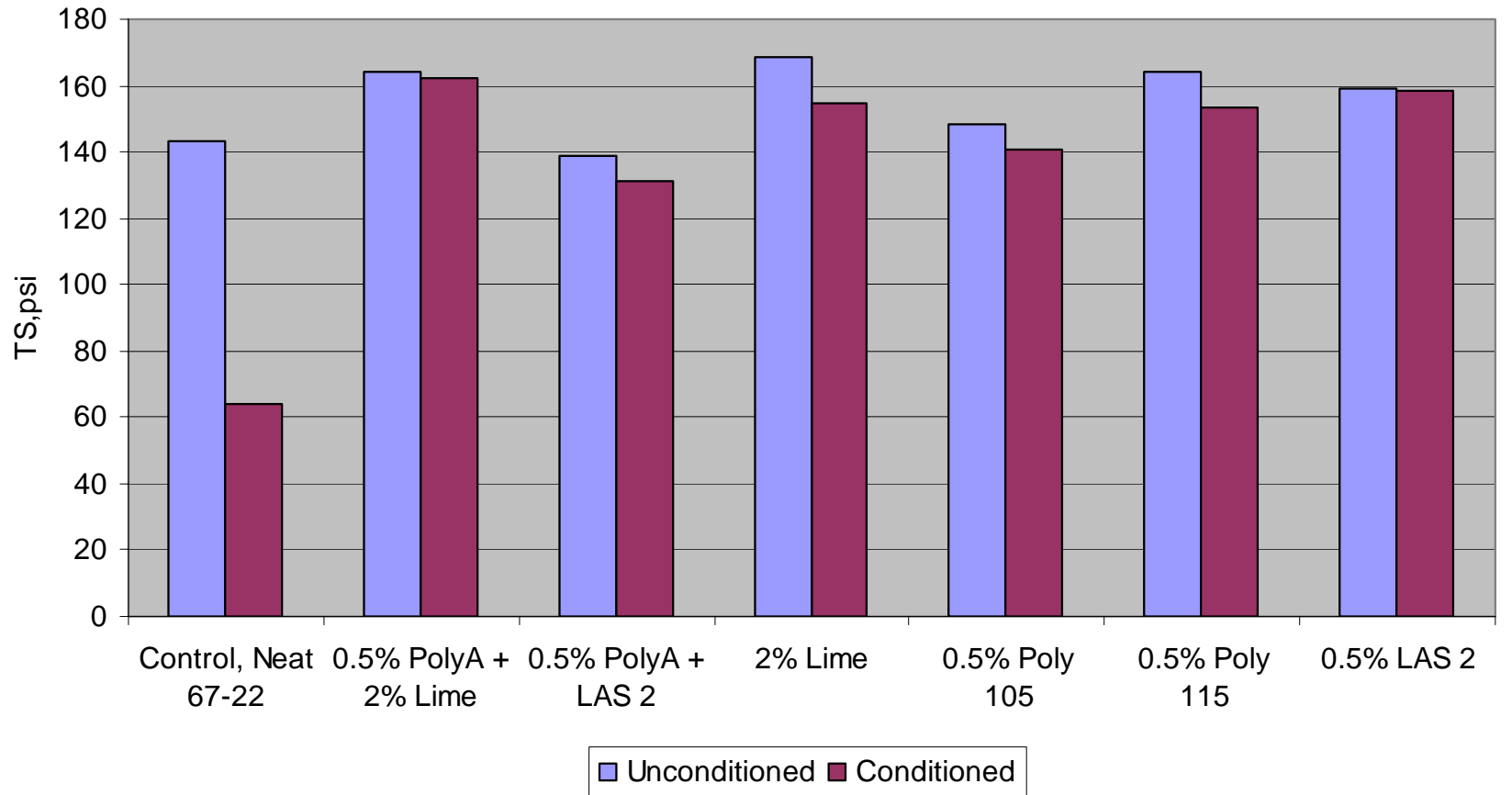
Estimated % Adhesion - Asphalt H



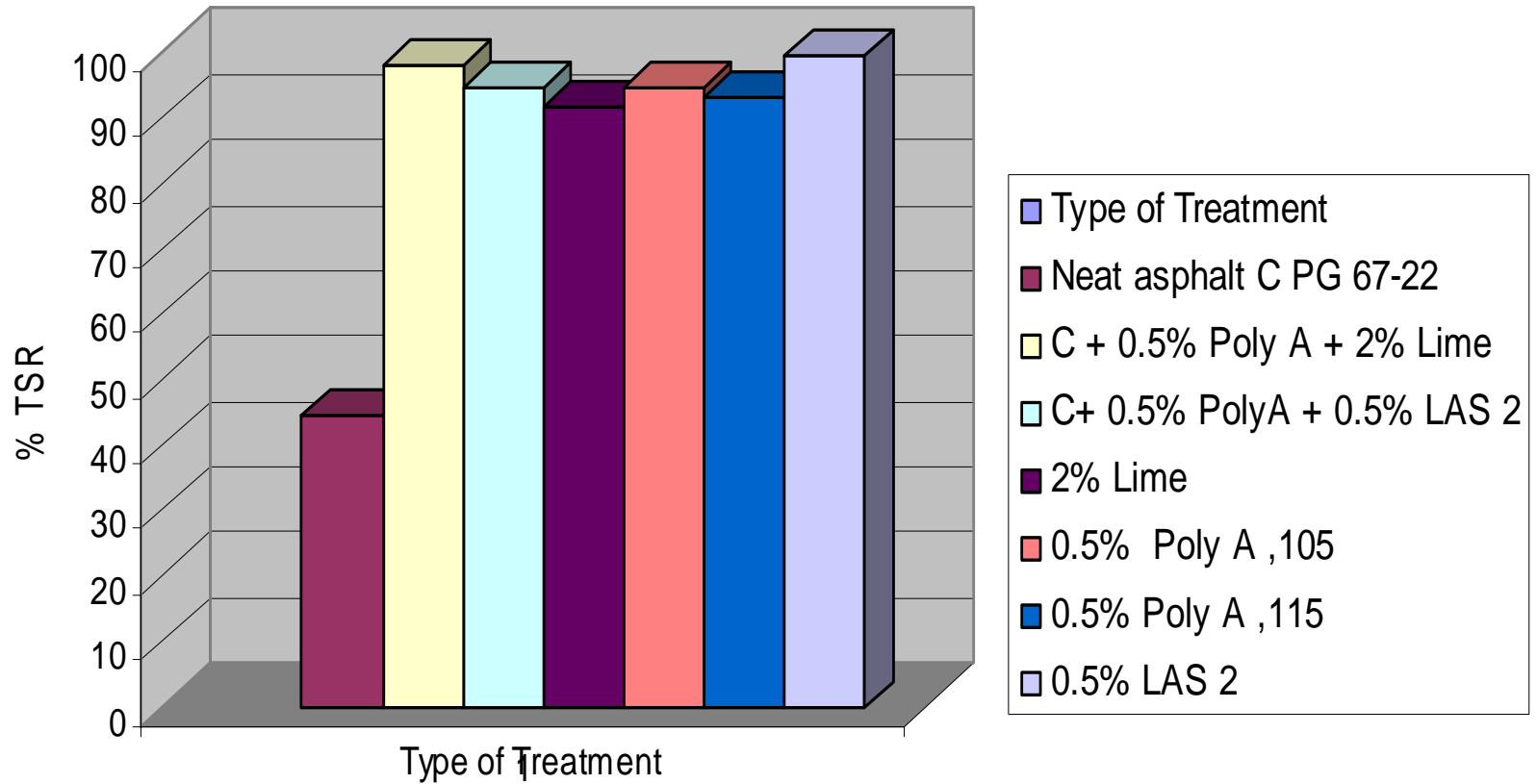
Lottman Assessments

- Aggregate Source: Lithonia Granite
- Asphalt: C PG 67-22
- Variables: Polyphosphoric acid, LAS 2, Lime

Tensile Strength



