A FUNDAMENTAL STUDY OF ALUMINUM PHOSPHATES
SYNTHESIZED IN VARIOUS REACTION MEDIUMS

by

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# TABLE OF CONTENTS

## I. INTRODUCTION

Page 1

## II. LITERATURE REVIEW

General Discussion of Aluminum Phosphate

Methods of Preparation and Processing

X-Ray Diffraction Studies of Aluminum Phosphates

Thermal Analysis of Aluminum Phosphates

Infrared Absorption Spectra of Phosphates

Chemistry of Dimethylformamide

## III. EXPERIMENTAL

Plan of Experimentation

Kinetic Studies

Differential Thermal Analysis

X-Ray Studies

Infrared Studies

Data and Results

Theory for Kinetic Studies

Sample Calculation
IV. DISCUSSION

Discussion of Experiments
Kinetic Studies
Differential Thermal Analysis
Infrared Studies
Discussion of Results
Kinetic Studies
Differential Thermal Analysis
X-Ray Diffraction Patterns
Infrared Spectra
Characteristics of Products Synthesized in Various Mediums
Recommendations
Limitations

V. CONCLUSIONS

VI. SUMMARY

VII. BIBLIOGRAPHY

VIII. ACKNOWLEDGMENTS

IX. VITA
X. APPENDIX ....................................... 101
  Materials ........................................ 101
  Apparatus ....................................... 104
  Temperature Versus Time Data ............... 109
  X-Ray Diffraction Patterns ................. 112
  Infrared Spectra ............................... 120
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>ASTM X-Ray Diffraction Data</td>
<td>9</td>
</tr>
<tr>
<td>II.</td>
<td>O-H Infrared Spectra in Pure Alumina Hydrate</td>
<td>20</td>
</tr>
<tr>
<td>III.</td>
<td>Physical Properties of N,N-Dimethyl Formamide</td>
<td>22</td>
</tr>
<tr>
<td>IV.</td>
<td>Specific Gravity and Vapor Pressure of N,N-Dimethyl Formamide</td>
<td>23</td>
</tr>
<tr>
<td>V.</td>
<td>Apparent Rate Constant of Reaction of Aluminum Hydroxide with Phosphoric Acid Using Water as Solvent</td>
<td>34</td>
</tr>
<tr>
<td>VI.</td>
<td>Apparent Rate Constant of Reaction of Aluminum Hydroxide with Phosphoric Acid Using N,N-Dimethyl Formamide as Solvent</td>
<td>35</td>
</tr>
<tr>
<td>VII.</td>
<td>Summary of X-Ray Results</td>
<td>47</td>
</tr>
<tr>
<td>VIII.</td>
<td>Temperature Versus Time Data of Aluminum Hydroxide-Phosphoric Acid Reaction in DMF</td>
<td>110</td>
</tr>
<tr>
<td>IX.</td>
<td>Temperature Versus Time Data of Aluminum Hydroxide-Phosphoric Acid Reaction in Water</td>
<td>111</td>
</tr>
</tbody>
</table>
1. Thermogram of Monoaluminum Phosphate
2. Characteristic Absorption Bands in Phosphorus Compounds
3. Temperature vs. Time Curve of $\text{Al(OH)}_3$-$\text{H}_2\text{PO}_4$ Reaction
4. Arrhenius Plot of Reaction Carried Out in Water
5. Arrhenius Plot of Reaction Carried Out in DMF
6. Thermogram of Diphenyl Carbazole and Diphenyl Benzidine
7. Thermogram of Products Synthesized Using a 1:1 Molar Ratio in Water
8. Thermogram of Products Synthesized Using a 1:1 Molar Ratio
9. Thermogram of Products Synthesized Using a 0.75:1 Molar Ratio
10. Thermogram of Products Synthesized Using a 0.5:1 Molar Ratio
11. Thermogram of Products Synthesized Using a 0.33:1 Molar Ratio
<table>
<thead>
<tr>
<th>No.</th>
<th>Figure Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>X-Ray Diffraction Pattern of Product Synthesized Using a 1:1 Molar Ratio in Absence of Solvent</td>
<td>45</td>
</tr>
<tr>
<td>13</td>
<td>X-Ray Diffraction Pattern of Product Synthesized Using a 1:1 Molar Ratio in DMF</td>
<td>46</td>
</tr>
<tr>
<td>14</td>
<td>Infrared Spectra of KBr and Al(OH)(_3) in High Frequency Range</td>
<td>48</td>
</tr>
<tr>
<td>15</td>
<td>Infrared Spectra of KBr and Al(OH)(_3) in Low Frequency Range</td>
<td>49</td>
</tr>
<tr>
<td>16</td>
<td>Infrared Spectra of Product at 400-1000 °C Using a 1:1 Molar Ratio in Absence of Solvent</td>
<td>51</td>
</tr>
<tr>
<td>17</td>
<td>Infrared Spectra of Product at 100-400 °C Synthesized Using a 1:1 Molar Ratio of Al(_2)O(_3)/P(_2)O(_5) in Absence of Solvent</td>
<td>52</td>
</tr>
<tr>
<td>18</td>
<td>Infrared Spectra of Product Synthesized Using a 0.33:1 Molar Ratio in Absence of Solvent</td>
<td>53</td>
</tr>
<tr>
<td>19</td>
<td>Infrared Spectra of Product Synthesized Using a 1:1 Molar Ratio of Al(_2)O(_3)/P(_2)O(_5) in DMF</td>
<td>54</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>20.</td>
<td>Infrared Spectra of Product Synthesized Using a 0.33:1 Molar Ratio in DMF</td>
<td>55</td>
</tr>
<tr>
<td>21.</td>
<td>X-Ray Diffraction Pattern of Product Synthesized Using a 0.5:1 Molar Ratio in Absence of Solvent</td>
<td>113</td>
</tr>
<tr>
<td>22.</td>
<td>X-Ray Diffraction Pattern of Product Synthesized Using a 0.5:1 Molar Ratio in DMF</td>
<td>114</td>
</tr>
<tr>
<td>23.</td>
<td>X-Ray Diffraction Pattern of Product Synthesized Using More DMF</td>
<td>115</td>
</tr>
<tr>
<td>25.</td>
<td>X-Ray Diffraction Pattern of Product Synthesized Using a 1:1 Molar Ratio in DMF</td>
<td>117</td>
</tr>
<tr>
<td>27.</td>
<td>X-Ray Diffraction Pattern of Gel-like Material Synthesized in Water</td>
<td>119</td>
</tr>
<tr>
<td>28.</td>
<td>Infrared Spectra of Product Synthesized Using a 0.75:1 Molar Ratio in Absence of Solvent</td>
<td>121</td>
</tr>
<tr>
<td>Figure</td>
<td>Infrared Spectra of Product Synthesized</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------</td>
<td></td>
</tr>
<tr>
<td>29.</td>
<td>Using a 0.5:1 Molar Ratio in Absence of Solvent</td>
<td>122</td>
</tr>
<tr>
<td>30.</td>
<td>Using a 0.75:1 Molar Ratio in DMF</td>
<td>123</td>
</tr>
<tr>
<td>31.</td>
<td>Using a 0.5:1 Molar Ratio in DMF</td>
<td>124</td>
</tr>
<tr>
<td>32.</td>
<td>Infrared Spectra of Products at 100 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>125</td>
</tr>
<tr>
<td>33.</td>
<td>Infrared Spectra of Products at 170 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>126</td>
</tr>
<tr>
<td>34.</td>
<td>Infrared Spectra of Products at 170 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>127</td>
</tr>
<tr>
<td>35.</td>
<td>Infrared Spectra of Products at 270 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>128</td>
</tr>
<tr>
<td>36.</td>
<td>Infrared Spectra of Products at 270 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>129</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>37.</td>
<td>Infrared Spectra of Products at 400 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>130</td>
</tr>
<tr>
<td>38.</td>
<td>Infrared Spectra of Products at 800 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>131</td>
</tr>
<tr>
<td>39.</td>
<td>Infrared Spectra of Products at 1000 °C Synthesized Using a 1:1 Molar Ratio</td>
<td>132</td>
</tr>
<tr>
<td>40.</td>
<td>Infrared Spectra of Products at 270 °C Synthesized Using a 0.5:1 Molar Ratio</td>
<td>133</td>
</tr>
<tr>
<td>41.</td>
<td>Infrared Spectra of Products at 400 °C Synthesized Using a 0.5:1 Molar Ratio</td>
<td>134</td>
</tr>
<tr>
<td>42.</td>
<td>Infrared Spectra of Products at 800 °C Synthesized Using a 0.5:1 Molar Ratio</td>
<td>135</td>
</tr>
<tr>
<td>43.</td>
<td>Infrared Spectra of Products at 1000 °C Synthesized Using a 0.5:1 Molar Ratio</td>
<td>136</td>
</tr>
</tbody>
</table>
44. Infrared Spectra of Gel-like Material from Room Temperature to 400 °C Synthesized Using a 1:1 Molar Ratio in Water .............. 137

45. Infrared Spectra of Gel-like Material at 400-1000 °C Synthesized Using a 1:1 Molar Ratio in Water .............. 138

46. Infrared Spectra of White Solid Material Synthesized Using a 1:1 Molar Ratio in Water .............. 139

47. Infrared Spectra of Products Synthesized Using Different Molar Ratios of Al₂O₃/P₂O₅ in Absence of Solvent .............. 140
I. INTRODUCTION

The necessity for high temperature materials has become more apparent in recent years with the advent of new processes in the chemical and nuclear fields. Most of the common construction materials lose their strength at temperatures higher than 600 °C and most of the metals and plastics become useless at temperatures far below 600 °C. Most ceramic materials are highly temperature-resistant but generally they require a high temperature heat treatment before use.

