JOURNAL OF MATERIALS SCIENCE **28** (1993) 4175–4182

Constitution and properties of phosphosilicate coatings

Part I *Influence of sodium phosphates on the constitution of sodium silicate coatings*

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The constitution and structure of sodium phosphosilicate coatings were investigated by paper chromatography, X-ray diffraction, and infrared spectroscopy. All the tests performed indicated that heating phosphosilicate coating samples resulted in the polymerization of the silicate to crystalline silica (α-crystobalite) while the phosphate depolymerized. The extent of the depolymerization of the phosphate depended on the total Na_2O in the phosphosilicate system. The assumption that the maximum quantity of Na_2O in the phosphosilicate system, up to a molar ratio of 3:1 $Na_2O:P_2O_5$, associates with the phosphate, gave a good estimate of the phosphate chain distribution in the phosphosilicate system.

1. Introduction

Intumescent coatings are important for fire protection due to their property of swelling (i.e. intumescing) to form a fire-protective barrier when exposed to fire. Previous work [1, 2] identified the mechanism of dehydration and intumescence of soluble silicate coatings. These studies also examined the effects of the 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.

There are limitations to such coatings, however, one being the relatively low melting point of 900–1000 °C. This, although far higher than organically based coatings, is still too low for some applications such as fuel fires or fires of long duration which increase continuously in temperature. Literature indicates that adding phosphate to sodium silicate glasses can increase the melting point [3] and it is believed that phosphate will provide the same increase in temperature for aqueous-based silicate coatings.

Although there is an abundance of literature on the constitution of phosphosilicate glasses, there is little information on phosphosilicate coatings. To understand the effect that phosphate has on the high-temperature stability, and intumescence of silicate coatings it is necessary first to understand the constitution of silicate and phosphate solutions and how combinations of the two can alter the melting point.

The purpose of the first part of this study was to determine the constitution of a sodium phosphate/sodium silicate coating. Particularly, the study investigated whether the phosphate reacts with silicate and the effect it has on the constitution, or, alternately, if the phosphate anions and silicate anions maintain their distinct nature in the coating. X-ray analysis, infrared spectroscopy, and paper chromatography were used to give direct information on the constitution of the phosphosilicate coatings.

2. Background

2.1. Constitution of alkali silicates

Soluble silicates form various ionic species in solution and this can be illustrated by the solubility curve of Fig. 1 [4]. At low concentration (area A, Fig. 1) mononuclear $Si(OH)_4$ is in equilibrium with its ionic species (e.g. $SiO(OH)_3^-$ and $SiO_2(OH)^{-2}$).

At higher concentrations (area B, Fig. 1) the equilibria in solution becomes extremely complex as monomeric $Si(OH)_4$, and its ionic species, form siloxane (–Si–O–Si–) units. As polymerization proceeds, condensation leads quickly to ring structures followed by addition of monomer and other cyclic units to form larger three-dimensional units. These condense to a compact state with –Si(OH) and –SiO$^-$ groups remaining on the outside. Such polymeric units can reach dimensions of 1–2 nm diameter. The number and size of the polymeric units depends on the concentration of silica and $SiO_2:M_2O$ (M = sodium, potassium, lithium) molar ratio. Increasing silica concentration and increasing $SiO_2:M_2O$ molar ratio [5–7] both result in increasing particle size.

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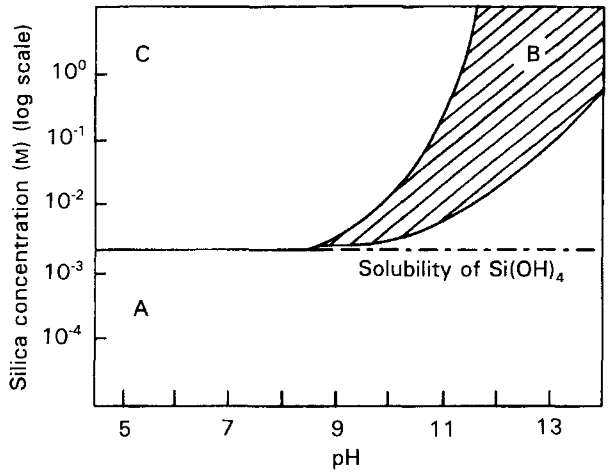

Figure 1 Species in equilibrium with amorphous silica at 25 °C [4] (A, mononuclear species; B, polysilicate ions in solution; C, solution unstable with respect to amorphous silica).

Upon drying, the cations in solution act as cross-links between particles through coordination with negatively charged oxygen atoms (surface SiO^- groups) [5, 8]. In the case of monovalent ions, such linkages are broken due to dissociation upon submersion in water, the rate of dissolution depending on the strength of the ionic bonds between particles. In the case of multivalent cations, such as Ca^{2+}, strong bonds link adjacent silicate particles and form insoluble precipitates when added to a silicate solution.