Tensile Strength Ratio



Tensile Strength Ratios

- Systems involving polyphosphoric acid and alkaline materials all gave good TSR's, when the polyphosphoric acid was used at a reasonable level

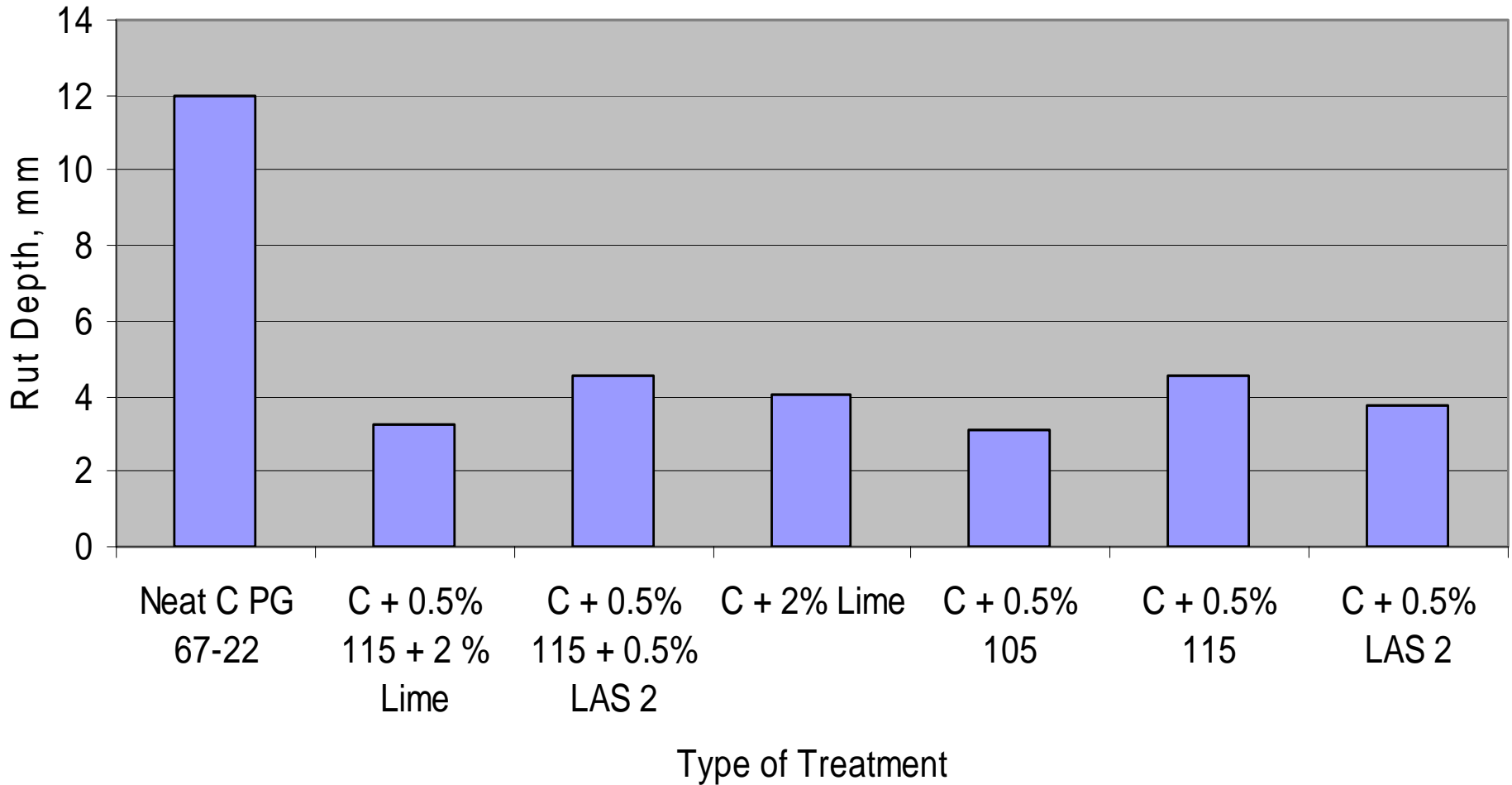
Sensitivity Analysis Results:

- Some synergy with liquid anti-strips
- 0.5% polyphosphoric acid is similar to 2% lime
- Polyphosphoric acid improves adhesion (dosage dependent)

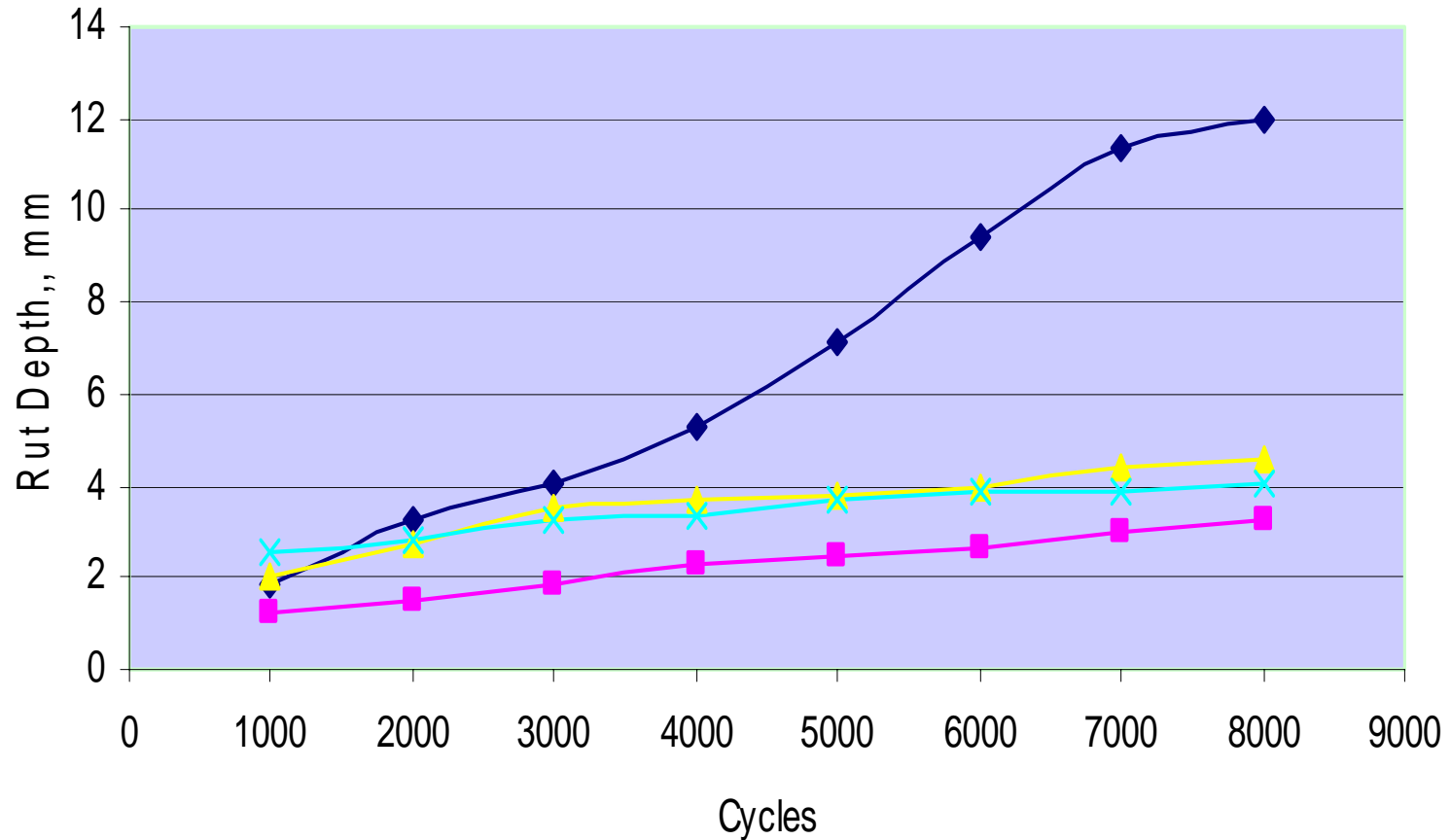
Hamburg Test Conditions-8000 cycles at 50 deg C, PG 67-22(4.5% binder)

