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A brief review of the chemistry of polyphosphoric acid (PPA) and bitumen

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Abstract

Bitumen finds great use in paving and roofing applications. To enhance or extend its performance, it is often modified with a polymer, including polyphosphoric acid (PPA). PPA is a reactive oligomer, a short chain polymer, whose reaction with bitumen is poorly understood. In an effort to better understand their reaction, the chemical characteristics of PPA and bitumen are reviewed. It is concluded that PPA cannot dissociate and react with bitumen unless enclaves of high dielectric constant exist in bitumen.

Introduction

Bitumen is used in over two hundred applications, most of which relate to civil engineering, and to paving and roofing in particular (1). In an attempt to change its characteristics and improve its performance, bitumen is often modified with an elastomer (2, 3), a plastomer (4, 5, 6, 7), a thermoset (8, 9), sulphur (10, 11), or a mineral acid (12). There is now much interest in the use of polyphosphoric acid (PPA) to modify bitumen. By itself or in combination with a polymer, PPA provides a means of bitumen modification usually produced more expensively with a polymer alone.

It is common for material formulators and developers to use bitumens of different sources as dictated by market forces. As bitumen changes, it is often difficult to predict the effect

of a modifier on bitumen and determine in advance the level of modifier required to achieve a given characteristic. In many cases, the modifier is dispersed in bitumen at high temperatures. In some cases, the modifier reacts with bitumen. This is the case of PPA, but the nature of the reaction is ill understood. In an effort to shed light on this reaction, and before PPA-modified bitumens are studied further, it is beneficial to better know the raw materials. Consequently, we briefly review here the chemistry and the composition of bitumen and PPA.

Bitumen

Bitumen is a residue of the distillation of crude oil. Most often this is a two-step process where atmospheric and vacuum distillations are combined, in which case *straight-run* bitumen is produced. When the distillation residue is oxidized in an effort to change its consistency, *blown* bitumen is obtained (13).

The characteristics and composition of bitumen depend in large part on the source of the mother crude oil, for instance, Canada, Mexico, Saudi Arabia, Venezuela (14). The chemical complexity of bitumen precludes any precise molecular identification. Consequently, it is often conveniently characterized by its chromatographic fractions, the maltenes and the asphaltenes (As), which are, respectively, soluble and insoluble in n-heptane. The maltenes can be fractionated further into saturates (S), aromatics (A) and resins (R) (15, 16). The SARAs terminology can be confusing, however, because the aromatics fraction (A) most often contains little conjugated ring structures (14). Table 1 provides the composition of the fractions in more classical terms.

[Table 1]

The molecular weight of the SARAs increase as S<A<R<As between 300 and 1000 Daltons (17, 18). Aromatic nuclei commonly have three to five condensed aromatic rings (19). The bitumen molecules can thus be fairly large, with alkanes and pending alkyl chains on aromatic nuclei providing for entanglements and viscoelastic properties. In contrast to viscoelastic polymers, however, bitumen molecules do not have identical repeat units. Bitumen can be regarded as an oligomer with about 10 repeat units, with each repeat unit different from the next, and where the molecular weight of the repeat unit varies from about 35 Da to 90 Da (20).

The SARAs fractions also increase in aromaticity and heteroatomic content in the order S<A<R<As (14). In bitumen, sulfur, oxygen and nitrogen can respectively attain about 8.5%, 1.2% and 1.5% by mass (21). Typical bitumen functional groups are shown in Figure 1.

[Figure 1]

The miscibility of the SARAs fractions and the dispersion of the various functional groups in bitumen are of great interest because they govern its chemical and physical characteristics. The miscibility of the fractions is addressed by the colloidal bitumen model, which states that asphaltenes are stabilized by the resins in a matrix of mixed saturates and aromatics (22). A more recent model addresses the dispersion of the heteroatomic functions in bitumen. It characterizes bitumen as a homogeneous mixture of

neutral and amphoteric molecules, where adjacent acidic and basic functions interact to form a viscoelastic network within the neutral fraction (23).

Notwithstanding the success of the colloidal and the amphoteric models, both are based on solvent fractionation of bitumen by chromatography, which provide an incomplete view of bitumen in its solid state, by neglecting for instance the existence of ordered material. The undisturbed solid-state structure of bitumen can be characterized by modulated differential scanning calorimetry, MDSC (20, 24), and atomic force microscopy, AFM (25, 26). These methods show that bitumen can contain at least six phases and that it is heterogenous on a 15 μm scale. MDSC shows that it can have four glass transition temperatures from distinct amorphous phases, along with endothermic transitions from crystalline paraffins, and from mesogenic (liquid-crystalline like) asphaltenes whose ordering is time dependent (27, 28). Given this complexity, it is not surprising that bitumens of identical classes can have different chemical compositions as illustrated in Table 2 (21) for bitumens with a 58-28 grade (29). For this reason, it is difficult to predict the stability or the reactivity of an additive in a mixture with bitumen.