Previous work indicated [1] that the rapid evolution of water vapour associated with ionically bonded water provided the main driving force for intumescence. However, only silicates with monovalent cations have the intumescence property. Apparently, the strong bonds formed by multivalent cations prevent expansion of the silicate matrix (i.e. intumescence) upon exposure to fire.

2.2. Constitution of alkali phosphates

The constitution of sodium phosphate glasses has been studied extensively by paper chromatography [9–21] and thin-layer chromatography [22–29]. These studies have demonstrated the dependence of the constitution on the Na : P ratio. Glasses with Na : P ratios of 1.0–2.0 are primarily linear chains with a distribution of chain lengths. The average chain length is given by the equation

$$\bar{n} = 2/(\mathrm{Na/P} - 1) \qquad (1)$$

The true $\bar{n}$ will be somewhat less than this due to the presence of cyclic polymers in the glass. The percentage of these cyclic polymers increases with the average chain length of the sodium phosphate glass going from 1% by weight, at $\bar{n} = 4.5$, to about 10% by weight at $\bar{n} = \infty$ (i.e. Na/P = 1, metaphosphate glass) [13, 19].

As long as Na:P is less than 2 ($\bar{n} > 2$), no orthophosphate ($\bar{n} = 1$) will be found in the glass [10, 14, 17, 30]. Only orthophosphate and pyrophosphate are found between Na:P > 2 and Na:P = 3 (i.e. between $\bar{n} < 2$ and $\bar{n} = 1$). At Na:P = 2, the glass contains about 90% pyrophosphate, with the remainder being split approximately equally between orthophosphate and triphosphate [30].

When NaH_2PO_4 is melted and rapidly cooled, the melt solidifies as a glass. This is referred to as Graham's salt having the chemical formula $(NaPO_3)_n$. Equation 1 would give an average chain length of infinity for this glass; however, it has been found experimentally that this glass also contains a distribution of chain lengths including metaphosphates, and the actual average chain length becomes dependent on the water vapour pressure present during melting because water is absorbed by the sodium phosphate glass and forms –P–OH end groups [31]. When this glass is annealed it is converted into Kurrol's sodium salt, Maddrell's salt, or one of three forms of sodium trimetaphosphate $Na_3(P_3O_9)$, depending on the temperature and water vapour pressure.

Glasses with Na:P ratio < 1 contain branching points which result in a cross-linked three-dimensional structure. These glasses are sometimes called ultraphosphates and contain a number of branch points, the number of which depends on the Na:P ratio.

In aqueous solution, the phosphate anions contained in the glass remain as discrete units [10, 14, 17]. These units are stable in water at and above pH 7, and 25 °C, but degrade at higher temperatures and lower pH. This degradation is referred to as hydrolysis and proceeds by monomeric phosphate units (orthophosphate) being removed from the end of the polymeric phosphate chains. A new –OH terminating unit is formed at the end of the chain [31, 32]. A second mechanism of degradation which becomes increasingly important as the chain length increases is the coiling of chains to form metaphosphates. This mechanism is also promoted by low pH and higher temperatures.

Cross-linked phosphates are hydrolysed preferentially at the cross-linking points and this hydrolysis proceeds relatively rapidly, as compared to linear chains, essentially causing all branching groups to be destroyed by the time dissolution is completed. The cross-linked structure is therefore not present in solution.

The dissolution rate of phosphate glasses has a minimum at a Na:P ratio of about 0.57–0.59 which corresponds to cross-linked phosphate glass [32]. It can be noted that while the dissolution rate of cross-linked phosphate glasses is low, the hydrolysis rate is relatively high, compared to polyphosphates, occurring predominately at the cross-links. The linear chain phosphates decrease in solubility rate as the length of the chain increases but still the dissolution rate is much higher than that of the cross-linked phosphates.

2.3. Constitution of sodium phosphosilicate glasses

Si^{4+} normally has a four-fold tetrahedral coordination with oxygen. P^{5+}, having a similar ionic size, also results in four-fold tetrahedral coordination with oxygen, with the extra charge on the P^{5+} atom being satisfied by the formation of a double bond with one of its neighbouring oxygen atoms. Sodium phosphosilicate glasses have been studied extensively to determine the constitution of these glasses and whether or not Si^{4+} and P^{5+} form mixed polymeric networks.