- Asphalt C PG 67-22, Polyphosphoric acid 105% and 115%, LAS 2 and Lime
- Lime added to aggregate prior to mixing with binder

Hamburg /Lithonia Granite/ 50 deg C

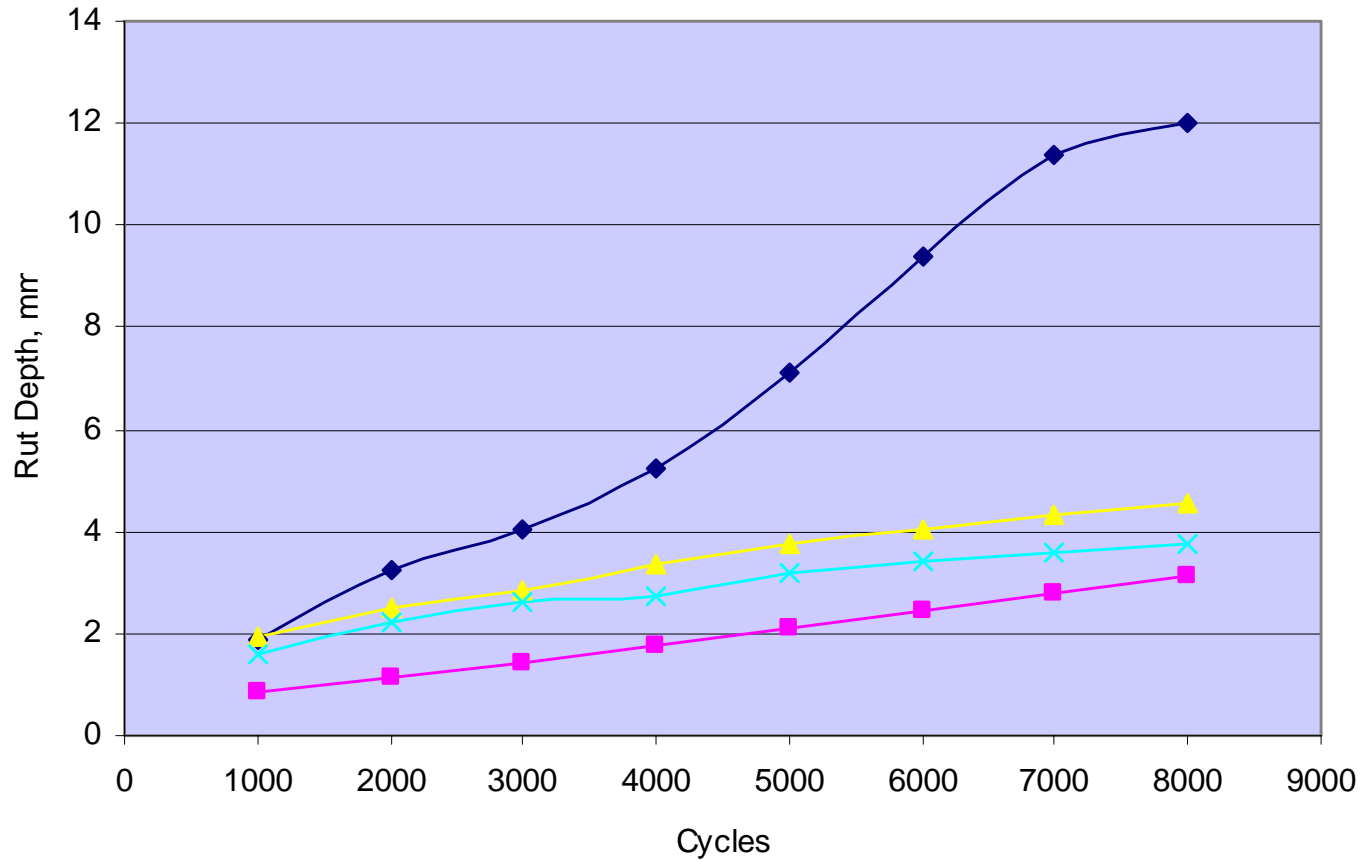