The bonding properties of phosphate materials have been recognized for many years; they are of particular interest in the field of refractories due to their high fusion temperature. A particular phosphate is aluminum phosphate which is formed by the reaction of aluminum hydroxide and phosphoric acid, releasing water as a condensation polymerization by-product. Aluminum phosphate is remarkable in that it may be prepared in a paste form which can be easily applied to reinforcement and cured at low temperature and pressure and yet is thermally stable up to 1000 °C.

The major problem with aluminum phosphate is the high functionality of the reactants which results in
liberation of large quantities of water. If a non-porous high quality laminate is to be produced, it is necessary to remove the condensation by-product from the laminate during cure. Unfortunately, a brittle non-flowing state is reached long before the reaction has been completed. This creates an inherent porosity in the matrix and a brittleness of the reacted matrix.

The purpose of this investigation was to develop an aluminum phosphate without the drawback mentioned above. One approach which tends to reduce the quantity of water involves a reaction where a reactive site would be blocked on the reactants and reactivated after the polymer chain is formed. The use of di-functional organophosphorous compounds seems to be the only possibility, but the degradation of the attached organic groups makes this approach impractical.

Another approach which could tend to reduce intermolecular forces would involve introducing a special solvent to the reaction system. In the past, chemists carried out reactions in water, assuming that it was inert, but now they recognize that using water as a solvent frequently changes the character of the dissolved species. In recent years, a new solvent
called di-methylformamide, has made practical a number of chemical reactions which were previously regarded as impractical simply because they had been tried before in water. The benefits of this solvent are: (a) increased reaction rate, (b) more homogeneous reaction mixture, (c) less complex reaction systems, and (d) production of solutions of workable viscosities.

The purpose of the present work was to study fundamentally the aluminum phosphates synthesized in various reaction mediums.
II. LITERATURE REVIEW

There has been a considerable amount of interest in aluminum phosphate recently for a variety of end uses. Although considerable patent literature relates to phosphate bonds, very little information concerning these materials is available in the general literature. The following reviews contain: (a) general discussion of aluminum phosphate, (b) methods of preparation and processing aluminum phosphates, (c) x-ray studies of phosphates, (d) thermal analysis of phosphates, (e) infrared spectra of phosphates, and (f) chemistry of di-methylformamide.

General Discussion of Aluminum Phosphates

Phosphoric acid has been used as a refractory patching cement composed of ground silica brick, silica flour, and ball clay(37). The ammonium phosphate may be used in place of the phosphoric acid(37). Other applications such as: (a) protecting coating compounds for coating metals(39), carbon(44), and glass fiber(7), (b) electric insulating materials(35,43), and (c) bonding agent for ceramic materials(6,44) and
cement (30) have been reported by many investigators in recent years. The methods of preparation and characteristic properties are also described.

The existence of monobasic and dibasic aluminum phosphate in solution of aluminum hydroxide and phosphoric acid at room temperatures was first reported by E. Erlenmeyer (37). Jones (32) indicated the existence of the dihydrate of aluminum orthophosphate in alkaline phosphate solution of aluminum hydroxide.

The ternary system Al₂O₃·P₂O₅·H₂O has been investigated and the following compounds have been found:

Al₂O₃·P₂O₅·7H₂O, Al₂O₃·P₂O₅·4H₂O,
2Al₂O₃·3P₂O₅·10H₂O, and Al₂O₃·3P₂O₅·6H₂O (22,24).

Many other ternary compounds have been found with higher phosphorous contents. Generally, however, these are unstable due to their great affinity for water.

The first comprehensive study of aluminum phosphate was made by Kingery. Later Rickles in a Ph. D. thesis amplified many of the points developed by Kingery. Kingery (24) pointed out that: (a) hydrated alumina and phosphoric acid produced gel monoaluminum phosphate with a modulus of rupture of 1260 pounds per square inch, (b) monoaluminum phosphate solution indicated
strong hydrogen bonding, (c) for optimum bonding, a weakly basic or amphoteric cation, with a moderately small ionic radius, is required so that a non-ordered structure is formed.

Another study was made by Rickles (37). The reaction was studied with regard to reaction temperature, starting reactants, particle size of the solid reactants, concentration of acid, ratio of reactants, and the relationship between these factors and the engineering properties. The following conclusions were reached: (a) The reaction rate is strongly dependent upon temperature. (b) Phosphoric acid reacts with aluminum hydroxide to form monoaluminum phosphate and a crystalline solid $2\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$. The equilibrium depends only on the ratio of two reactants. Temperature (25 to 125 °C), particle size of aluminum hydroxide (40 to 200 mesh), and concentration of acid had no effect upon the equilibrium. (c) A mixture of alumina and aluminum hydroxide should be employed instead of only aluminum hydroxide in order to reduce the water content of castings. (d) The voidage in the resultant casting is a result of the dehydration of monoaluminum phosphate and $2\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$.
(e) Castings containing monoaluminum phosphate possess high strength due to its non-uniform polymeric structure and hydrogen-bound chains.

Methods of Preparation and Processing

Rickles suggested the following procedures were the best method for the preparation of aluminum phosphate: Liquid 100 parts by weight of 100 per cent phosphoric acid, prepared by evaporation of 15 parts of water from 100 parts of 85 per cent phosphoric acid at 200 to 250 °C. Solid 80 parts by weight prepared by blending 30 parts of -325 mesh alpha alumina and 70 parts of -325 mesh aluminum hydroxide. Mix slowly keeping cool at 25 °C for working pot life of 100 minutes, then cured by the following schedule: 21 hours at 80 °C, 16 hours at 95 °C, 2 hours at 105 °C, and 2 hours at 115 °C. By these procedures a material of optimum thermal and mechanical properties, and least voidage is obtained.

Chase and Copeland (7) reported an optimum receipt of:

<table>
<thead>
<tr>
<th>%</th>
<th>Component</th>
<th>Volume</th>
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<tbody>
<tr>
<td>39.0%</td>
<td>Al(OH)₃</td>
<td></td>
</tr>
<tr>
<td>54.5%</td>
<td>H₃PO₄</td>
<td></td>
</tr>
<tr>
<td>6.5%</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>85%</td>
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The reactants were allowed to react at room temperature for 24 hours. The product was ground in a ball mill for 2 hours. The resulting powder was mixed 50-50 by weight with phosphate binder paste then cured under pressure at 120 °C.

Water, acetone, and alcohol have been used with the mixture to obtain a stoichiometric ratio, and water proved to be the satisfactory liquid. Early in 1946, Greger reported that solid aluminum phosphate could be prepared by treating \( \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \) with concentrated phosphoric acid, but if the reaction was not controlled, the product solidified to a hard mass. This could be improved by dispersing aluminum hydroxide in kerosene then mixed with kerosene-diluted phosphoric acid.

**X-Ray Diffraction Studies of Aluminum Phosphates**

X-Ray diffraction patterns have been considered as reliable means to identify the structure of aluminum phosphates. Standard patterns for some aluminum phosphates are shown in Table I. Kingery, in 1950, studied the structure changes versus temperature of mono-aluminum phosphate by x-ray diffraction patterns in the temperature range from 105 °C up to 500 °C and found
<table>
<thead>
<tr>
<th>Alpha Alumina Trihydrate</th>
<th>ALPO₄</th>
<th>Al(PO₃)₃</th>
<th>3Al₂O₃·2P₂O₅·3H₂O</th>
<th>4Al₂O₃·3P₂O₅·3OH₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>I/I₀</td>
<td>d</td>
<td>I/I₀</td>
<td>d</td>
</tr>
<tr>
<td>4.82</td>
<td>10</td>
<td>4.27</td>
<td>8</td>
<td>4.38</td>
</tr>
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<td>4.33</td>
<td>9</td>
<td>3.97</td>
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<td>3.30</td>
<td>6</td>
<td>3.32</td>
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<td>3.08</td>
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<td>2.78</td>
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<tr>
<td>2.44</td>
<td>8</td>
<td>2.25</td>
<td>1</td>
<td>1.87</td>
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<tr>
<td>2.37</td>
<td>8</td>
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<td>2.28</td>
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<td>1</td>
<td>1.48</td>
<td>1</td>
<td>1.75</td>
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</table>

that the crystallinity was improved with increasing temperature.