Chakraborty and Chondrate [33] investigated sodium phosphosilicate glasses with 1:1 $SiO_2:P_2O_5$ molar ratio (i.e. SiP_2O_7 glass) by infrared and Raman spectroscopy and concluded that the structure of this glass was significantly different from that of its SiP_2O_7 crystalline polymorphs. The glass contained PO_4 tetrahedral units with $P=O$ bonds, and SiO_4 tetrahedral units without any indication of six-fold coordination (i.e. SiO_6 units) which occurs in crystalline SiP_2O_7. Devitrification of the glass resulted in a change from four-fold silicon coordination to six-fold coordination. This change occurs as P–O–Si bonds are formed at the expense of $P=O$. When Na_2O was added to the glass, the silicate network retained its bridged structure, whereas the Na_2O associated with the phosphate to form non-bridging PO^-. The result was an amorphously phase-separated glass, with one region rich in silica and the other region rich in sodium metaphosphate. The devitrification products of a 1:1 $SiO_2:P_2O_5$ molar ratio glass with 5 mol % Na_2O was a mixture of cubic SiP_2O_7, $3SiO_2 \cdot 2P_2O$, and $Na_4P_2O_7$.

The absence of P–O–Si bonds in sodium phosphosilicate glasses, and the increased polymerization of the silicate region of the glass at the expense of the depolymerization of the phosphate region of the glass, are independently confirmed through Raman spectroscopy by Nelson and Tallant [34, 35], and through NMR spectroscopy by Yang and Kirkpatrick [36]. The depolymerization effect on phosphate has also been confirmed by paper chromatographic investigations on the dissolved glasses in the $MO–P_2O_5–SiO_2$ system (where MO = PbO, BaO, MgO, CdO, SrO, Bi_2O_3, TeO_2, and MnO) [37, 38].

There is also an ample amount of literature [39–42] that indicates that P–O–Si bonds are formed in phosphosilicate and sodium phosphosilicate glass at certain concentrations. Whereas Yang and Kirkpatrick conducted their NMR experiments on alkaline earth phosphosilicate glasses with a maximum of 10 wt % P_2O_5, Sekiya *et al.* [39] conducted NMR experiments on samples of $SiO_2:P_2O_5$ glass with 28 mol % P_2O_5 and 50 mol % P_2O_5. At 28 mol % P_2O_5, no six-coordinated Si^{4+} (i.e. SiO_6 units) was found as in Yang and Kirkpatrick's investigation; however, at 50 mol % P_2O_5, both four-coordinated and six-coordinated Si^{4+} were found in the glass. It is interesting to note that Nelson and Tallant [34] not only indicated that discrete phosphate and silicate regions were formed, they also indicated the possible substitution of P^{5+} for Si^{4+} in the silicate network at high phosphorus levels.

The consensus seems to be that Si^{4+} remains four-coordinated with oxygen at low to intermediate P_2O_5 levels but six-coordinated Si^{4+} may be present at high P_2O_5 levels, thus indicating the formation of P–O–Si bonds in phosphosilicate glass.

P–O–Si bonds which may be present in the phosphosilicate glass are not expected to be stable in aqueous solution. Saeki *et al.* [43] demonstrated that crystalline $Si_3(PO_4)_4$ decomposes rapidly in aqueous solution to form silicate anions and orthophosphate anions. At pH 11 and 20 °C the $Si_3(PO_4)_4$ was 50% decomposed after 90 min.

3. Experimental procedure

3.1. Sample preparation

Samples prepared by the following two methods were compared in terms of constitution.

(a) Coatings prepared from mixtures of aqueous solutions of sodium silicate "N" (3.33 molar ratio, 37.6% in water) and sodium phosphate (chain length = 9, 37.6% in water).

(b) Glasses prepared by combining sodium silicate "SS-65 PWD" (3.33 molar ratio, anhydrous powder) and phosphate glass (chain length = 9, anhydrous powder) by melting together at high temperature (1350–1550 °C).

The compositions shown in Table 1 were prepared by the two methods.

3.2. X-ray analysis

Selected samples were ground and sifted through a 200 mesh sieve tray. These powdered samples were analysed using a Phillips X-ray diffractometer with CuK_α radiation providing a wavelength of 0.154 16 nm.

3.3. Paper chromatography

Separations of the phosphate chains were performed using cellulose on polyester thin-layer chromatography (TLC) sheets, silica on polyester TLC sheets, and chromatography paper, using various solvents. A satisfactory method was found to be paper chromatography, using Schleicher and Schuell no. 589 White Ribbon.

The selected solvent was acidic consisting of 70 ml isopropanol, 20 ml trichloroacetic acid (25%), 10 ml water, and 0.3 ml ammonia (30%) [46].

The paper sheets were cut as described by Huhti and Gartaganis [46] as shown in Fig. 2. This method of cutting the paper gives a dramatic improvement in the separation of the phosphate bands. A 15 wt % solution of sample was applied along a 1 cm line drawn at the top of the 1 cm × 3 cm tab. Five to six applications were normally sufficient, drying each application with a blow dryer prior to applying the next. To get good distinct separations, the line must be kept as thin as possible (1 mm wide or less). These sheets were placed in a developing tank, maintained at 4 °C in a refrigerator to minimize hydrolysis, for 16–20 h.