Hamburg Rut Depth, 50 deg C

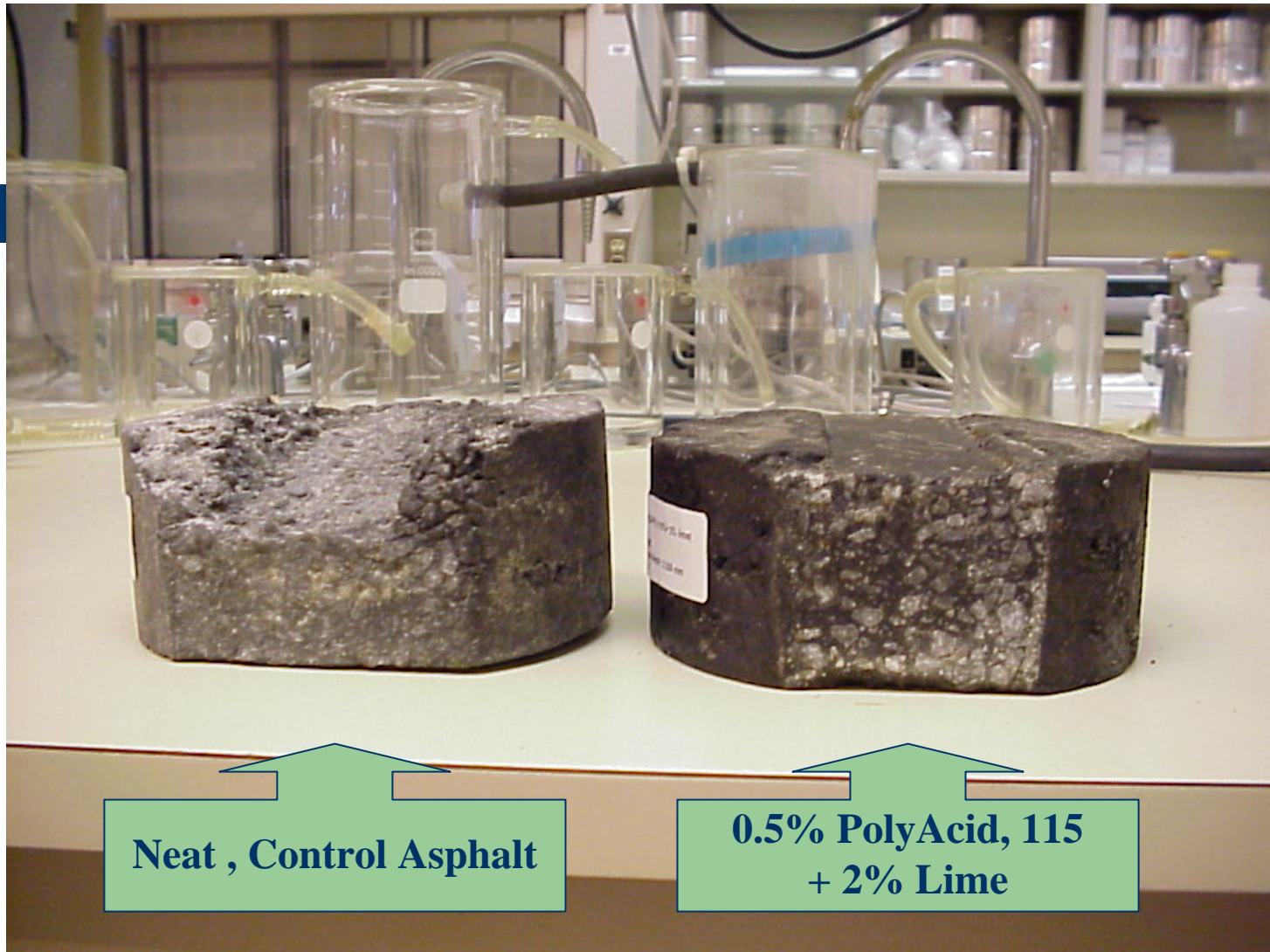


—◆— Control, C 67-22 —■— C+0.5% 115+ 2% Lime
—▲— c+ 0.5% 115 + 0.5% LAS 2 —x— C + 2.0% Lime