X-Ray powder patterns were observed for Al(H₂PO₄)₃ using Cu Kα and Co Kα radiation by Remy and d’Yvoire (14,36). They theorized that Al(H₂PO₄)₃ was isomorphous. Parameters and densities were listed for four forms; the methods of preparation were also reported.

The equilibrium compositions of the Al₂O₃ • P₂O₅ • H₂O system greatly depend on the molar ratio of aluminum hydroxide to phosphoric acid and the reaction temperature. By a careful study of the literature, the reaction products are reported to be mono- and di-basic aluminum phosphate (24). Kingery pointed out that the reaction products of aluminum hydrate and phosphoric acid are a mixture of amorphous material which is monoaluminum phosphate and the hydrated aluminum. Rickles (37) reported that the end product of this system was found to be a mixture of amorphous monoaluminum phosphate and a crystalline solid having the chemical composition 3Al₂O₃ • 2P₂O₅ • 3H₂O.

Dehydrations occur gradually when the reaction product is heated. Guerin and Martin (20) reported that
monoaluminum phosphate became $\text{Al}(\text{PO}_3)_3$ at 130 °C. The x-ray parameters have been reported\(^{(13)}\). At higher temperatures, orthoaluminum phosphate is obtained. X-Ray data for $\text{AlPO}_4$ have been reported by many investigators\(^{(2,15,16,38)}\); its analogy to $\text{SiO}_2$ has also been described.

**Thermal Analysis of Aluminum Phosphates**

Structure versus temperature can be investigated by determining the rate of weight loss versus temperature, by differential thermal analysis, and by x-ray diffraction patterns at various temperatures as mentioned in the previous section.

On heating monoaluminum phosphate at a constant rate of temperature increase, Kinger\(^{(24)}\) found that the rate of weight loss versus temperature showed peaks at 250 °C and 490 °C. The weight loss is completed at 800 °C with the formation of aluminum metaphosphate. He also studied thermal behaviors by DTA and pointed out that a large endothermic peak was observed at 255 °C which developed into a slightly exothermic reaction that continued until about 900 °C and an endothermic effect was noted at about 450 °C, as shown in Figure 1.

Henry Guerin\textsuperscript{(20)} reported that Al\((\text{H}_2\text{PO}_4)\)\textsubscript{3} became $3\text{P}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3$ at 180 °C and then $2\text{P}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3$ at 800 °C, $3\text{P}_2\text{O}_5 \cdot 2\text{Al}_2\text{O}_3$ at 820 °C, AlPO\textsubscript{4} at 880 °C, and P\textsubscript{2}O\textsubscript{5} and Al\textsubscript{2}O\textsubscript{3} above 1000 °C.

The effect of heat upon the structure of monoaluminum phosphate was described by Rickles using DTA; the sample was heated from 25 to 1650 °C. An endothermic peak was noted at 200 °C. Another endothermic peak was noted at 500 °C. After this peak there were no other noticeable peaks until an endothermic peak was observed, at 1300 °C. By doing this he was able to say that in the temperature interval 175-230 °C, metaphosphate was obtained, at 500 °C metaphosphate chains broke and formed ionically bound aluminum orthophosphate, and at 1530 °C, Al\textsubscript{2}O\textsubscript{3} and P\textsubscript{2}O\textsubscript{5} were obtained. He also studied the crystalline solid $3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ in a similar manner and the results were:

at the temperature interval 190-245 °C

$$3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_4 \cdot 8\text{H}_2\text{O} \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 + 8\text{H}_2\text{O}$$

and at 500 °C

$$3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \rightarrow \text{Al}_2\text{O}_3 + 4\text{AlPO}_4 .$$
A study\(^{(25)}\) was made on the phase transformation of a mixture containing phosphoric acid and aluminum hydroxide with the molar ratio of \(P_2O_5 : Al_2O_3\) equal to 1.0, 1.5, 3.0 at 105 to 500 °C. In the system studied, six phases were found: \(Al(H_2PO_4)_3\), \(AlPO_4\) (\(\alpha\)-quartz and \(\alpha\)-tridymite forms), \(Al_2(H_2PO_4) \cdot 3H_2O\), \(Al(PO_3)_3\), and a new compound arbitrarily designated as \(\beta-Al(PO_3)_3\). In the light of the condensation process of the phase change of acidic aluminum phosphate adhesive and the conditions of hardening in binding corundum aggregates were discussed.

The investigation of phase inversion of \(AlPO_4\) has also been reported\(^{(15)}\).

**Infrared Absorption Spectra of Phosphates**

The infrared spectrum is said to be one of the most characteristic properties of a compound. The range is from 0.75 to 200 microns. However, the so-called infrared region usually only covers the range between 2.5 to 16 microns. Infrared light is also expressed in terms of wave-numbers, which are the reciprocal of wavelength expressed in centimeter units.
The first major study of infrared analysis of phosphorus compounds was undertaken by Daasch and Smith (11) who published the spectra of 60 organo-phosphorus derivatives. Bellamy and Beecher (3,4,5) have examined the spectra of over 120 compounds. Miller and Wilkins (32) reported the spectra of a few ortho-phosphates, including tri-, di-, and mono-basic phosphates. A systematic study of inorganic phosphate compounds has been made by Corbridge and Lowe (8,9,10). In their work, the spectra of phosphorus salts have been examined as fine powder in 5000-400 cm\(^{-1}\) region. Characteristic absorption bands in phosphorus compounds have been suggested as shown in Figure 2. Infrared absorption spectra for aluminum phosphate binders used for refractories and thin layer coatings for metals have been studied by Medadewa, Mededev, and Tananaev (31). Wave-numbers for maximum absorption bands for Al\(_4\)(P\(_2\)O\(_7\))3 and AlH\(_3\)(PO\(_4\))\(_2\) \cdot 3H\(_2\)O are given as well as for aluminum phosphate binders heat treated at different temperatures. AlH\(_3\)(PO\(_4\))\(_2\) \cdot 3H\(_2\)O has a characteristically different infrared spectra than the spectra of the samples obtained at various temperatures. They reported that five stages phase changes occurred during heat treatment:
Figure 2. Characteristic Absorption Bands in Phosphorus Compounds

$8\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$

$4\text{Al(H}_2\text{PO}_4)_3$ \quad 170 °C \quad \text{No change}$

$2\text{Al}_2(\text{HPO}_4)_3$

\[ \xrightarrow{270 \ ^\circ \text{C}} \]

$4\text{AlH}_2\text{P}_3\text{O}_{10} + 4\text{AlPO}_4 + 32\text{H}_2\text{O}$

$4\text{AlH}_2\text{P}_3\text{O}_{10} + 8\text{H}_2\text{O}$

$2\text{Al}_2(\text{HPO}_4)_3$

\[ \xrightarrow{400-800 \ ^\circ \text{C}} \]

$4\text{AlP}_3\text{O}_9 + 4\text{AlPO}_4 + 4\text{H}_2\text{O}$

$4\text{AlP}_3\text{O}_9 + 4\text{H}_2\text{O}$

$\text{Al}_4(\text{P}_2\text{O}_7)_3 + 3\text{H}_2\text{O}$

\[ \xrightarrow{1000-1200 \ ^\circ \text{C}} \]

$\text{Al}_4(\text{P}_4\text{O}_{12})_3 + 4\text{AlPO}_4$

$\text{Al}_4(\text{P}_4\text{O}_{12})_3$

$4\text{AlPO}_4 + \text{P}_2\text{O}_5$

\[ \xrightarrow{1300 \ ^\circ \text{C}} \]

$8\text{AlPO}_4 + 4\text{P}_2\text{O}_5$

$4\text{AlPO}_4 + 4\text{P}_2\text{O}_5$

$4\text{AlPO}_4$

\[ \xrightarrow{1500-1800 \ ^\circ \text{C}} \]

$16\text{AlPO}_4$

\[ \xrightarrow{1800 \ ^\circ \text{C}} \]

$\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$
Arlidge\(^{1}\) reported the spectra for AlPO\(_4\) \cdot 2H\(_2\)O and two anhydrous forms of AlPO\(_4\). The results have served to identify the type of phosphate ion present, to distinguish between structural hydroxyl groups and water of crystallization. Spectra-structure correlations of phosphorus compounds can be summarized as follows:

(a) P-H stretching: 2440-2280 cm\(^{-1}\), a sharp absorption usually of medium intensity\(^{2}\).

(b) P-O bending: 1150-950 cm\(^{-1}\) has been suggested\(^{3}\).

(c) P-OH stretching: A broad and shallow absorption at 2700-2650 cm\(^{-1}\) with strong hydrogen bonding effects\(^{3}\).

(d) P-OH deformation in acid salt: 1400-1200 cm\(^{-1}\)(10).

(e) P-OH bending: 1050-850 cm\(^{-1}\)(10).

(f) P=O stretching: Normally occurs in the range 1300-1250 cm\(^{-1}\), but hydrogen bonding effects can cause shifts to lower frequencies (1250-1150) with an increase of intensity\(^{3}\).