Once the chromatograms were developed, they were allowed to dry and then sprayed with an acid molybdate solution (5 ml perchloric acid – 60 wt %, 10 ml 1N HCl, 60 ml water, 25 ml ammonium molybdate tetrahydrate solution – 4 wt%). The chromatograms were dried 4–5 min at 80–90 °C in an oven, and then exposed to ultraviolet radiation for

TABLE I Compositions prepared

Na-silicate ($SiO_2:Na_2O = 3.33$) (wt %)	Na-phosphate ($Na_2O:P_2O_5 = 1.22$) (wt %)	$Na_2O:P_2O_5:SiO_2$ (molar ratio)	$Na_2O:P_2O_5:SiO_2$ (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

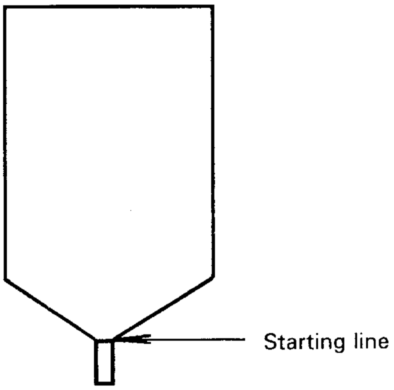

Figure 2 Paper chromatography sheets after cutting.

several minutes; the phosphomolybdate complex was reduced to form blue bands [47].

The phosphate bands were then cut from the chromatogram, including a blank band, and placed in separate solutions of 25.00 ml of 0.1N ammonium hydroxide for 1 h. Aliquots of 20.00 ml of each solution were then transferred to Erlenmeyer flasks and 1.5 ml Lucena-Conde and Prat's molybdate reagent [13] was added. Each of the flasks was then heated in the same water bath (100 °C) for 1 h. These solutions were diluted to 50 ml with 0.1 N ammonium hydroxide and the transmission was measured at 840 nm with a Bausch and Lomb Spectronic 20 using the blank sample as the reference.

Normally, orthophosphate through hexaphosphate could be clearly separated and sometimes heptaphosphate. Small amounts of cyclic units would be obscured by the tetraphosphate and pentaphosphate bands, without using a second basic solvent to do a two-dimensional chromatogram. The results of the tests, however, were such that this was not a significant factor.

3.4. Infrared spectroscopy

Infrared spectroscopy was used to gain information on the change in structure of the phosphosilicate coating upon heating. The tests were conducted in the 1500–600 cm^{-1} range using a Perkin–Elmer model 681 IR spectrometer.

4. Results and discussion

4.1. Paper chromatography results

The paper chromatography results provided an excellent insight into the reactions that occur between the sodium phosphate and sodium silicate.

The initial chain length distribution of the $\bar{n} = 9.09$ sodium phosphate glass, which was used in all the prepared sodium silicate/sodium phosphate compositions, is given in line 12 of Table II. Tests were carried out on a newly prepared 50%/50% solution to determine if the silicate in a phosphosilicate solution would interfere with the chromatographic results. Comparing line 12 with lines 13 and 14, it appears that the silicate causes little or no interference. This is probably due to the use of the strongly acidic solvent which would tend to polymerize the silicate to high molecular weights thereby preventing the silicate from moving up the chromatography paper. A good separation of the individual phosphate bands was achieved.

The paper chromatography results indicated that adding sodium phosphate to sodium silicate, when heated, resulted in the depolymerization of the phosphate. The simple assumption that the maximum quantity of Na_2O in the phosphosilicate system, up to a molar ratio of 3:1 $Na_2O:P_2O_5$, associates with the phosphate, gave a good estimate of the phosphate chain distribution in the phosphosilicate system. This redistribution of Na_2O results in the polymerization of the silicate regions. The $Na_2O:P_2O_5:SiO_2$ molar ratios for each composition (given in Table I) were rewritten in terms of $Na_2O:P_2O_5/SiO_2:Na_2O$ and the assumed chain length for the $Na_2O:P_2O_5$ molar ratio was calculated from Equation 1 and is given in Table II.