Hamburg Rut Depth, 50 deg C

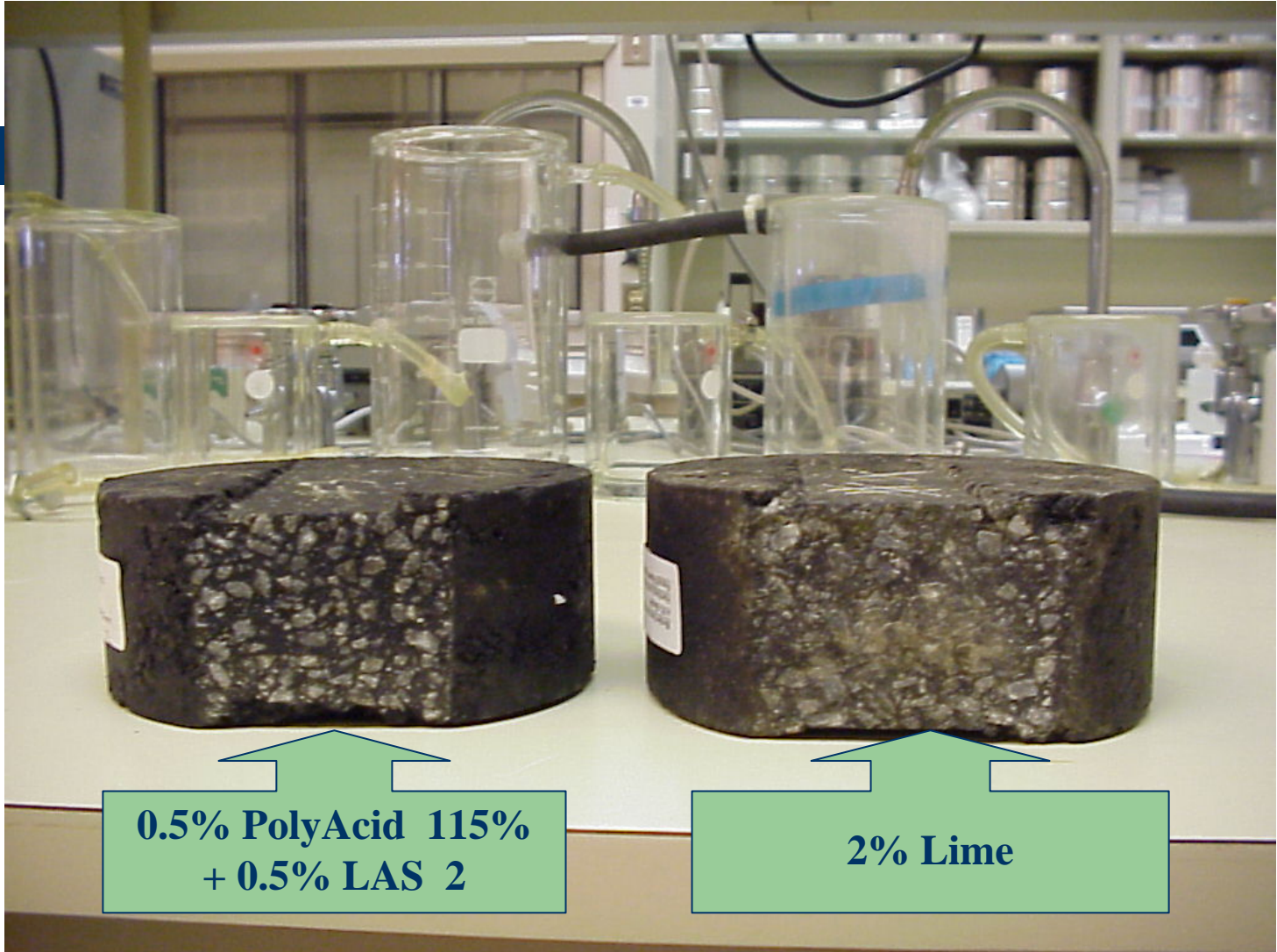


—◆— C 67-22, Neat —■— C + 0.5% 105 —▲— C + 0.5% 115 —×— C + 0.5% LAS 2



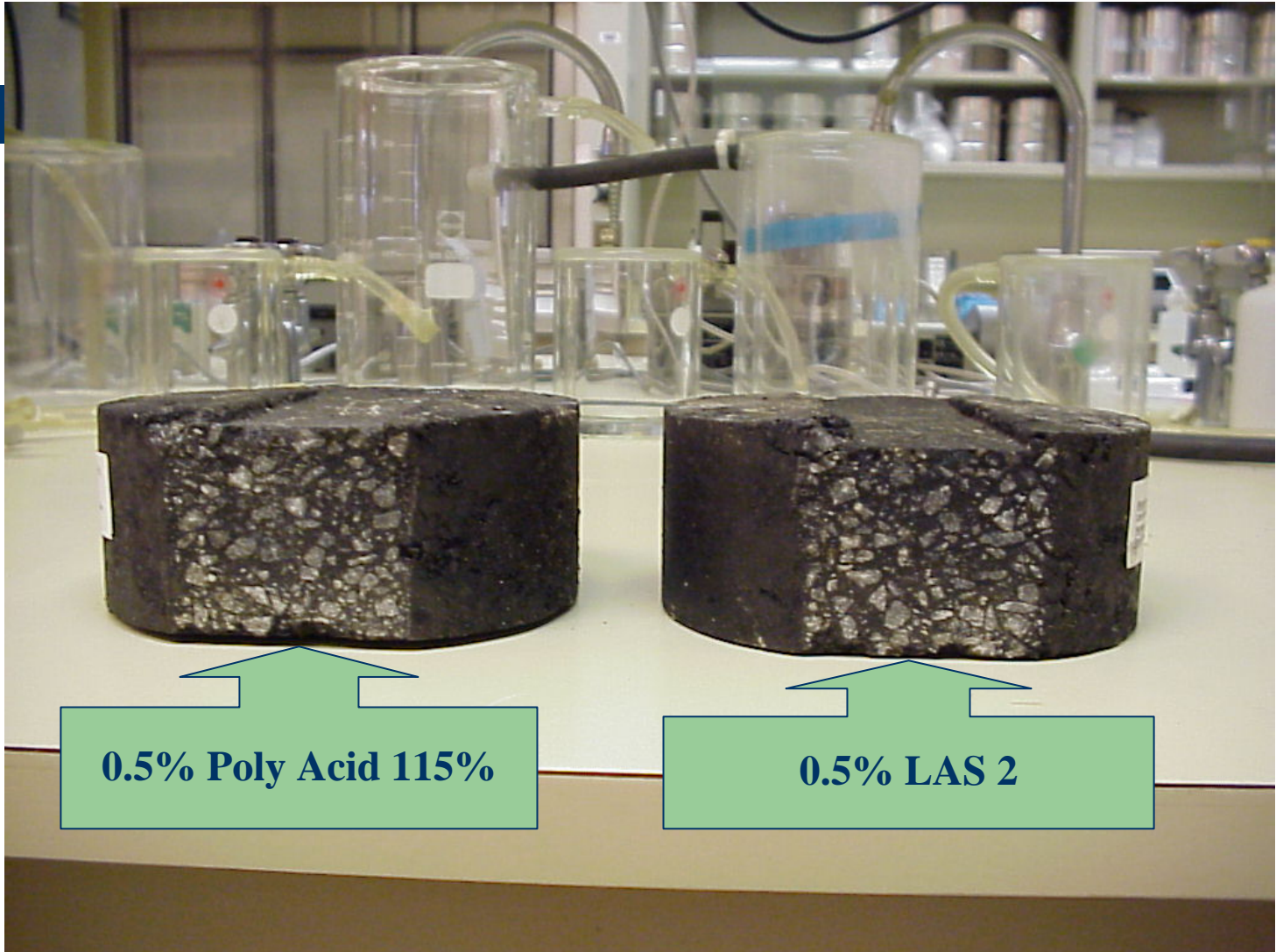
Neat, Control Asphalt

**0.5% PolyAcid, 115
+ 2% Lime**



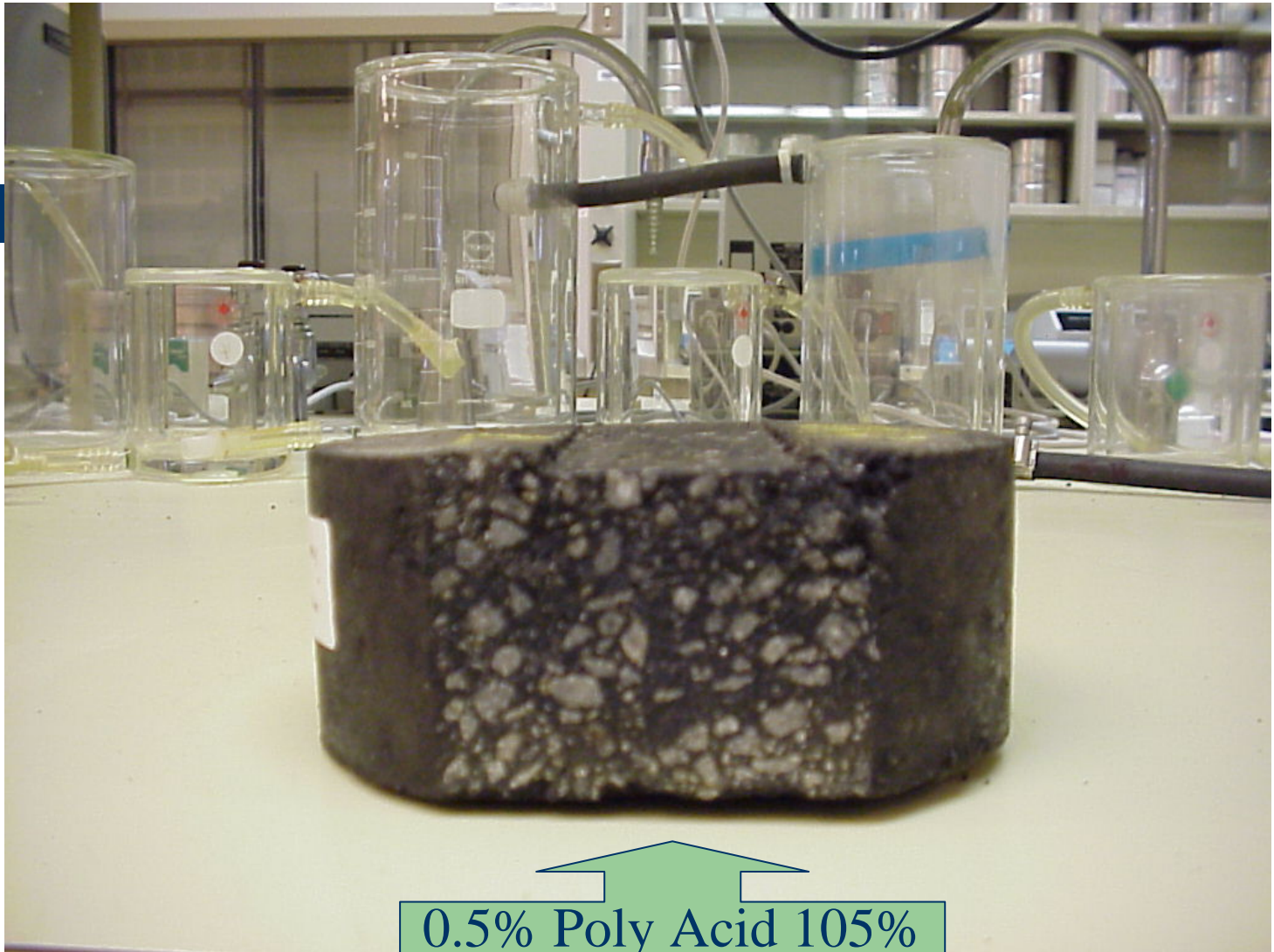
**0.5% PolyAcid 115%
+ 0.5% LAS 2**

2% Lime

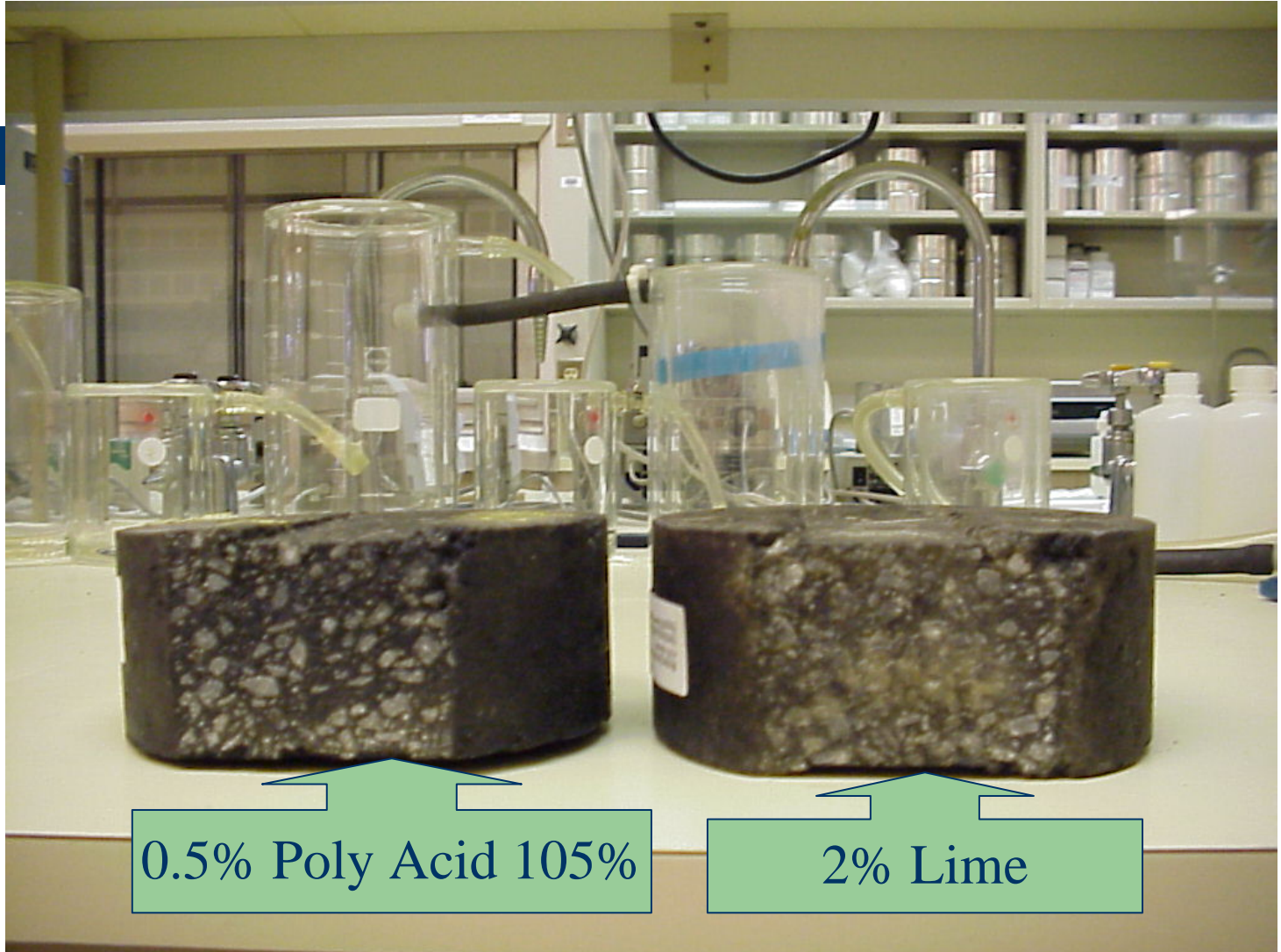


0.5% Poly Acid 115%

0.5% LAS 2



0.5% Poly Acid 105%



0.5% Poly Acid 105%

2% Lime

Conclusions

- Data suggests that Polyphosphoric acid improves water sensitivity
- The combination of Polyphosphoric acid and commercially available anti-strip products did not adversely affect the adhesion

Conclusions: *(9 Different Asphalts and Various Grades tested)*

- Performance Grade, PG
 - **Improved High Temperature Grades**
 - **No Adverse Cold Temperature (PAV) Properties**
 - **Improved Resistance to Oxidative Aging (PAV)**
 - **Improved DTT % Strains — some asphalts**

Conclusions Continued: *(9 Different Asphalts and Various Grades tested)*

- Exhibits “Stable” Terminal Storage Properties
- No adverse effects by Overheating
- Improved Adhesion
- Improved Resistance to Water
 - Texas Boil Tests
 - Lottman (T-283)
 - Hamburg Loaded Wheel Tester
- Compatibility w/ conventional Anti-Strip Additives

RECOMMENDATION:

- Polyphosphoric Acid is the material to use. It is a clear, colorless, odorless liquid.
- It is not orthophosphoric acid, or green acid
- One should use it with all the proper testing techniques

Food for Thought/Path Forward

- Dispersion Chemistry - Degree and Stability