[Table 2]

Polyphosphoric acid

Synthesis and composition

The basic compounds for the production of polyphosphoric acid (PPA) are phosphorus pentoxide (P_2O_5) and phosphoric acid (H_3PO_4), as shown in Figure 2. Phosphorus is first oxidized to phosphorus pentoxide, which crystallizes as P_4O_{10} . Upon its reaction with water, phosphoric acid is produced. This route to H_3PO_4 is known as the *dry* process,

which is used to provide high purity material (30, 31). A cheaper *wet* process provides H_3PO_4 from the reaction of sulphuric acid on ground apatite phosphate rock, $\text{Ca}_3(\text{PO}_4)_2\text{CaF}_2$ (30, 31).

[Figure 2]

PPA is an oligomer of H_3PO_4 . High purity material is produced either from the dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO_4 (32). Figure 3 illustrates the equilibria for these reactions, which produce different chain lengths and distributions. The dehydration method tends to produce short chains, whereas the dispersion method usually produces chains with more than 10 repeat units (32).

[Figure 3]

PPA is available in various grades, the naming of which can be confusing as the percentage can exceed 100% (Table 3). One hundred percent phosphoric acid contains 72.4% P_2O_5 as calculated from the formula weight ratio $\text{P}_2\text{O}_5/\text{H}_3\text{PO}_4$. Similarly, pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) contains 79.8% P_2O_5 as calculated from the ratio $\text{P}_2\text{O}_5/\text{H}_4\text{P}_2\text{O}_7$. The ratio of these P_2O_5 contents provides a relative phosphoric acid content, which for pyrophosphoric acid is $79.8\%/72.4\% = 110\%$. Other examples are provided in Table 3.

The production of PPA provides a distribution of chain lengths, where the number of repeat units in the PPA chain, n in Figure 3, varies from one chain to the next. Jameson (32) characterized this distribution and found that 100% phosphoric acid is a mixture of H_3PO_4 (orthophosphoric acid) with about 10% dimer (pyrophosphoric acid) by weight.

Figure 4 shows the distribution of chain lengths for three common commercial grades used to modify bitumen. The 105% PA grade contains for the most part short monomeric and dimeric segments, ortho and pyro phosphoric acids. In contrast, the 110% grade has the same dimeric content, but little monomer, converted to segments with $n > 3$. In the higher 114% grade, little monomer is left. They have all been converted to chains with 2 to 14 units. This increase in chain length leads to chain entanglements and explains the increased viscosity of the higher grades (33).

[Table 3]

[Figure 4]

Dissociation and reactions with PPA

Koebner and Robinson (34) pioneered the use of PPA as a reagent in organic synthesis when they produced a steroid skeleton after the cyclisation of a carboxylic acid. In the seventy years since then, PPA has been found to be an effective reagent and solvent for numerous synthetic applications, as detailed in several reviews (35, 36, 37), including alkylation, acylation, cyclisation, halogenation, dehydration, hydrolysis, polymerization, and phosphorylation, amongst several others. Figure 5 illustrates some examples of possible interest to the bitumen scientist (38, 39, 40, 41).

[Figure 5]

All phosphoric acids are acidic without being oxidizing, in contrast to mineral acids like nitric acid (31). In water, the dissociation of the phosphoric acid and the release of the protons follow the equilibria shown in Figure 6. Orthophosphoric acid has only one strongly ionizing proton, with a pK_1 of 2.1. The second proton, with a pK of 7.2, is not more acidic than those of water. As the phosphoric acid chain length increases, however, the acidity increases. The dimeric pyrophosphoric acid has two acidic hydrogens and the

trimeric triphosphoric acid has three (31). This increased acidity must be related to the ability of the longer chains to stabilize multiple negative charges by tautomerization and delocalization as shown in Figure 7 for the dimer. The longer the PPA chain, the greater its acidity as each repeat unit can release a proton and stabilize the charge by resonance. On a weight basis, however, the acidity of PPA is equal to that of H_3PO_4 , which also releases one proton per phosphorus atom. Moreover, upon dissolution of PPA in water, the equilibrium shown in Figure 3a is shifted to the left so that PPA reverts back to H_3PO_4 . On an equal weight basis, the acidity of PPA in water is thus independent of chain length.