Compositions of 5%/95% to 30%/70% sodium phosphate/sodium silicate, all have sufficient Na_2O to give a 3.00:1.00 molar ratio of $Na_2O:P_2O_5$ (the maximum amount). If the assumption that the maximum amount of Na_2O becomes associated with the phosphate were true, then the only phosphate unit in these compositions would be orthophosphate (i.e. $\bar{n} = 1.00$). This is shown to be true for the samples intumesced from room temperature to 905 °C (lines 1–4 in Table II). Compositions of 40%/60% and 50%/50% sodium phosphate/sodium silicate do not contain sufficient Na_2O to completely convert to orthophosphate and

TABLE II Paper chromatography results

Line	Composition, sodium phosphate/ sodium silicate (wt %)	Ortho	Pyro	Tri	Tetra	Penta	Hypoly	Rewritten molar ratio $Na_2O:P_2O_5$: $SiO_2:Na_2O$ ^{a}(100% SiO_2 in silicate region)	Assumed (actual^b) phosphate chain length, $\tilde{n}$
Intumesced samples (room temperature – 905 °C in 45 min)									
1	5%/95%	100%						3.00:1.00/52.48:14.00	1.00
2	10%/90%	100%						3.00:1.00/24.87:5.67	1.00
3	20%/80%	100%						3.00:1.00/11.07–1.54	1.00
4	30%/70%	100%						3.00:1.00/6.45:0.15	1.00
5	40%/60%	66.0%	34.0%					2.46:1.00/4.14:0.00^a	1.37
6	50%/50%	15.6%	76.1%	8.3%				2.05:1.00/2.76:0.00^a	1.90
Melted samples (5/95, 10/90, at 1350 °C; 20/80, 50/50 at 1450 °C, 40/60 at 1550 °C; each for 2 h)									
7	5%/95%	100%						3.00:1.00/52.48:14.00	1.00
8	10%/90%	84.2%	15.8%					3.00:1.00/24.87:5.67	1.00
9	20%/80%	81.6%	18.4%					3.00:1.00/11.07:1.54	1.00
10	40%/60%	80.7%	19.3%					2.46:1.00/4.14:0.00^a	1.37
11	50%/50%	17.0%	83.0%					2.05:1.00/2.76:0.00^a	1.90
Solutions prepared by mixing individual phosphate and silicate solutions									
12	100% Na-phos. (0 days)	1.1	2.2	4.5	8.7	7.7	75.9	1.22:1.00/0.00:0.00	9.09^b
13	50%/50% (1 day)	1.4	2.4	6.5	8.8	6.7	74.1	2.05:1.00/2.76:0.00^a	1.90
14	50%/50% (8 days)	1.0	1.5	5.6	8.7	7.5	75.7	2.05:1.00/2.76:0.00^a	1.90
15	50%/50% (78 days)	8.5	7.8	23.3	14.5	6.6	39.3	2.05:1.00/2.76:0.00^a	1.90
Coatings (solutions which were dried at ambient conditions)									
16	100% Na-phos. (112 days)	29.5	60.3	4.1	2.5	1.4	2.5	1.22:1.00/0.00:0.00	9.09^b
17	50%/50% (72 days)	20.7	38.9	38.7	1.2		0.6	2.05:1.00/2.76:0.00^a	1.90
18	50%/50% (114 days)	20.8	53.1	25.0	0.9		0.3	2.05:1.00/2.76:0.00^a	1.90
Reference data									
19	1:5:1 Li:Na:K phos. [17]	1.26	2.00	5.97	9.89	9.34	71.54	$M_2O:P_2O_5$ = 1.22:1.00	9.00^b
20	1:1 Li:Rb phos. [47]	0.7	2.2	6.1	10.5	9.0	71.5	$M_2O:P_2O_5$ = 1.22:1.00	9.00^b
21	1:1 Li:Rb phos. [47]	57.1	40.8				2.1	$M_2O:P_2O_5$ = 2.60:1.00	1.25^b
22	1:1 Li:Rb phos. [47]	36.0	62.4				1.6	$M_2O:P_2O_5$ = 2.33:1.00	1.50^b
23	1:1 Li:Rb phos. [47]	16.7	82.0				1.3	$M_2O:P_2O_5$ = 2.14:1.00	1.75^b
24	1:1 Li:Rb phos. [47]	4.6	91.8	3.4			0.2	$M_2O:P_2O_5$ = 2.00:1.00	2.00^b

thus also contain pyrophosphate, and pyrophosphate and tripolyphosphate, respectively. Equation 1 gives assumed chain lengths of 1.37 and 1.90 for the 40%/60% and 50%/50% compositions, respectively. These chain lengths cannot be prepared with sodium phosphate glasses; however, Murthy and Westman [30] were successful in forming lithium–rubidium phosphate glasses with chain lengths as low as 1.25. They also found that the cation had only a minimal influence on the chain-length distribution, as can be seen for the chain length equal to 9.00 phosphate glasses shown in lines 19 and 20 in Table II. It is thus reasonable to use the lithium–rubidium phosphate data for comparison purposes.