(g) Ionic P-O stretching: 1170-1000 cm\(^{-1}\)(3).
(h) $P^+ - O^-$ ionized linkages: All phosphorus compounds containing ionized $P^+ - O^-$ linkages absorption, often in several places, in the ranges 1300-970 cm$^{-1}$ (stretching modes) and 580-460 cm$^{-1}$ (deformation modes)\(^{(9)}\).

(i) $PO_4^{3-}$ ions: 1100-1000 cm$^{-1}$, very strong. The tetrahedral ion has fundamental vibration frequencies at 1082 and 515 cm$^{-1}$\(^{(8)}\).

(j) $HPO_4^{2-}$ and $H_2PO_4^-$: 1070-1050 and 1090-1030 cm$^{-1}$, respectively\(^{(3)}\).

(k) P-O-P stretching: Near 900 and 700 cm$^{-1}$.

The P-O-P stretching near 900 cm$^{-1}$ appear to shift towards lower frequencies with increasing length of the P-O-P chain. The cyclic metaphosphates show absorption near 700 cm$^{-1}$ and also near 770 cm$^{-1}$, the latter band replacing the one near 900 cm$^{-1}$ in the chain compounds.

Table II shows the absorption spectra for hydrated aluminas.
TABLE II

O-H Infrared Spectra in Pure Alumina Hydrate

<table>
<thead>
<tr>
<th>Phase</th>
<th>Frequencies cm⁻¹</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stretching</td>
<td>Bending</td>
</tr>
<tr>
<td>α-Al₂O₃ monohydrate</td>
<td>3070</td>
<td>1145</td>
</tr>
<tr>
<td></td>
<td>3262</td>
<td>1073</td>
</tr>
<tr>
<td>β-Al₂O₃ monohydrate</td>
<td>2900</td>
<td></td>
</tr>
<tr>
<td>α-Al₂O₃ tri-hydrate</td>
<td>3361</td>
<td>1020</td>
</tr>
<tr>
<td></td>
<td>3378</td>
<td>967</td>
</tr>
<tr>
<td></td>
<td>3428</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3518</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3616</td>
<td></td>
</tr>
<tr>
<td>β-Al₂O₃ tri-hydrate</td>
<td>3401</td>
<td>1024</td>
</tr>
<tr>
<td></td>
<td>3454</td>
<td>975</td>
</tr>
<tr>
<td></td>
<td>3518</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3533</td>
<td></td>
</tr>
</tbody>
</table>

Chemistry of Dimethylformamide

Dimethylformamide (DMF), HCON(CH$_3$)$_3$, can be classified as a base which donates electrons. Ionic materials dissolved in this solvent yield anions which have much greater energies than the anions produced from salts dissolved in water. There is little tendency of anions and cations to aggregate in DMF, partly because this solvent strongly stabilizes the cations through dipole-cation interactions and partly because the high dielectric constants minimize the electrostatic attraction between anion and cation. The positive charge on the very small hydrogen atoms of water can come very much closer to an anion than can a positive charge on an atom other than hydrogen; hence hydrogen bonding is weaker in DMF. In DMF there is neither ion pairing nor hydrogen bonding, only a little weak ion-dipole interaction, hence the energy of the reactants remains high. It has now been found that the rates of many anionic reactions are some $10^3$ to $10^9$ times faster in DMF than in conventional solvents$^{(33)}$. The physical properties are shown in Tables III and IV.
### Table III

**Physical Properties of N,N-Dimethyl Formamide**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point at 760 mm Hg</td>
<td>153 °C</td>
</tr>
<tr>
<td>Freezing point</td>
<td>-61 °C</td>
</tr>
<tr>
<td>Refractive index at 25 °C</td>
<td>1.4269</td>
</tr>
<tr>
<td>Specific heat at 20 °C</td>
<td>0.5 cal/gr</td>
</tr>
<tr>
<td>Latent heat of evaporation</td>
<td>248 Btu/lb</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>11,280 Btu/lb</td>
</tr>
<tr>
<td>Viscosity at 25 °C</td>
<td>0.302 cp</td>
</tr>
<tr>
<td>Dielectric constant at 25 °C</td>
<td>26.6</td>
</tr>
</tbody>
</table>

### TABLE IV

**Specific Gravity and Vapor Pressure of N.N-Dimethyl Formamide**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Specific Gravity</th>
<th>Vapor Pressure mm Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>0.979</td>
<td>0.68</td>
</tr>
<tr>
<td>0</td>
<td>0.970</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.960</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.950</td>
<td>2.65</td>
</tr>
<tr>
<td>30</td>
<td>0.941</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.931</td>
<td>8.95</td>
</tr>
<tr>
<td>50</td>
<td>0.922</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.912</td>
<td>26.8</td>
</tr>
<tr>
<td>70</td>
<td>0.902</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.893</td>
<td>68.0</td>
</tr>
<tr>
<td>90</td>
<td>0.883</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.874</td>
<td>150</td>
</tr>
<tr>
<td>110</td>
<td>0.864</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.854</td>
<td>295</td>
</tr>
<tr>
<td>130</td>
<td>0.844</td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>0.835</td>
<td>540</td>
</tr>
<tr>
<td>153</td>
<td></td>
<td>760</td>
</tr>
</tbody>
</table>

III. **EXPERIMENTAL**

The following section contains the plan of experimentation, kinetic studies of aluminum hydroxide-phosphoric acid reaction, differential thermal analysis, x-ray studies, infrared studies, data and results, theory for kinetic studies, and a sample of the calculations.

**Plan of Experimentation**

A careful survey of the literature was made, covering reaction kinetics, reaction mechanism, bonding mechanism of aluminum phosphate, and chemistry of di-methylformamide.

**Kinetic Studies**

The reaction of aluminum hydroxide and phosphoric acid is strongly exothermic. This means that the reaction rate can be estimated from the rate of temperature rise under adiabatic conditions. As the total temperature rise is a measure of the amount of reaction, so also the rate of temperature rise is a measure of the rate of reaction.
Some studies were made before developing the procedure and selecting the apparatus. The temperature versus time curve was first studied in a beaker, using a thermometer to measure the temperature rises. This information helped to select the thermocouple system. Also, in order to provide satisfactory mixing, the optimum amount of solvent was determined.

A three-necked flask of 1000 milliliters capacity was used as the reaction vessel. In order to minimize the heat loss during reaction, the flask was insulated with a layer of asbestos and cotton, then placed in a wooden box. A glass stirrer was used to provide better mixing. The stirring speed was kept constant by a transformer. The temperature of reaction mixture was measured at a fixed point in the flask with a 30 gage iron-constantan thermocouple, and recorded on a Texas Instrument Company recorder. A 50 milliliter buret with stopcock was used to feed phosphoric acid to the flask.

One hundred and seventeen grams of RH-730 aluminum hydroxide were dispersed in 300 milliliters of DMF (or water) in a 600 milliliter beaker. The mixture was kept at 20 °C before it was poured into the reaction flask.
After a warm-up period of 30 minutes, the solution was poured into the flask and mixed by the glass stirrer; 103 milliliters of 85 percent phosphoric acid were used. This corresponded to a 1:1 ratio of Al₂O₃/P₂O₅. The acid was added at different rates, but kept constant in each run, controlled by opening the buret stopcock. As soon as the acid was added, the temperatures were continuously recorded using a 0.2 inch per minute chart speed. A period of 3 hours was used in this experiment. At the end of the reaction, the reaction mixture was poured into a beaker and marked with data and acid rate, and retained for analysis.

**Differential Thermal Analysis**

The basic technique in differential thermal analysis is as follows. The sample being studied along with a material of a known specific heat and thermal conductivity, are placed separately on a differential thermocouple, which in turn is placed in a furnace. The furnace is heated at a rate as close to a constant rate as is possible. Its temperatures are recorded by another thermocouple. With a knowledge of the specific heat of the unknown
and the entire heat history of the inert, characteristic temperature changes can then be determined.

The equipment used in this study was a "Model DTA 12B Series" furnace, manufactured by the Robert L. Stone Company. The furnace temperatures were recorded on a Leeds and Northrup Minimax recorder and were plotted versus the differential thermocouple readings on a X-Y recorder. The sample holder used was a small dish made of aluminum foil. The dish containing the sample of material to be tested was placed on the right-hand ring of the differential thermocouple. Any inert material of known specific heat could be used as a reference. However, it was convenient to use a number of aluminum foil discs which were stacked and folded together to make a small wad that would fit into the reference cup.

