

# Constitution and properties of phosphosilicate coatings

## Part II *Influence of sodium phosphates on the properties of sodium silicate coatings*

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The properties of sodium phosphosilicate coatings were studied by fire exposure tests, differential scanning calorimetry, thermal gravimetric analysis, water absorption tests, and water solubility tests. The results indicated that addition of up to 5% sodium phosphate gave significant improvement in the sodium silicate-based intumescent coating, with satisfactory low-temperature intumescence (550 °C) and improved high-temperature resistance (905 °C). Additions of 10 wt% or more sodium phosphate resulted in a dramatic decrease in the degree of intumescence. This resulted from the polymerization of the silicate regions of the coating that meant that less sodium cation and, therefore, less ionically bonded water, was associated with the silicate regions of the coatings. Although more ionically bonded water would be associated with the depolymerized phosphate regions, these regions do not have a physical structure which results in intumescence when heated.

### 1. Introduction

Intumescent coatings swell (i.e. intumescence) when exposed to fire, to provide an insulating barrier to the protected substrate. Previous work [1, 2] identified the mechanism of dehydration and intumescence of soluble silicate coatings. Those studies also examined the effects of the  $\text{SiO}_2:\text{Na}_2\text{O}$  molar ratio, and the cations (lithium, sodium, potassium) on the properties of intumescence, water absorption, and solubility. This information provided means of improving such coatings.

A previous study [3] examined the effect that sodium phosphate had on a sodium silicate-based intumescent coating. That study indicated that the silicate polymerized to a higher  $\text{SiO}_2:\text{Na}_2\text{O}$  molar ratio while the phosphate region depolymerized.

Preliminary tests indicated that the addition of sodium phosphate to the sodium silicate-based coating increased the high-temperature resistance of the intumescent coating. This is important for some applications such as fuel fires, or fires of long duration which increase continuously in temperature. The increase in the high-temperature resistance of the coating would result from the polymerization of the silicate regions of the coating to a higher  $\text{SiO}_2:\text{Na}_2\text{O}$  molar ratio (i.e. becoming more like silica with its corresponding higher melting point).

In addition to a higher melting point, the phosphosilicate coating must have satisfactory intumescence, water absorption resistance (i.e. low hygroscopicity), and low water solubility. Tests were therefore conducted to determine the water solubility, water absorption, and degree of intumescence to give data on the suitability of any particular composition for use as a coating. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to give information on the mechanism of dehydration and intumescence of the phosphosilicate coating compositions.

### 2. Background

#### 2.1. Mechanism of dehydration and intumescence of sodium silicate

The water retained in a room-dried silicate sample can be considered to consist of “free” water and “bound water”. The bound water includes (1) water hydrogen bonded to surface silanol groups of polysilicate particles [4–6], (2) ionic hydration, and (3) water present as SiOH groups on the polysilicate ions (structural water) [7, 8].

Previous work indicated that free water and water hydrogen bonded to silanol groups were given off at

low temperatures (room temperature–130 °C), whereas ionically hydrated water in the sodium silicate system was given off in the 130–200 °C temperature range. It was this rapid evolution of water vapour associated with the ionically bonded water that provided the main driving force for intumescence. Structural water (i.e. that water present as –OH groups) is released at relatively high temperatures, in the 200–500 °C temperature range. At these temperatures the polysilicate particles begin to join by condensation of SiOH groups to form –Si–O–Si–, and at around 900 °C the sodium silicate begins to melt to form sodium silicate glass.

## 2.2. Mechanism of dehydration of sodium phosphate

The mechanism of dehydration of a sodium phosphate coating should be mainly ionic because no –OH groups are present. This would change if a significant degree of hydrolysis has taken place in which phosphate chains degrade to orthophosphate with the addition of –OH endgroups. However, the previous study indicated that the mechanism of depolymerization in phosphosilicate coatings was due mainly to the redistribution of Na<sub>2</sub>O from the silicate region to the phosphate region.