The phosphate chain distribution for the intumesced 40%/60% composition (line 5) with an assumed $\tilde{n} = 1.37$ compares quite well with the lithium–rubidium phosphate glass with $\tilde{n} = 1.25$ (line 21). The intumesced 50%/50% sample with assumed $\tilde{n} = 1.90$ (line 6) compares well with the lithium–rubidium glass with $\tilde{n} = 1.75$ (line 23), although no tripolyphosphate would be expected for this chain length.

The glass samples which were prepared by melting the sodium silicate and sodium phosphate powders together at high temperature (lines 7–11 in Table II) showed the same general pattern as the intumesced samples. The one important difference was the presence of pyrophosphate in all the samples, excluding the 5%/95% sample. This is believed to be an indication of the formation of Si–O–P bonds containing silicon phosphate components ($SiO_2:P_2O_5$, $3SiO_2:2P_2O_5$) which give pyrophosphate upon dissolution in water (as indicated by paper chromatography tests). Apparently, the higher temperatures and longer heating period (2 h), compared to the intumesced samples, was required to produce the silicon phosphate in appreciable quantities. It appears that the 5%/95% sample contained insufficient phosphate to form silicon phosphates, which is in agreement with Turkdogan *et al.*'s results for the Na_2O–P_2O_5–SiO_2 ternary system with P_2O_5 content between 0 and 7.5 mol% [3].

Tests were performed to investigate the stability of the coating in solution and when dried. Line 15 indicates a significant degree of depolymerization of the phosphate in the 50%/50% sodium phosphate/sodium silicate coating solution after 78 days. Comparing this with line 17, it can be seen that the rate of degradation is even higher in the 50%/50% sample which had been dried at ambient conditions for a period of 72 days.

Comparing the 100% sodium phosphate coating dried at ambient conditions for 112 days (line 16) with the 50%/50% coating dried at ambient conditions for 114 days (line 18), it can be seen that the 100% sodium phosphate coating degraded at a slightly faster rate. It cannot, therefore, be said that the sodium phosphate and sodium silicate react to depolymerize at ambient conditions based on the paper chromatography data. However, formation of a silicate precipitate and the brittleness of the 50%/50% coating indicates that polymerization of the silicate does occur and this may be the cause of the depolymerization of the phosphate through reassociation of the Na_2O from the silicate region to the phosphate region. In the 100% sodium phosphate sample, the mechanism of depolymerization would simply be hydrolysis.

4.2. X-ray diffraction results

Coating samples of differing sodium phosphate/sodium silicate weight percents were intumesced in a furnace from room temperature–905 °C over 45 min following the ASTM E119 (1983) temperature rise curve. These are the same samples which were tested by paper chromatography with the results shown in lines 1–6 of Table II. Portions of each intumesced sample were crushed to a powder and analysed on the X-ray diffractometer. The results are shown in Fig. 3.

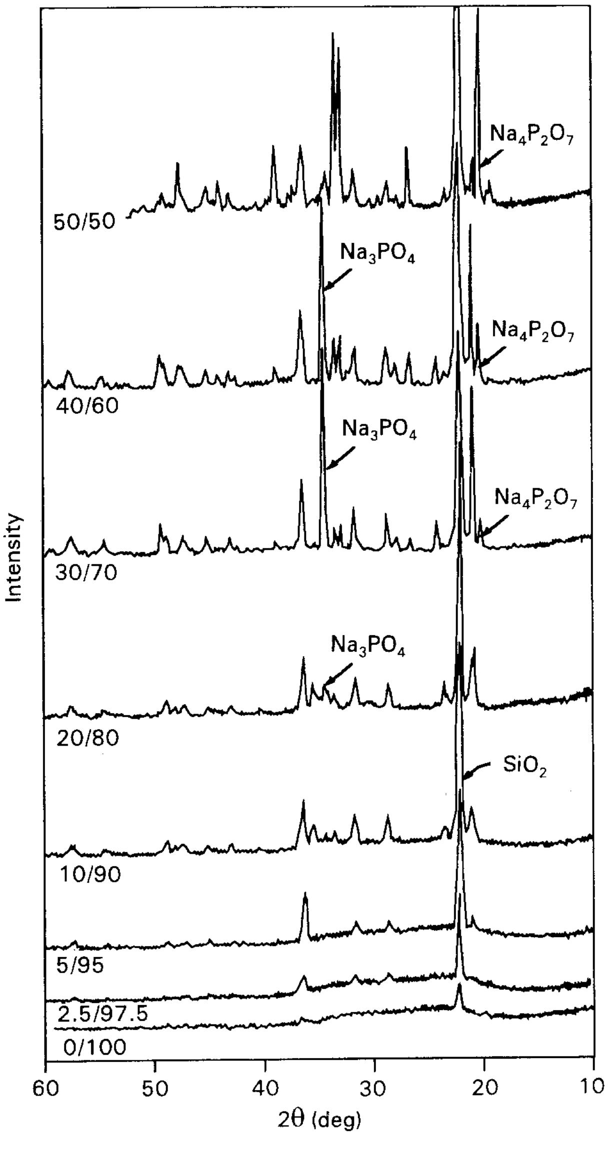

Figure 3 X-ray diffraction patterns of phosphosilicate coating samples after intumescing by heating from RT–905 °C. The sample compositions, as labelled on the chart, are from 0/100 sodium phosphate/sodium silicate to 100/0 sodium phosphate/sodium silicate.