The heating rate was predetermined in such a way as to maintain a steady temperature increase over the range of interest. Usual temperature rise rate was about 10 °C per minute. This rate was fast enough to obtain sharp peaks and slow enough to permit accurate readings of the temperature.\(^{(37)}\).
The entire unit was checked by observing the action of di-phenyl carbazole and di-phenyl benzidine. The results were:

<table>
<thead>
<tr>
<th></th>
<th>Observed</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>di-phenyl carbazole</td>
<td>155-158 °C</td>
<td>155 °C</td>
</tr>
<tr>
<td>di-phenyl benzidine</td>
<td>244-248 °C</td>
<td>242-245 °C</td>
</tr>
</tbody>
</table>

In order to obtain zero base-line drift, an exact balance must be determined for the amount of reference versus sample, i.e., \((\text{weight of reference}) \times (\text{specific heat of reference}) = (\text{weight of sample}) \times (\text{specific heat of sample})\). Since the specific heat of the material to be tested was unknown, a value of 0.2 calorie per gram was estimated\(^{[37]}\).

X-Ray Studies

Specimens were prepared from DMF and water synthesized aluminum phosphates. The samples were:

(a) products synthesized using a 1:1 molar ratio of \(\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5\) in DMF at different rates of acid addition;
(b) both phases of a product synthesized using a 1:1 molar ratio in water; (c) product synthesized using
a 1:1 molar ratio without any solvent; (d) product synthesized using a 0.5:1 molar ratio in DMF; (e) product synthesized using a 0.5:1 molar ratio without solvent; and (f) product synthesized using a 1:1 molar ratio in different amounts of DMF.

X-Ray diffraction patterns were made of products after simple air drying and also of the same products after subjection to vacuum drying at 95 °C and 170 °C. Slides were prepared by two methods. At temperatures below 100 °C, the slurry was put on the slides and dried under 25 inches of mercury vacuum for 2 hours. At higher temperatures the specimens on the slide surface would crack, hence a different technique was used. Powder of the material was ground and mixed on the slide surface with a small amount of collodion which had been diluted with amyl acetate, then dried at 60 to 70 °C for 5 minutes.

The instrument used in this study was an XRD-5 x-ray diffraction unit, manufactured by General Electric Company. The procedures followed the operation manual of the instrument.
Infrared Studies

Pellet samples for studying were prepared using a pressed medium technique. This involved the following steps: A few milligrams of solid powder were ground and mixed in an agate with finely powdered KBr (-325 mesh) which had been dried under vacuum at 70 °C for 24 hours. The mixture was then inserted in a die made of steel. The inner die surfaces were polished to a smooth mirror finish and an evacuation port was provided so that air could be removed from the powder before it was pressed. If this were not done, air pockets in the pellet might render it cloudy.

A pressure of 20,000 pounds was applied with a Carver laboratory press for about five minutes. At this pressure many of the KBr crystals became quite plastic and flowed together into a transparent pellet. Pressure was then released, and the pellet was removed from the die and placed in a holder in the spectrometer.

The doublebeam Perkin-Elmer Model 337 spectrophotometer was used in this study and covered a total range from 2.5 to 25 μ (4000 to 400 cm⁻¹) with two gratings. One operated in the range from 25 to 8.33 μ⁻¹ (4000 to 1200 cm⁻¹); the other from 7.5 to 25 μ (1333
to 400 cm\(^{-1}\)). Two standard scanning speeds, an eight-minute scan and a 24 minute scan, were provided in each range.

The procedure followed the suggested general method outlined by the operational manual for the Perkin-Elmer instrument. Air was used as the reference for the samples during each analysis. The reference chamber was empty. The operating conditions were standard for each analysis of the spectra of the products. After a warm-up period of 30 minutes, each analysis was commenced at the upper limit of the instrument, 4000 cm\(^{-1}\), and scanned to 400 cm\(^{-1}\). The scanning time setting was 24 in the range 2000-1300 cm\(^{-1}\), while in the other range, a setting of 8 was used.

The samples to be tested were heat-treated at different temperatures, including air dried, 100, 170, 270, 400, 800, and 1000 °C. The sample at 100 °C was dried under 25 inches of mercury vacuum for 2 hours while the others were dried in an oven or furnace for 4 hours.
Data and Results

Experimental data of DTA, x-ray, infrared, and kinetic studies, results calculated from the experimental data, and charts prepared from experimental or calculated results are given in the following paragraphs.

**Kinetic Data.** Temperature versus time plots were obtained for reactions carried out in DMF and in water. Two such plots are presented in Figure 3, and the remainder of them are found in the Appendix. Note that the maximum temperature rises are different for the two solvents used. The reaction rate constants were calculated at several temperatures from the temperature-time plots and are listed in Tables V and VI.

The Arrhenius plots from Tables V and VI are found in Figures 4 and 5, respectively, the slopes of which were determined and used to evaluate activation energy as shown in the figures.

**Differential Thermal Analysis.** The experimental differential thermal analysis data for products synthesized using different ratios of $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ in DMF and without DMF are presented in Figures 8 through 11. Data were made from room temperature to 500 °C. Endothermic peaks were noted near
### TABLE V

**Apparent Rate Constant of Reaction of Aluminum Hydroxide with Phosphoric Acid Using Water as Solvent at Different Temperatures and Acid Addition Rates**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Acid Rates, ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>℃</td>
<td>9.36</td>
</tr>
<tr>
<td>25</td>
<td>1.120</td>
</tr>
<tr>
<td>30</td>
<td>0.746</td>
</tr>
<tr>
<td>35</td>
<td>0.531</td>
</tr>
<tr>
<td>40</td>
<td>0.349</td>
</tr>
</tbody>
</table>
TABLE VI

Apparent Rate Constant of Reaction of Aluminum Hydroxide with Phosphoric Acid Using N,N-Dimethylformamide as Solvent at Different Temperatures and Acid Addition Rates

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Acid Rate, ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>℃</td>
<td>7.63</td>
</tr>
<tr>
<td>30</td>
<td>0.923</td>
</tr>
<tr>
<td>40</td>
<td>0.427</td>
</tr>
<tr>
<td>50</td>
<td>0.289</td>
</tr>
<tr>
<td>60</td>
<td>0.162</td>
</tr>
<tr>
<td>70</td>
<td>--</td>
</tr>
</tbody>
</table>
Fig. 4 Log K vs. 1/T plot of reaction carried out in water.
FIG. 5  LOG K VS. 1/T PLOT OF REACTION CARRIED OUT IN DMF
FIG. 6 THERMOGRAM OF DIPHENYL CARBAZONE AND DIPHENYL BENZIDINE.
Fig. 7 ThermoGram of products synthesized using a 1:1 molar ratio in water.
FIG. 8 THERMOGRAM OF PRODUCTS SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 9 THERMOGRAM OF PRODUCTS SYNTHESIZED USING A 0.75:1 MOLAR RATIO.
FIG. 10. THERMOGRAM OF PRODUCTS SYNTHESIZED USING A 0.5:1 MOLAR RATIO.
FIG. 11. THERMOGRAM OF PRODUCTS SYNTHESIZED USING A 0.33:1 MOLAR RATIO.
175-240 °C and 450 °C. The whole test unit had been checked by two organic compounds, i.e., di-phenyl carbazole and di-phenyl benzidine. The result is shown in Figure 6.

**X-Ray Diffraction Patterns.** X-Ray diffraction patterns of products synthesized using a 1:1 molar ratio of Al₂O₃/P₂O₅ without solvent are presented in Figure 12. Diffraction patterns for products synthesized in DMF are found in Figure 13. Data were also made for (a) products synthesized using 0.5:1 molar ratio in DMF and without using DMF, (b) two phases in product synthesized in water, and (c) products synthesized using different amounts of DMF. The results are summarized in Table VII. Patterns are given in the Appendix.

**Infrared Spectra of Potassium Bromide and Aluminum Hydroxide.** Infrared spectra data are presented graphically. Figures 14 and 15 show the absorption spectra of pure aluminum hydroxide and potassium bromide. There is some water moisture in the potassium bromide as indicated by the absorption near 3430 cm⁻¹ and 1640 cm⁻¹ which are stretching and bending of OH, respectively. As far as OH stretching
FIG. 12. X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIZED USING A 1:1 MOLAR RATIO IN ABSENCE OF SOLVENT.
FIG. 13. X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIZED USING A 1:1 MOLAR RATIO IN DMF.
## TABLE VII

**Summary of X-Ray Results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>Figure</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1 in DMF</td>
<td>air dried</td>
<td>13</td>
<td>amorphous + Al(OH)₃</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>13</td>
<td>amorphous + Al(OH)₃</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>25</td>
<td>crystalline + Al(OH)₃</td>
</tr>
<tr>
<td>1:1 no solvent</td>
<td>air dried</td>
<td>12</td>
<td>amorphous + Al(OH)₃</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>12</td>
<td>amorphous + small amount of Al(OH)₃</td>
</tr>
<tr>
<td>0.5:1 in DMF</td>
<td>air dried</td>
<td>22</td>
<td>amorphous</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>22</td>
<td>amorphous</td>
</tr>
<tr>
<td>0.5:1 no solvent</td>
<td>air dried</td>
<td>21</td>
<td>crystalline</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>21</td>
<td>amorphous</td>
</tr>
<tr>
<td>1:1 gel-like</td>
<td>air dried</td>
<td>27</td>
<td>amorphous</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>27</td>
<td>crystalline</td>
</tr>
<tr>
<td>1:1 white solid</td>
<td>air dried</td>
<td>26</td>
<td>amorphous + Al(OH)₃</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>26</td>
<td>crystalline + Al(OH)₃</td>
</tr>
<tr>
<td>1:1 more DMF</td>
<td>air dried</td>
<td>23</td>
<td>amorphous + Al(OH)₃</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>23</td>
<td>amorphous + Al(OH)₃</td>
</tr>
<tr>
<td>1:1 less DMF</td>
<td>air dried</td>
<td>24</td>
<td>amorphous + small amount of Al(OH)₃</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>24</td>
<td>amorphous + small amount of Al(OH)₃</td>
</tr>
</tbody>
</table>
FIG. 14. INFRARED SPECTRA OF KBr AND Al(OH)$_3$ IN HIGH FREQUENCY RANGE.
FIG. 15. INFRARED SPECTRA OF KBr AND Al(OH)₃ IN LOW FREQUENCY RANGE.
is concerned, the absorption bands of aluminum hydroxide higher than 3500 cm\(^{-1}\) show strong evidence of free OH bond stretching.