[Figure 6]

[Figure 7]

Despite tabulated dissociation constants and the known acidic nature of PPA, its mechanism of action is ill understood. It is often thought to be a reaction catalyst (38), possibly because the anion PPA^- , e.g. H_2PO_4^- , is amphoteric. Its dual acidic and basic character is shown by the multiple equilibria in Figure 6. The action of PPA on alcohols is a good example of its amphoteric activity, as the PPA^- anion adds to alcohols to provide a phosphorylated product (35, 38).

PPA is also blended and reacted with bitumen (42). With the many functional groups in bitumen, however, the exact reaction between PPA and bitumen can only be inferred. Giavarini et al. (43) alluded to a reaction of PPA with asphaltenes, and Orange et al. showed that it can occur by phosphorylation (44). Baumgardner et al. (45) concluded that many competing reactions were possible.

It is noteworthy that PPA may be a very weak acid when mixed with bitumen. For PPA to dissociate into PPA^- and H^+ , the medium must be of sufficiently high dielectric constant (ϵ). Water is very polar. It has the highest dielectric constant of all solvents, closely followed by H_3PO_4 , as shown in Table 4 (46, 47). Consequently, a hydration sphere can stabilize the charges of dissociated anions and cations (48). This stabilization is gradually lost when water protons are replaced with non-polar alkyl groups (49). The reduced potential for charge stabilization is shown, for example, by the reduced dielectric constant for ethanol and ether in Table 4. Below a dielectric constant of 15, it is generally considered that charge stabilisation is not possible (48). Consequently, in non-polar bitumen ($\epsilon = 3$), PPA is unlikely to dissociate to its charged moieties, PPA^- and H^+ . Any dissociation of PPA and reaction with bitumen would have to be localized to bitumen enclaves with high dielectric constant, the existence of which is speculative, but not incompatible with the grouping of several amphoteric groups (23), and nanodomains (26).

[Table 4]

Summary and conclusion

It is increasingly common that polyphosphoric acid (PPA) is used to modify the rheological characteristics of bitumen. However, it is difficult to identify bitumens that react with PPA and establish the level of PPA required for a given application. This is in great part because the mechanism of PPA action on bitumen is unknown. To better understand their reaction, or lack of, the characteristics of PPA and bitumen were briefly reviewed. PPA has a high dielectric constant whereas that of bitumen is low, which

renders the dissociation of PPA into its acidic and basic moieties ineffective. PPA is thus a very weak acid in bitumen. It can thus be postulated that PPA can only dissociate and react with bitumen in enclaves of high dielectric constants formed from the aggregation of amphoteric heteroatomic groups into nanodomains.

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Captions

Table 1. Typical composition of SARAs fractions*

Table 2. Composition of some bitumens with an identical grade*

Table 3. Grades and designations of phosphoric acids (PA)

Table 4. Dielectric constants of some compounds (47)

Figure 1. Typical organic functions in bitumen. Dotted bonds indicate possible extensions.

Figure 2. Production and reaction of phosphorus pentoxide.

Figure 3. Production of PPA from the dehydration (a) and dispersion (b) methods. n is an integer.

Figure 4. Distribution of chain lengths in three PPA grades.

Figure 5. Selected examples of synthetic applications of the effect of PPA on a starting material.

Figure 6. Dissociation of orthophosphoric acid and its constants. pK values are from (30).

Figure 7. Stabilization of double charges by tautomerization (left) and delocalisation in pyrophosphoric acid. Not all possible structures are shown.

Table 1. Typical composition of SARAs fractions*

Fraction	Composition
Saturates	n- and iso-alkanes
Aromatics	Alkylated cyclopentanes and cyclohexanes
Resins	Alkylated and cycloalkylated aromatic rings
Asphaltenes	Alkylated condensed aromatic rings

* From reference 14.

Table 2. Composition of some bitumens with an identical grade*

Bitumen Source	AAA-1 Lloydminster	AAK-2 Boscan	AAS-2 Arab Heavy
Saturates	11	8	6
Naphtene Aromatics	32	31	46
Polar Aromatics	37	39	30
Asphaltenes (n-heptane)	16	19	17

* From (29).