The 100 wt % sodium silicate sample showed a weak SiO_2 pattern corresponding to α-cristobalite. This SiO_2 pattern intensified with increasing sodium phosphate content, and was present in all the samples tested. This supports the hypothesis that the polymerization of the silicate is a result of the Na_2O preferentially associating with the phosphate phase in the system.

The X-ray diffraction data agree quite well with the paper chromatography results. Sodium orthophosphate was first distinguishable as a very weak pattern at 5 wt % sodium phosphate and increased in intensity as the proportion of sodium phosphate to sodium silicate increased up to and including 40%/60%. At 50/50 wt % sodium phosphate/sodium silicate, the orthophosphate decreased to only a faint pattern.

Sodium pyrophosphate showed a very weak pattern, starting at 30/70 wt % sodium phosphate/sodium silicate, which intensified to its maximum at 50/50 wt % sodium phosphate/sodium silicate. This follows the trend indicated by the paper chromatography results with the exception that no pyrophosphate was detected by paper chromatography at 30%/70%.

Fig. 4 shows the stability of the room-dried coating over a period of time when left at ambient conditions. Clearly, a considerable amount of crystallization occurs in the 50%/50 wt % sample over time. As in the heated samples, the silicate polymerizes and forms a precipitate if the film is dissolved; however, it remains amorphous and therefore is not evident in the diffraction patterns shown in Fig. 4.

The sample tested at 27 days showed only a $Na_4P_2O_7 \cdot 10H_2O$ diffraction pattern, whereas the 71 day sample showed only a weak $Na_4P_2O_7 \cdot 10H_2O$ pattern and a well-defined $Na_5P_3O_{10} \cdot 6H_2O$ pattern. The paper chromatography results for this same sample aged 72 days showed 38.9 wt % pyrophosphate (line 17, Table II). Possibly, the crystallization of the $Na_5P_3O_{10} \cdot 6H_2O$ resulted in the partial decrystallization of $Na_4P_2O_7 \cdot 10H_2O$. The fact that the

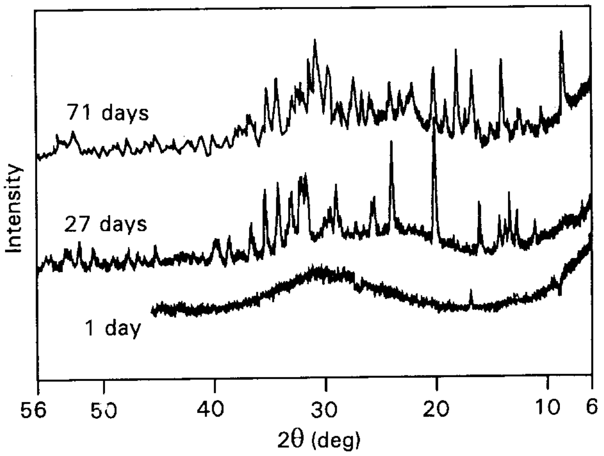

Figure 4 X-ray diffraction curves of 50/50 wt% sodium phosphate/sodium silicate coatings left at ambient conditions for the indicated periods of time.

products are not hydrogen phosphates (e.g. $Na_2H_2P_2O_7 \cdot H_2O$) indicates that the mechanism is the reassociation of the Na_2O from the silicate to the phosphate region, as opposed to the hydrolysis that occurs in the 100% sodium phosphate samples resulting in sodium hydrogen phosphates.

4.3. Infrared spectroscopy results

A 30% sodium phosphate/70% sodium silicate coating solution was spread on three NaCl plates and these were then placed in a muffle furnace which was raised in temperature from room temperature–750 °C. Individual samples were taken out at temperatures of 300, 600 and 750 °C, corresponding to times of 5, 25 and 35 min, respectively. These data give information on the transformations that occur in the coating structure as it is intumesced. The samples were tested in the 1500–600 cm^{-1} range using a single pass directly through the samples. The results are shown in Fig. 5.