**Infrared Spectra of Products.** Infrared spectra of products synthesized in the absence of solvent from 1:1 and 0.33:1 ratios of Al\(_2\)O\(_3\)/P\(_2\)O\(_5\) at different stages of curing are presented from Figures 16 to 18.

Figures 19 and 20 show the data of products synthesized in DMF. Little difference is observed between products from 1:1 and 0.75:1 ratios both in DMF and in the absence of solvent. Data of the products heat-treated from air dried to 1000 \(^\circ\)C indicate the existence of monoaluminum phosphate, di-aluminum phosphate, hydrated meta-aluminum phosphate, meta-aluminum phosphate, orthoaluminum phosphate, and probable unreacted aluminum hydroxide.

The comparisons of products synthesized in DMF and without using DMF at different temperatures and Al\(_2\)O\(_3\)/P\(_2\)O\(_5\) ratios are presented from Figures 32 to 43 of the Appendix. When water was used as the solvent, two phases were formed in the reaction mixture; a gel-like and a white solid material could be separated.
FIG. 16. INFRARED SPECTRA OF PRODUCT AT 400–1000°C USING A 1:1 MOLAR RATIO IN ABSENCE OF SOLVENT.
FIG. 17. INFRARED SPECTRA OF PRODUCT AT 100-400°C SYNTHESIZED USING A 1:1 MOLAR RATIO OF $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ IN ABSENCE OF SOLVENT.
FIG. 18. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 0.33:1 MOLAR RATIO IN ABSENCE OF SOLVENT.
FIG. 19. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 1:1 MOLAR RATIO OF $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ IN DMF.
FIG. 20. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 0.33:1 MOLAR RATIO IN DMF.
The data of these two materials are presented from Figures 44 to 46 in the Appendix.

At temperatures below 270 °C, a significant absorption band is not observed because of the strong hydrogen bonding and complexity of the system. All these results will be interpreted and discussed in more detail in the Discussion section of this thesis.

Theory for Kinetic Studies

The rate of temperature rise under adiabatic conditions for the reaction of phosphoric acid and aluminum hydroxide is a measure of the reaction rate\(^{(41)}\), since the reaction is exothermic. The apparatus and procedures used in this study meet the assumptions of an ideal semi-batch adiabatic reactor. Phosphoric acid was added gradually, hence a first order reaction with regard to the concentration of acid may be assumed. For a semi-batch reactor, the
following material balance for phosphoric acid can be made:

\[ V \frac{dc}{dt} = F - kVc \]  \hspace{1cm} (1)

where:

- \( V \) = volume of reactor at time \( t \), \( \text{min} \)
- \( c \) = concentration of acid at time \( t \), \( \text{mole/ml} \)
- \( k \) = rate constant, \( \text{min}^{-1} \)
- \( t \) = time, \( \text{min} \)
- \( F \) = flow rate of acid, \( \text{mole/min} \)

The volume of reactor changes with time, and can be expressed as:

\[ V = V_0 + Rt \]  \hspace{1cm} (2)

where \( V_0 \) is the initial volume of the reaction mixture, and \( R \) is the flow rate of acid in milliliters per minute.

The rate of reaction, \( \frac{dc}{dt} \), is proportional to the rate of temperature rise, \( \frac{dT}{dt} \):

\[ m \frac{dT}{dt} = \frac{dc}{dt} \]  \hspace{1cm} (3)
Integrating this equation, we find

\[ m\Delta T = -\Delta C. \]

The total amount of acid added \( \Delta C \) was 1.5 mole per volume of reactor, and \( \Delta T \) were approximately 50 °C and 35 °C for reaction in DMF and in water, respectively. Hence in the system involving DMF, \( m \) equaled \( -10^{-4} \), while in the system involving water, \( m \) was found to be \( -1.43 \times 10^{-4} \).

Substituting equations (2) and (3) into equation (1):

\[ (V_0 + Rt)m \frac{dT}{dt} = F + k(V_0 + Rt)m\Delta T. \]

Simplifying, we find

\[ k = \frac{1}{\Delta T} \left\{ \frac{dT}{dt} - \frac{F}{m(V_0 + Rt)} \right\} \]

\( \frac{dT}{dt} \) was read from a temperature-time plot at temperature \( T \), and \( \Delta T \) was the difference between \( T \) and \( T_0 \) which was the initial temperature of the reactor.
Sample Calculation

The following is an example of the method used to calculate the apparent reaction rate constants for the data obtained in the kinetic studies. The rate constants were calculated according to the following equation:

\[
k = 1/\Delta T \left[ \frac{dT}{dt} - F/(V_0 + Rt)m \right]
\]

as derived in the preceding section.

Substituting the data for the reaction carried out in DMF with an acid addition rate of 12.12 milliliters per minute, at 40 °C:

\[
\begin{align*}
\frac{dT}{dt} &= 11.65 \\
\Delta T &= 20 \degree C \\
F &= 0.1765 \text{ mole/min} \\
V_0 &= 320 \text{ ml} \\
R &= 12.12 \text{ ml/min} \\
t &= 1.7 \text{ min} \\
m &= 10^{-4} \text{ mole/ml °C.}
\end{align*}
\]

This yields:

\[
k = \frac{16.83/20}{20} = 0.842 \text{ min}^{-1}.
\]
An Arrhenius equation, $k = A_0 e^{-E/RT}$, was then used to estimate activation energy $E$. The slope in log $k$ versus $1/T$ plot gave the value of $E$ equal to 11.55 kilocalories per mole.
IV. DISCUSSION

The procedures, equipment, results, and limitations for this investigation as well as recommendations for future work are discussed in these paragraphs.

Discussion of Experiments

This section contains a discussion of the kinetic studies, differential thermal analysis, and infrared studies.

**Kinetic Studies.** The accuracy of the temperature readings was the basic requirement of this study. Both potentiometer and recorder were checked by standard battery. Since the recorder set point tended to drift after a certain period of operation, it was necessary to readjust the unit. At the beginning of the reaction, a fluctuation of temperature readings was observed, due to the non-uniform heat distribution.

Temperature readings involved a certain amount of error. The heat loss of the reaction vessel lowered the temperature of the reaction mixture. The amount of error was determined as follows: 117 grams of aluminum hydroxide were dispersed in 300 milliliters of water,
heated to 65 °C, and then poured into the reaction vessel. The temperature-time plot was made. It was found that:

<table>
<thead>
<tr>
<th>Temperature range, °C</th>
<th>dT/dt, °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-57</td>
<td>0.7</td>
</tr>
<tr>
<td>57-53</td>
<td>0.4</td>
</tr>
<tr>
<td>53-50</td>
<td>0.2</td>
</tr>
<tr>
<td>50-45</td>
<td>0.16</td>
</tr>
<tr>
<td>45-30</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The temperature range of interest was 25 to 40 °C, hence heat loss could be neglected.

The same procedures were carried out using DMF as the solvent. The data showed:

<table>
<thead>
<tr>
<th>Temperature range, °C</th>
<th>dT/dt, °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>77-73</td>
<td>2.0</td>
</tr>
<tr>
<td>73-71</td>
<td>1.0</td>
</tr>
<tr>
<td>71-67</td>
<td>0.6</td>
</tr>
<tr>
<td>67-65</td>
<td>0.4</td>
</tr>
<tr>
<td>65-63</td>
<td>0.3</td>
</tr>
<tr>
<td>63-58</td>
<td>0.2</td>
</tr>
<tr>
<td>58-53</td>
<td>0.1</td>
</tr>
<tr>
<td>53-40</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The temperature range of interest was 30-70 °C. At 70 °C, the amount of error was less than 2.0 percent. Based upon the data, heat loss was neglected.

A metal stirrer could not be used, because the reaction mixture was an electrolyte solution. This meant that the induced magnetic field would influence the electric properties of the solution affecting the thermocouple readings.