Table 3. Grades and designations of phosphoric acids (PA)

PA	Formula 1	Formula 2	Formula 3	Designation	P ₂ O ₅ %	PA%	P ₂ O ₅ /H ₂ O*
Ortho	H ₃ PO ₄	P ₂ O ₅ •3H ₂ O	HO(HPO ₃)H	Solid anhydrous	72.4	100	0.33
		P ₂ O ₅ •2.35H ₂ O		Super-PA	75.9	105	0.40
Pyro	H ₄ P ₂ O ₇	P ₂ O ₅ •2H ₂ O	HO(HPO ₃) ₂ H		79.8	110	0.50
Tri	H ₅ P ₃ O ₁₀	3P ₂ O ₅ •5H ₂ O	HO(HPO ₃) ₃ H		82.6	114	0.60
Meta	H ₂ P ₂ O ₆	P ₂ O ₅ •H ₂ O	(HPO ₃) _n	Meta-PA	88.8	123	1.00

* molar ratio

Table 4. Dielectric constants of some compounds (47)

Name	Structure	ε
Water	HOH	79
Phosphoric acids	HOP(O)(OH)OH	61*
Ethanol	HOCH ₂ CH ₃	24
Ethyl ether	CH ₃ CH ₂ OCH ₃ CH ₂	4
Bitumen	Hydrocarbon mixture	3
Benzene	C ₆ H ₆	2
Hexane	C ₆ H ₈	2

* From (48)

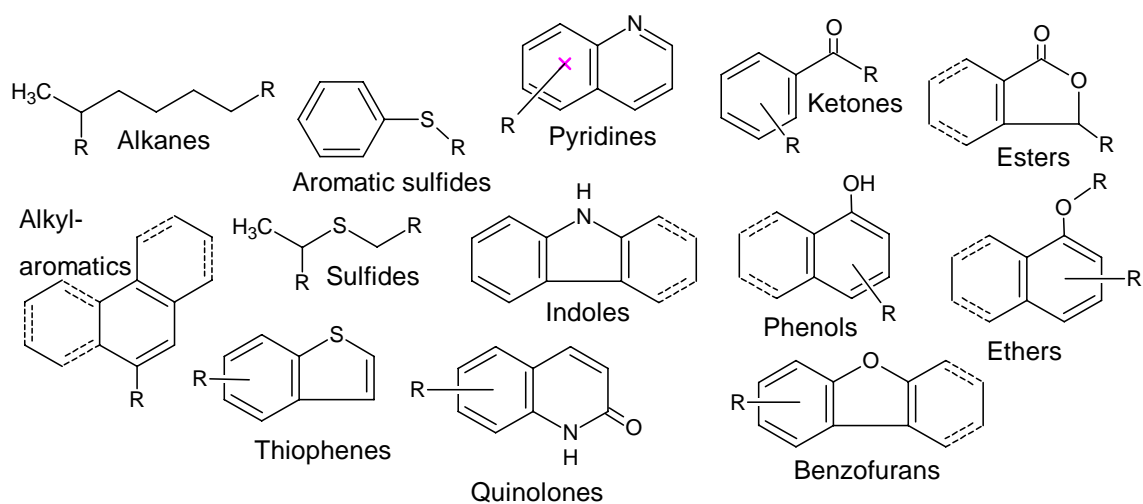


Figure 1. Typical organic functions in bitumen. Dotted bonds indicate possible extensions.

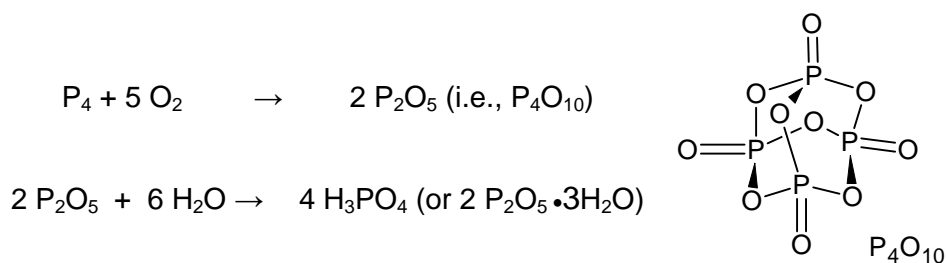


Figure 2. Production and reaction of phosphorus pentoxide.