## 2.3. Mechanism of dehydration of a sodium phosphosilicate coating

The mechanism of dehydration of a sodium phosphosilicate coating should depend on the degree of polymerization of the silicate region, and depolymerization of the phosphate region. As the silicate region polymerizes, less water will be ionically associated with it because the SiO<sub>2</sub>:Na<sub>2</sub>O molar ratio decreases, thus decreasing the concentration of Na<sup>+</sup> cations in the region. On the other hand, as the phosphate region polymerizes, the Na<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> ratio increases, thus increasing the amount of water associated with the phosphate.

## 3. Experimental procedure

### 3.1. Sample preparation

Sample coatings were prepared by mixing aqueous solutions of sodium silicate “N” (3.33 molar ratio, 37.6 % in water) and sodium phosphate (average

chain length = 9, 37.6 % in water). The compositions shown in Table I were prepared.

### 3.2. DSC and TGA

Samples were thermogravimetrically analysed using a DuPont model 951 TGA analyser. These tests were conducted in the 25–600 °C range at a heating rate of 5 °C min<sup>-1</sup> to 200 °C and at 10 °C min<sup>-1</sup> to 600 °C.

DSC tests were performed on a DuPont DSC 2910 analyser. The temperature range and heating rate was identical to that of the TGA runs.

### 3.3. Degree of intumescence

Sample coatings were applied to suitable substrates (aluminium and porcelain) to a thickness of about 1 mm and were allowed to dry at 40 % relative humidity for 1 week. Two sets of samples were tested in a gas furnace. The first set of samples was heated from room temperature–550 °C in 5 min, and the second set was heated from room temperature–905 °C in 45 min, both according to the ASTM E119 (1983) standard temperature rise curve. The degree of intumescence was determined by dividing the final intumesced thickness by the initial thickness.

### 3.4. Water absorption

The purpose of this test was to determine the amount of water retained by the different coating compositions at various relative humidities. Coating solution (2 g) was introduced into each sample dish (5 cm diameter) and allowed to dry at 40 % relative humidity for a period of 1 week. Sets of samples, corresponding to the compositions given in Table I, were placed in humidity chambers at relative humidities of 4 %, 25 %, 56 %, 82 %, and 95 %, at 22 °C. The relative humidity in each chamber was set by using sulphuric acid–water solutions in accordance with ASTM E104-85 (1985).

Samples were allowed to equilibrate, and this was checked by weighing the samples daily until the weights were constant.

### 3.5. Water solubility

A set of sample solutions were placed in aluminium dishes (5 cm diameter) and dried for 1 week at 40 %

TABLE I Compositions prepared

Na-silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 3.33) (wt %)	Na-Phosphate (Na <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub> = 1.22) (wt %)	Na <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> (molar ratio)	Na <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> (mol %)
0	100	1.22:1.00:0.00	55.0:45.0:00.0
50	50	2.05:1.00:2.76	35.3:17.2:47.5
60	40	2.46:1.00:4.14	32.4:13.1:54.5
70	30	3.15:1.00:6.45	29.7:9.4:60.9
80	20	4.54:1.00:11.07	27.3:6.0:66.7
90	10	8.67:1.00:24.87	25.1:2.9:72.0
95	5	17.00:1.00:52.48	24.1:1.4:74.5
97.5	2.5	33.57:1.00:107.74	23.6:0.7:75.7
100.0	0	1.00:0.00:3.33	23.1:0.0:76.9

relative humidity. The dried samples were placed in individual containers of 500 ml distilled water at 21 °C, for 1 h. Each container of water was manually stirred every 5 min. After the test, the samples were again dried at 40 % relative humidity for 1 week and then weighed for weight loss.

The weight loss of each sample was expressed in terms of weight loss (g) per exposed surface area (cm<sup>2</sup>) per hour.

## 4. Results and discussion

### 4.1. Intumescence results

The results of the intumescence tests are shown in Fig. 1. When the samples were intumesced by heating from room temperature to 550 °C, the intumescence of the samples decreased with increasing sodium phosphate content.

