Polyphosphoric Acid in Asphalt Modification

by

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

- Objective: Discuss what polyphosphoric acid is, its 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, $\text{H}_3\text{PO}_4$, has a $\text{P}_2\text{O}_5$ content of 72.4%.
- There is an analytical procedure to determine $\text{P}_2\text{O}_5$ content.
- Now—How do you get anything greater than 100%? It is a relative measure. You set up a ratio.
- $100\% \text{ acid} / 72.4\% \text{ P}_2\text{O}_5 = X / 83.2\% \text{ P}_2\text{O}_5$
  $X = 115\%$ Polyphosphoric Acid
Literature References:

- Arnold Hoiberg, US Pat # 2,450,756—10/5/1948, assigned to Lion Oil Division, Monsanto Company


- 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

- A, AC-20
- A + 0.5% (105)
- B + 0.45%, 115
- C - AC 20
- C + 0.5%, 105
- C + 0.45%, 115
Softening Point, deg F

- A-AC 20
- A+0.5% 105
- A+ 0.45%, 115
Penetration @ 25 deg C

Penetration, (dmm)

- A-AC20
- A+0.5%, 105
- A+0.45%, 115
Penetration @ 4 deg C

Penetration (dmm)

A-AC 20 | A+0.5%, 105 | A+0.45%, 115

Penetration @ 4 deg C
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)

- Asphalt-VEN., initial
- Asphalt-VEN., 7 days @ 350 F
- Asph. VEN + 0.5% 115, initial
- Asphalt VEN + 115- 7 days at 350 F

DSR, kPa
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 B

S, MPa

20 hr PAV
30 hr PAV

64-28 Neat
64-28 + 0.5%
64-28 + 0.45%

105
115
Extended Oxidative Aging - Asphalt C

S, MPa

64-22  64-22 +  64-22 +
Neat    0.5% 105    0.45% 115

20 hr PAV
30 hr PAV
Extended Oxidative Aging - Asphalt A - DTT

- 20 hr PAV
- 30 hr PAV

Direct Tension, %

- 64-22 Neat
- 64-22 + 0.5% 105
- 64-22 + 0.45% 115
Extended Oxidative Aging - Asphalt B - DTT

Direct Tension, %

- 64-28, Neat
- 64-28 + 0.5%
- 64-28 + 0.45%

20 hr PAV
30 hr PAV
Extended Oxidative Aging - Asphalt C - DTT

- Direct Tension, %

64-22, Neat
64-22 + 0.5% 105
64-22 + 0.45% 115

20 hr PAV
30 hr PAV
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

![Bar Graph]

- Type C, AC 30
- Type D AC 30
- Type S
- Type A, 64-22
- Type C, AC 30
- Type H

% Adhesion

Type of Asphalt

- Neat
- With 0.5% Polyacid
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

Control, AC 30
Control, with conditioning
AC30+105+conditioning

Tensile Strength, psi

0 20 40 60 80 100 120 140

Control, AC 30
Control, with conditioning
AC30+105+conditioning
Tensile Strength, Limestone Aggregate
Asphalt D

Tensile Strength (psi)

Control, no conditioning
Control + conditioning
AC 30 +0.5%
105% with cond.
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

- V- PG 64-22 + 0.5%LAS1
- V + 0.5% LAS 2
- V + 0.5 % LAS 2 +0.5%A
- V + 0.5% A+2% Lime
- V + 2.0%A +2% Lime
- V + 2.0%A + 0.5% LAS 2
- V + 2.0%A + 0.5% LAS 1
- V + 2% Lime
- V + 0.5% A
- Asphalt V, Neat
Est. % Adhesion - Asphalt C

Type of Treatment
- C PG 67-22 + 0.5% 105 + 2% Lime
- C + 0.5% 105 + 0.5% LAS1
- C + 0.5% LAS 1
- C + 0.5% 105 + 0.5% LAS 2
- C + 2% 105 + 2% Lime
- C + 0.5% LAS 2
- C + 2% Lime
- C + 2% 105 + 0.5% LAS 1
- C + 0.5% 105
- C + 2% 105 + 0.5% LAS 2
- C + 235 105
- Neat Asphalt 67-22
Estimated % Adhesion - Asphalt H

- Type of Treatment
- Asp H PG 58-22+ 0.5% 105 +2% Lime
- H+ 0.5% 105 + 0.5% LAS 2
- H + 0.5% LAS 1
- H + 0.5% 105 + 0.5% LAS 2
- H + 2% 105 + 2 % Lime
- H + 2% Lime
- H + 0.5% LAS 2
- H + 0.5% 105
- H + 0.5% 105
- Neat Asphalt, 58-22
Lottman Assessments

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

- Neat asphalt C PG 67-22
- C + 0.5% Poly A + 2% Lime
- C + 0.5% Poly A + 0.5% LAS 2
- 0.5% Poly A, 105
- 0.5% Poly A, 115
- 0.5% LAS 2

% TSR

Tensile Strength Ratio

Type of Treatment

Neat asphalt C PG 67-22
C + 0.5% Poly A + 2% Lime
C + 0.5% Poly A + 0.5% LAS 2
0.5% Poly A, 105
0.5% Poly A, 115
0.5% LAS 2
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
The diagram shows the rut depth (in mm) for different treatments on Hamburg/Lithonia Granite at 50 degrees Celsius. The treatments include:

- Neat C PG 67-22
- C + 0.5% Lime
- C + 0.5% LAS 2
- C + 2% Lime
- C + 0.5% 105
- C + 0.5% 115
- C + 0.5% LAS 2

The rut depth for Neat C PG 67-22 is significantly higher compared to the other treatments.
Hamburg Rut Depth, 50 deg C

- Control, C 67-22
- C+0.5% 115 + 2% Lime
- c+ 0.5% 115 + 0.5% LAS 2
- C + 2.0% Lime
Neat, Control Asphalt

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

2% Lime
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