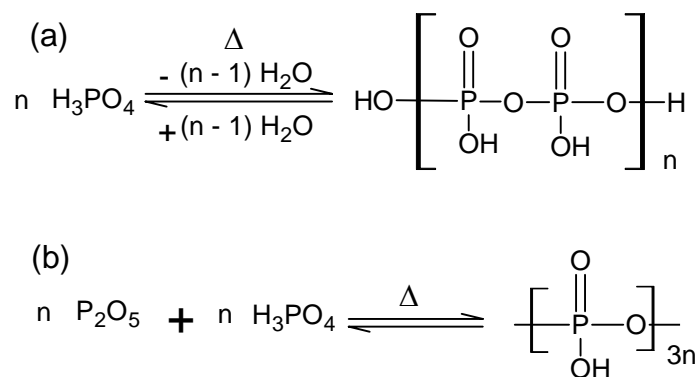


Figure 3. Production of PPA from the dehydration (a) and dispersion (b) methods. n is an integer.

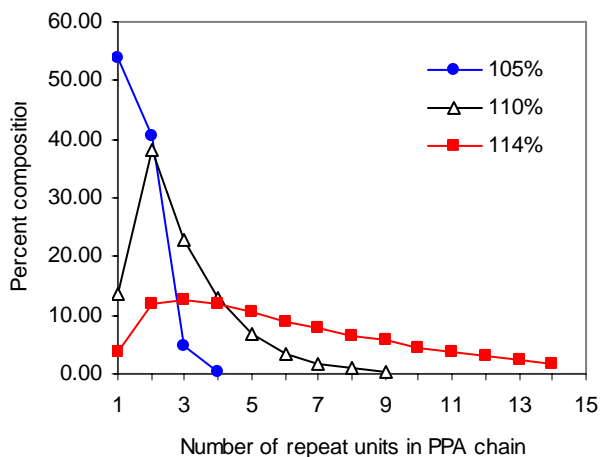


Figure 4. Distribution of chain lengths in three PPA grades.

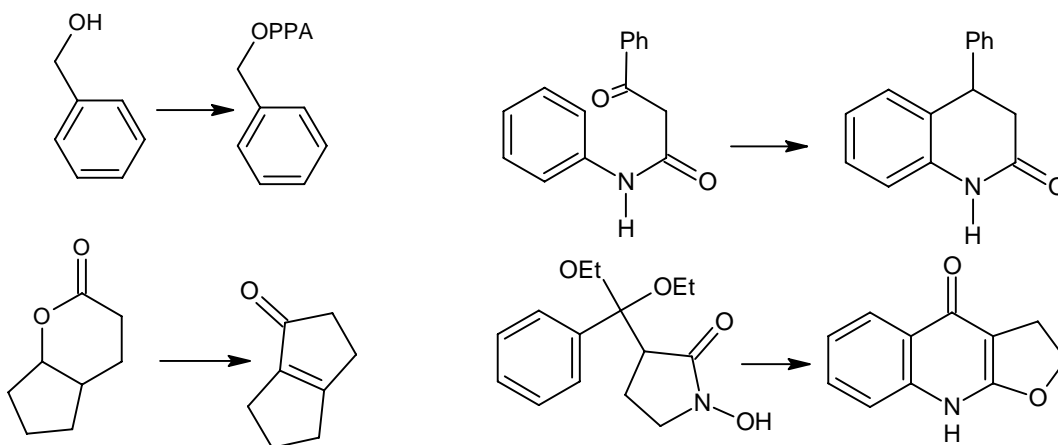


Figure 5. Selected examples of synthetic applications of the effect of PPA on a starting material.

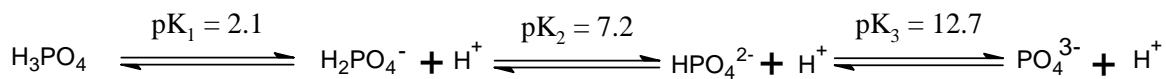


Figure 6. Dissociation of orthophosphoric acid and its constants. pK values are from (30).

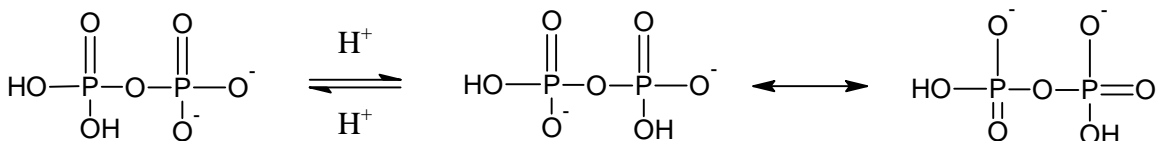


Figure 7. Stabilization of double charges by tautomerization (left) and delocalisation in pyrophosphoric acid. Not all possible structures are shown.