A previous study [3] indicated that when phosphosilicate coatings were heated, the Na<sub>2</sub>O became increasingly associated with the phosphate region. The simple assumption that the maximum possible amount of Na<sub>2</sub>O becomes associated with the phosphate region, with the remainder being associated with the silicate region, gives a good qualitative evaluation of what occurs in the heated ternary system. Using this assumption the compositions in Table I can be rewritten as in Table II. Comparing the degree of intumescence in Fig. 1 for 40 %/60 % sodium phosphate/sodium silicate, and 50 %/50 % sodium phosphate/sodium silicate with Table II, it can be seen that according to the above assumption, the silicate region would consist of 100 % SiO<sub>2</sub> with no associated sodium cations. Because the driving force for intumescence comes primarily from the water associated with the cation, the silicate region would contribute little to the overall intumescence. The degree of intumescence for these samples, which was minimal, would be due to the water associated with the sodium cation in the phosphate region. However, as can be seen in Fig. 1,

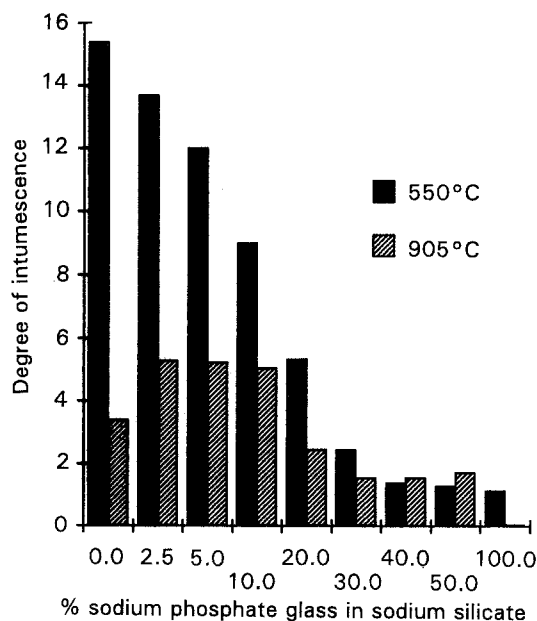


Figure 1 Degree of intumescence results for sodium phosphate/sodium silicate compositions.

TABLE II Compositions rewritten assuming the maximum amount of Na<sub>2</sub>O is associated with the phosphate region with the remainder associated with the silicate region

Composi- tion phos- phate/ silicate (wt %)	Rewritten molar ratio Na <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> :Na <sub>2</sub> O	Phosphate	Silicate
		region Na <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub>	region SiO <sub>2</sub> :Na <sub>2</sub> O
5/95	3.00:1.00/52.48:14.00	3.00:1.00	52.48:14.00
10/90	3.00:1.00/24.87:5.67	3.00:1.00	24.87:5.67
20/80	3.00:1.00/11.07:1.54	3.00:1.00	11.07:1.54
30/70	3.00:1.00/6.45:0.15	3.00:1.00	6.45:0.15
40/60	2.46:1.00/4.14:0.00	2.46:1.00	100 % SiO <sub>2</sub>
50/50	2.05:1.00/2.76:0.00	2.05:1.00	100 % SiO <sub>2</sub>

the intumescence of sodium phosphate is negligible. Apparently, the sodium phosphate does not possess a structure which results in intumescence.

Referring to Fig. 1 and Table II, the lower the assumed SiO<sub>2</sub>:Na<sub>2</sub>O molar ratio (i.e. the higher the amount of sodium cation associated with the silicate region) the higher is the degree of intumescence.

The samples which were intumesced to 905 °C show a similar pattern, except that the samples with up to 10 % sodium phosphate maintain their intumesced structure better than the 100 % sodium silicate sample (0 % sodium phosphate). This would be a result of the higher temperature resistance of the higher SiO<sub>2</sub>:Na<sub>2</sub>O molar ratio in the silicate region.

### 4.2. DSC and TGA results

The DSC and TGA results are shown in Fig. 2. The DSC and TGA results show that for 100 % sodium silicate, primary dehydration occurs between 120 and 190 °C and appears as a series of endothermic peaks on the DSC curve and as a steep rate of weight loss in the TGA curve. This characteristic dehydration curve of sodium silicate is predominant up to and including 20 %/80 % sodium phosphate/sodium silicate. At 30 %/70 % sodium phosphate/sodium silicate, the DSC and TGA curves change shape to indicate that the primary dehydration is occurring in the phosphate region. The 30 %/70 %, 40 %/60 %, and 50 %/50 % DSC curves all show endothermic peaks between 70 and 80 °C. This is characteristic of Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O which decomposes between 73.3 and 76.7 °C [9].