**Differential Thermal Analysis.** The three most important requirements in differential thermal analysis technique are (a) selection of a heating rate, (b) maintenance of a constant heating rate, and (c) a continuous and accurate recording of sample temperature and temperature differences with the inert sample. A heating rate of 10 °C per minute was used; this rate was fast enough to obtain sharp peaks and slow enough to permit accurate reading of the temperatures, as reported by Rickles. The thermocouple should be calibrated and checked. In this study, the whole unit had been checked by the melting point of two organic compounds. The results checked well with those reported. This indicated that both heating rate and temperature readings were satisfactory. However, some error could evolve due to the incorrect reading of furnace temperatures.
The apparatus and procedure used in this study had two limitations: (a) The capacity of the furnace was restricted to temperatures below 550 °C; no studies at higher temperatures were conducted. Actually some reactions for the system studied occur at higher temperatures as indicated by other analyses \((24,37)\). (b) The sample tested was not a simple compound, and its specific heat was unknown.

Heat transfer was also an important problem in DTA studies. To attain better heat distribution in the sample, the solid powder was ground and placed in the center of a dish which, in some way, should be placed on the right position on the differential ring.

**Infrared Studies.** The pressed medium technique has become very popular, perhaps partly because the technique for pellet preparation appears to be more quickly learned and perhaps partly because the physical labor is greatly eliminated. Various alkali halides have been used successfully for making discs; however, KBr is the popular compromise. It has no absorption in the infrared region from 4000 to 400 \(\text{cm}^{-1}\). This is one of the advantages over the mull technique.
The pressed medium technique also has certain difficulties. As the alkali halide powder cannot be kept absolutely dry, an OH stretch absorption is almost always observed to a greater or lesser extent in the region of 3300 cm$^{-1}$ because of trace amounts of moisture in the KBr powder. The press medium technique can perform quantitative analysis directly, but the quantitative analysis in the solid state is unreliable because of the complications of the Christiansen effect, polymorphism and amorphism effects, and difficulty of uniform beam coverage.

**Discussion of Results**

A discussion of the results obtained during the course of this investigation is presented in the following paragraphs.

**Kinetic Studies.** The rate constants calculated from the pseudo first order reaction model generally fit the Arrhenius equation quite well. However, at high acid rates, some deviations from the Arrhenius equation were observed. This was because the reaction was no longer first order and the rate of reaction was proportional not only to the concentration of phosphoric acid but also to that of aluminum hydroxide.
The rate constants were obtained from 30 °C to 40 °C for the reaction using water as the solvent. Many factors influenced the temperature readings at the beginning of the reaction, as mentioned previously. This made the calculated rate constants below 30 °C unreliable. At temperatures higher than 40 °C, the derived equation for evaluating the rate constant could not be used, since there was no acid input at that time.

For the reaction using DMF as the solvent, rate constants were obtained from 30 °C to 70 °C. The activation energies were found in the Arrhenius plot using the least squares method to determine the slopes and were found to be 8 to 12 kilocalories per mole, while for the reaction using water as the solvent, the activation energies were found to be 12 to 16 kilocalories per mole.

No activation energy data for aluminum phosphate or other phosphates were found in the literature. An average activation energy of 25 kilocalories per mole for the splitting of P-O-P linkage had been reported\(^\text{40}\). However, this situation was quite different from the reaction of aluminum hydroxide and phosphoric acid.
An empirical value of activation energy was estimated for the aluminum hydroxide-phosphoric acid reaction. \(^{(18,21)}\)

Hirschfelder proposed several rules relating to bond energies and enthalpies of activation for different types of reactions. The activation energy for a three-center reaction, \(A + BC = AB + C\) could be estimated by the following equation:

\[
E = 0.05 \, D_{BC} \quad \text{for exothermic reaction}
\]

where \(D_{BC}\) was the heat of dissociation of molecule BC. Some heat of dissociation data have been reported by Daniels\(^{(12)}\).

It was assumed that the mechanism of the reaction was that the hydrogen ions dissociated from phosphoric acid to form an activated complex molecule with aluminum hydroxide, eliminating water and forming the final product. Hirschfelder's rule was then used to estimate the activation energy. \(D_{BC}\) was found to be 113 kilocalories per mole for C-H\(^{(12)}\). The activation energy was then:

\[
E = 0.05 \, D_{BC} \\
= (0.05)(113) \\
= 5.65 \, \text{kcal/mole.}
\]
This value was approximately of the same order of magnitude as the experimentally determined activation energies.

Actually the coefficient for the foregoing rule has been shown to range from 0 to 0.1\(^{(18)}\). This then would mean that the estimated activation energy could be as large as 11.3 kilocalories per mole. The heat of formation of monoaluminum phosphate reported by Rickles\(^{(37)}\) was of the same order of magnitude.

It is of interest to call attention here to the fact that the energy of activation is, in general, considerably less than the energy required to break the bonds in the reacting molecules. The reason for this is that new bonds are formed in the activated state, and the energy of activation is the difference between the energy needed in the formation of these bonds and the amount necessary to break the bonds in the reactants.

Higher total temperature rise in the DMF system was observed due to the smaller specific heat of DMF, and had nothing to do with the rate of the reaction. Comparison of the activation energies experimentally determined for reactions carried out in DMF and in
water showed that the rate of reaction was faster in DMF. This could also be seen from the apparent rate constants. At 40 °C, the rate constant was 1.232 min\(^{-1}\) in DMF at an acid rate of 20.70 milliliters per minute, while it was 0.47 min\(^{-1}\) in water at an acid rate of 21.70 milliliters per minute.

The temperature-time data also showed that temperatures continued to rise when there was no acid input in the water system, while temperatures stopped rising as soon as the acid input ended in the DMF system. This provided additional evidence for the higher reaction rate in DMF.

**Differential Thermal Analysis.** Differential thermal analysis data were taken for products from 1:1 to 0.33:1 ratios of Al\(_2\)O\(_3\)/P\(_2\)O\(_5\). Almost the same weight of sample was used, hence a rough quantitative comparison could be made. All the samples showed a strong endothermic peak near 150-180 °C. The peak split into several peaks as the ratio of Al\(_2\)O\(_3\)/P\(_2\)O\(_5\) decreased. Actually this peak started from 100-120 °C, and became sharper at 130-140 °C, indicating the evolution of water molecules. Products from the 1:1 and 0.75:1 ratios showed a moderate endothermic
reaction near 180-190 °C. This corresponds to the formation of metaphosphate (3,20). Also, a weak endothermic peak occurs near 280 °C.

As the ratio of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \) decreased, the peak near 180-190 °C increased its intensity. Evidently more metaphosphates were formed, because the amount of monoaluminum phosphate was increased as the ratio of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \) decreased (37).

An interesting endothermic peak is noted at 235 °C. Rickles postulated that \( \text{Al}(\text{H}_3\text{PO}_4)_3 \rightarrow \text{Al}(\text{PO}_3)_3 \) at 175-235 °C. However, Guerin and Martin (20) indicated that this reaction occurred at 180 °C. A careful study of the thermogram reported by Rickles indicated that an endothermic reaction occurred at 200 °C and ended at 450 °C. His data were poor because of the limitations of the apparatus he used. Therefore, we could not definitely characterize the peak at 235 °C. It appeared likely, however, that metaphosphates were formed in the temperature region 175-240 °C. The slight exothermic peak at 300-400 °C occurred because of increasing crystallinity. Another endothermic peak occurring at 460 °C is possibly due to the formation of \( \text{AlPO}_4 \) (37), or the elimination of water from \( \text{Al}(\text{PO}_3)_3 \cdot \text{xH}_2\text{O} \) (31).
In the thermogram of the 0.5:1 ratio, in addition to the peak for the loss of free water, there was an endothermic peak at 165-175 °C indicating the formation of metaphosphate.

A slurry sample was used for the 0.33:1 ratio, since no solid powder could be obtained. This difference in heat history of samples gave different thermograms.

Gel-like phase in the product synthesized in water gave thermograms similar to products from the 0.33:1 ratio. Endothermic peaks were observed near 195 °C and 280 °C. These two peaks were all noted in the thermograms of the products from different ratios of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \). The peak near 175 °C became stronger as the ratio decreased, as discussed previously, while the peak near 230 °C disappeared as the ratio decreased to 0.5:1. At a high ratio of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \), compounds of \( x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O} \) may be formed\(^{(37)}\). They could lose the water of crystallization near 190-245 °C\(^{(37)}\), or form hydrated metaphosphate and \( \text{AlPO}_4 \) at 270 °C\(^{(31)}\). At low ratios of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \), the amount of these compounds was very small, and most of the products were monoaluminum phosphate.
Products synthesized in DMF had somehow different thermograms. At a 1:1 ratio, metaphosphates were formed near 175-250 °C. Then an endothermic peak was noted near 280 °C, as mentioned previously. Hence more $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ compounds were present when products were synthesized in DMF. As the ratio decreased, a more complicated thermal behavior was noted near 175-205 °C. This was due to more complicated hydroxy groups as indicated above; also, probably partly due both to the sample not being dried completely, and because the products were rich in $\text{Al(H}_2\text{PO}_4)_3$. A slight exothermic peak occurs just after the formation of metaphosphate. This was probably a gradual increase in crystallinity. Near 410 °C an exothermic peak was noted, which was probably a change of metaphosphate from linear to cyclic structure.