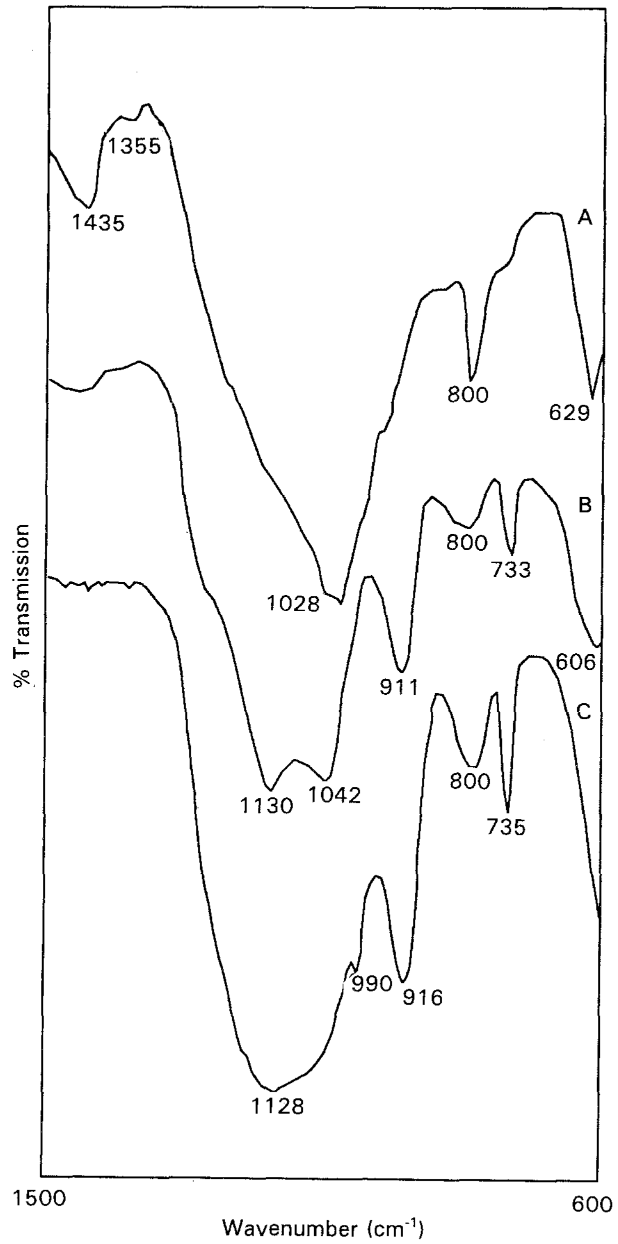

Figure 5 IR spectroscopy results. Curves correspond to 30/70 sodium phosphate/sodium silicate films spread on NaCl plates and heated at A) 25 °C to 750 °C in 35 minutes, B) 25 °C to 600 °C in 25 minutes, C) 25 °C to 300 °C in 5 minutes.

Studies on the infrared spectra of alkaline silicates were briefly reviewed in a previous paper [1]. The strongest peak observed in siliceous materials is around 1100 cm^{-1} and is attributed to an Si–O–Si stretching vibration. This peak is quite broad for amorphous alkaline silicates due to the irregularity of the silicate matrix but becomes narrower and shifts to a lower wave number for crystalline silicas in which the SiO_2 has an ordered structure. This can be observed in the 750 °C sample; however, this peak is confounded with a phosphate peak in the same region and does not give definite proof of the ordering of the silica regions. A peak observed near 800 cm^{-1}, ascribed to an O–Si–O bond bending mode, is weak in amorphous silica and strong in crystalline silicas. The narrowing and intensifying of this peak observed in the 750 °C sample gives more definite proof of the increased order in the silicate regions, as was apparent in the X-ray diffraction results.

The sample which was heated to 300 °C shows characteristic peaks of linear sodium polyphosphates at 735, 916, 990, and 1128 cm^{-1}. The 1128 cm^{-1} peak, which is obscured by the silicate peak in this region, is attributed to ionic P–O stretching. The peaks at 735, 916, and 990 can be assigned to P–O–P vibrations [42, 48]. The absence of these peaks in the 750 °C curve indicates the break up of the polyphosphate chains into orthophosphate. Sodium orthophosphate shows only a broad peak in the 1100–1000 cm^{-1} range with a maximum absorbance at 1028 cm^{-1} [48], as is the case in the 750 °C sample.

5. Conclusion

All the tests performed indicated that heating phosphosilicate coating samples resulted in the polymerization of the silicate to crystalline silica (α-crystobalite) while the phosphate depolymerized. The extent of the depolymerization of the phosphate depended on the total Na_2O in the phosphosilicate system. The assumption that the maximum quantity of Na_2O, up to a molar ratio of 3:1 $Na_2O:P_2O_5$, associates with the phosphate gave a good estimate of the phosphate chain distribution in the phosphosilicate system.

Acknowledgements

The authors thank the Defence Research Establishment Atlantic (DREA) for providing the financial support to undertake this study, and Gillian Minc for her assistance in the experimental work.

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Received 22 July 1992
and accepted 4 January 1993