The results agree with the rewritten molar ratios of Table II, which indicates that most of the sodium cation would be associated with the phosphate regions at compositions of 30 %/70 %, 40 %/60 % and 50 %/50 % sodium phosphate/sodium silicate. At compositions of 0 %/100 % to 20 %/80 % sodium phosphate/sodium silicate, most of the sodium cation is still associated with the silicate region and thus the typical sodium silicate DSC curves are observed.

### 4.3. Water absorption test results

The water absorption samples required a long time duration in order to reach equilibrium. For some samples, 2 months were required before the equilibrium was reached. This is due to the changing nature

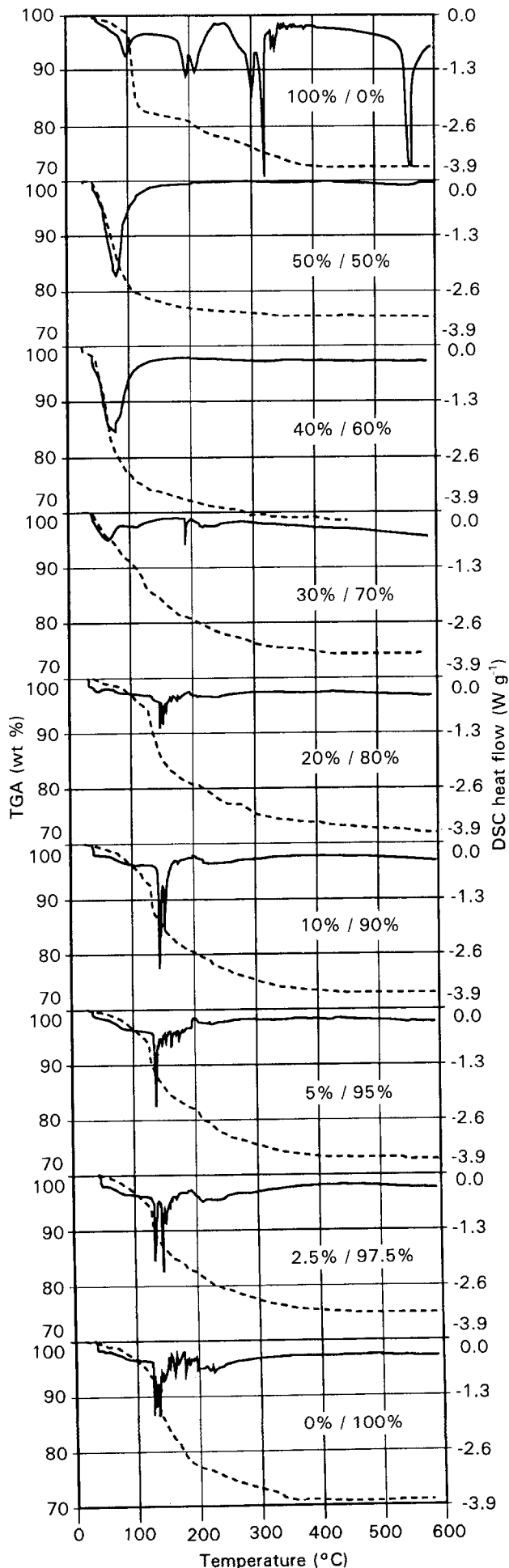


Figure 2 (—) DSC and (---) TGA results for compositions from 100%/0% sodium phosphate/sodium silicate to 0%/100% sodium phosphate/sodium silicate.

of the samples as the sodium phosphate and sodium silicate slowly reacted, resulting in the polymerization of the silicate regions and depolymerization of the phosphate regions.

The results of the water absorption tests are shown in Fig. 3. The amount of water absorbed by the coating decreases with increasing sodium phosphate added to the sodium silicate; however, 100 % sodium phosphate does not follow this rule. If the amounts of water absorbed were directly proportional to the amounts of sodium phosphate and sodium silicate in the sample, then all curves would be expected to lie between 100 % sodium silicate and 100 % sodium phosphate. Because this is not the case, it is reasonable to assume that a reaction takes place between the sodium phosphate and sodium silicate. It has been shown previously that this reaction involves the depolymerization of the phosphate and polymerization of the silicate. The polymerization of the silicate regions results in a decrease of sodium cation associated with these regions, thus decreasing the amount of ionically bonded water. Because the phosphate regions depolymerize, a larger amount of water would be associated with the higher concentration of sodium cations in the phosphate regions. The net effect, as observed in Fig. 3, is an overall decrease in the amount of ionically bonded water.

#### 4.4. Water solubility test results

The water solubility test results are shown in Fig. 4. The 100 % sodium phosphate sample showed the highest rate of dissolution. If sodium phosphate and sodium silicate remained as distinct regions in the coating system without any reaction occurring, the rate of dissolution would be expected to increase with increasing sodium phosphate content. However, the dissolution rate was independent of the sodium phosphate added. All compositions, other than 100 % sodium phosphate, showed similar rates of dissolution of the coatings.

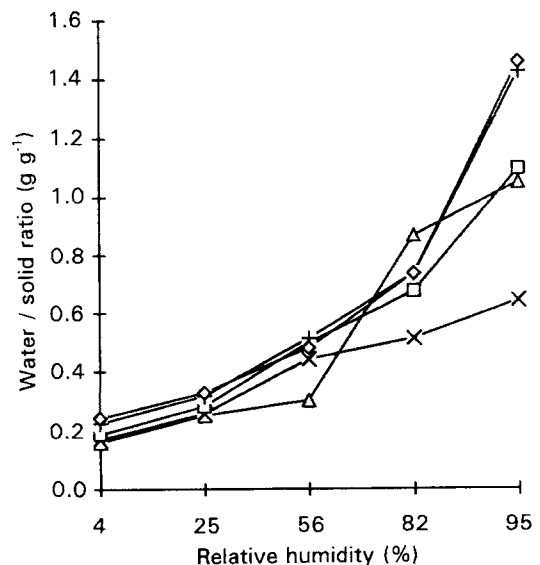


Figure 3 Water absorption results. ( $\Delta$ ) 100%/0%, (X) 50%/50%, ( $\square$ ) 30%/70%, (+) 10%/90%, ( $\diamond$ ) 0%/100% sodium phosphate/sodium silicate.

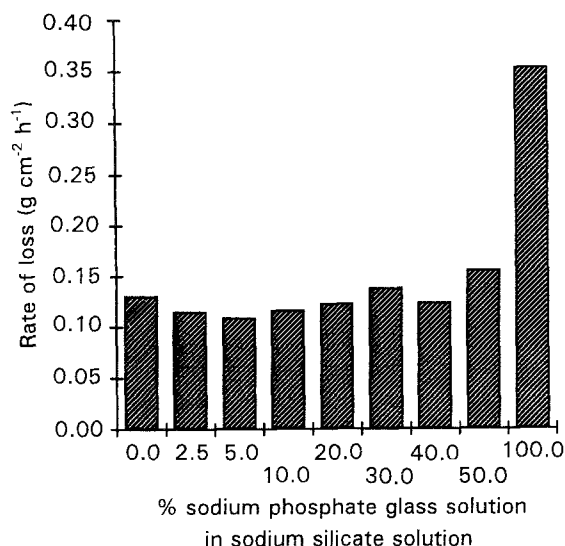


Figure 4 Rate of dissolution of sodium phosphate/sodium silicate coating samples.

Apparently, the increase in sodium phosphate concentration is offset by the increase in polymerization of the silicate region, which would decrease the solubility in this region.

## 5. Conclusion

The results indicated that addition of up to 5% sodium phosphate gave significant improvement in the sodium silicate-based intumescent coating, with satisfactory low-temperature intumescence (550 °C) and improved high-temperature resistance (905 °C). Additions of 10 wt % or more sodium phosphate res-

ulted in a dramatic decrease in the degree of intumescence. This resulted from the polymerization of the silicate regions of the coating that meant that less sodium cation and, therefore, less ionically bonded water was associated with the silicate regions of the coatings. Although, more ionically bonded water would be associated with the depolymerized phosphate regions, these regions do not have a physical structure which results in intumescence when heated.

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