X-Ray Diffraction Patterns. Figure 12 showed that the reaction mixture, which was air dried only, from a 1:1 ratio of $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ without DMF, was essentially amorphous material together with some unreacted aluminum hydroxide, which was shown by d values of 4.87, 4.33, 3.32, 3.17, 2.46, and 2.38 (37). When this product was
subjected to vacuum drying at 95 °C, reaction continued, as shown in the figure.

Products synthesized using this molar ratio in DMP had the same pattern, showing the presence of aluminum hydroxide which did not disappear when subjected to vacuum drying at 95 °C. The data are shown in Figure 13.

To study the incomplete reaction, data were made for the products synthesized using a 0.5:1 ratio of Al$_2$O$_3$/P$_2$O$_5$. Figure 21, the diffraction pattern of the product synthesized without DMP, which was simply air dried, showed that crystalline material was formed. Unfortunately, data did not coincide with reference patterns (37). However, compounds of $x$Al$_2$O$_3$ · $y$P$_2$O$_5$ · $z$H$_2$O composition were probably formed (31, 37).

At 95 °C the data showed no crystallinity. Monoaluminum phosphate was believed to form at this temperature (24). Hence, it appeared that the products from the 1:1 ratio contained unreacted aluminum hydroxide which could be eliminated either by using excess acid or by subjecting to heat. It was of interest to note that no crystalline materials were
found in the products synthesized using the 0.5:1 ratio in DMF, including those air dried and heat-treated at 95 °C, as shown in Figure 22.

In summary we could say: (a) products synthesized in DMF and without using solvent had different crystallinities, and (b) when DMF was used as the solvent, the conversion of Al(OH)₃ was decreased.

In order to study solvent effects, products were made in different amounts of DMF. The x-ray data showed that the more DMF was used the less was the conversion of aluminum hydroxide, as shown in Figures 23 and 24.

Improvement of crystallinity by heat treatment was noted by heating the product synthesized in DMF to 170 °C. Figure 25 showed that some aluminum hydroxide still existed. However, the whole diffraction pattern showed that the crystalline materials other than aluminum hydroxide were formed. Two phases separated from the product synthesized in water were also analyzed. These materials were found to be amorphous at room temperature, and crystalline as the temperature increased. The patterns are presented in Figures 26 and 27.

**Infrared Spectra.** As far as the infrared spectra are concerned, the author is not supposed to interpret
the data in detail, instead, trying to point out the evidences of the presence of certain types of bonding in the sample to be tested. The difficulties in the interpretation of the data are due to the complexity of the products in which more than one type of phosphate bonds are believed to exist. Especially at low temperatures, say below 270 °C, more than one type of OH bond including P-OH, H-O-H, water of crystallization, and hydrogen bonding makes the interpretation even more difficult. However, at a higher temperature, say 300-1000 °C, almost standard absorption spectra can be obtained, such as orthophosphate and cyclic metaphosphate.

The discussions of infrared spectra data in this section are based upon the work by Corbridge(8,9,10), Arlidge(1), and Medadeva(31). Corbridge and Arlidge reported the spectra of cyclic metaphosphate $\text{Al}_4(\text{P}_4\text{O}_{12})_3$ and orthophosphate $\text{AlPO}_4$, while Medadeva reported the data of aluminum phosphate at different temperatures.

The infrared spectra data obtained indicated the presence of the following compounds in the reaction mixture when heated from room temperature to 1000 °C:
linear metaphosphate, cyclic metaphosphate, orthophosphate, and probably some unreacted aluminum hydroxide. At low temperatures, i.e., below 270 °C, the reaction mixture without heat treatment contained mono- and di-aluminum phosphate, and probably a compound of $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ composition (31,37). Owing to the complexities of $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, and bonding water moisture, the characteristic absorption bands of ionic P-O stretching were broadened. Also, whole absorption bands became diffused, making interpretation difficult. As the temperature was increased, solid state polymerization probably occurred with evolution of water molecules. The data showed the formation of linear metaphosphate, cyclic metaphosphate, and orthophosphate in the order of temperature rising. The relative amount of each compound depended both upon the ratio of the two reactants and solvent effects. Some water of crystallization was also probably involved in the formation of these compounds.

The data of products synthesized in DMF and in the absence of solvent from a 0.33:1 ratio showed no solvent effects on the structure when the products were heat-treated above 270 °C. No solid powder could
be obtained below 170 °C at this molar ratio. Data of these products indicated the formation of cyclic metaphosphate at 800 and 1000 °C(3). At 400 and 270 °C there were some evidences of the -P-O-P- linkage. These absorptions were checked with those reported by Medadova and are believed to be metaphosphate. At 270 °C some water of crystallization might exist, which gave a broadened absorption near 980-1300 cm⁻¹.

Products from the 0.5:1 ratio at 800 and 1000 °C appeared to be Al₄(P₄O₁₂)₃. At 800 °C the same spectra were obtained from products made in DMF and in the absence of solvent. However, at 1000 °C, the strong and sharp absorption near 1100 cm⁻¹ showed the presence of AlPO₄ in the DMF sample. This solvent effect was emphasized by the data at 400 and 270 °C at which metaphosphates were formed(31). No differences were observed between products made in DMF and in the absence of solvent at 170 °C.

Products made from 1:1 and 0.75:1 ratios in the absence of solvent showed no significant difference in the infrared spectra. Metaphosphates formed at 170 °C, and changed to cyclic metaphosphate gradually as the temperature increased. Data showed strong evidence of
$\text{AlPO}_4$ at 1000 °C. The products synthesized in DMF showed quite different spectra below 800 °C. At 800 °C there were no evidences indicating the presence of metaphosphate; instead, it was a standard $\text{AlPO}_4$ absorption spectra. There were two possibilities, first, different compounds were formed in DMF, and second, the reaction was incomplete having some unreacted aluminum hydroxide. To investigate these solvent effects, the following were carefully studied: (a) infrared spectra of pure aluminum hydroxide, (b) the spectra of samples from different ratios of $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$, and (c) the spectra of each phase of products synthesized in water.

Figures 32, 33, and 34 are the comparisons of the spectra of products made in DMF and in the absence of solvent. It was obvious that DMF samples had more absorption bands. These were at 2450, 1660, 1480, 1425, 875, 855, 680, 640, and 580 cm$^{-1}$. The weak and broad band near 2450 cm$^{-1}$ was characteristic absorption of P-OH stretching$^{(10)}$, while O-H bending was noted near 1600-1660 cm$^{-1}$. The spectra of $\text{Al(OH)}_3$ had the same absorption as that of the product made in the absence of solvent. Together with the additional absorptions in the lower range, it might be said that new compounds
were probably formed in DMF. However, the spectra of samples from different ratios of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \) indicated that the intensities of 375, 855, 680, 640, and 580 cm\(^{-1}\) decreased as the ratio of \( \text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 \) decreased, and there was no solvent effect at the 0.33:1 molar ratio. This was evidence of incomplete reaction; hence, no definite conclusion could be made. However, the absorption bands of the DMF sample near 2450 and 1600-1660 cm\(^{-1}\) did indicate that the OH bonding was quite different in the two materials at temperatures below 270 °C. Furthermore, the additional P-OH stretching and OH bending in the DMF sample gave some evidence that hydrogen bonding was reduced when DMF was used as the solvent.

The ranges near 3300-3650 cm\(^{-1}\) were the characteristic absorption bands of hydroxyl group stretching, while the appearance of absorption near 3630-3525 cm\(^{-1}\) indicated the loosely bonded OH groups\(^{(1)}\). Samples made from a 1:1 molar ratio in the absence of solvent, except the gel-like material, at 170 °C and below, gave absorption at 3630, 3525, 3440, and 3380 cm\(^{-1}\) indicating some of the OH groups were loosely bonded. While the gel-like material showed strong hydrogen bonding, two factors influenced the
absorptions near this range, i.e., temperature and ratio of reactants. There were no absorptions at this range when the temperature was increased to 400 °C at which time no hydroxyl groups were present. More $H_2PO_4^-$ and $HPO_4^{2-}$ were formed when the ratio of the reactants decreased. This led to the strong hydrogen bonding as seen from the spectra.

**Characteristics of Products Synthesized in Various Mediums**

The major problem with aluminum phosphate is that large quantities of water are formed as a condensation by-product. If a non-porous, high quality laminate is to be produced, the condensation by-product had to be removed from the laminate during cure. Unfortunately, a brittle non-flowing state was reached long before the reaction was completed. This created an inherent porosity and brittle matrix.

During the course of this investigation, it was found that dimethyl formamide led to the reaction mixture of workable viscosity and greatly increased the working pot life of the product. The product made using a 1:1 molar ratio of reactants without using DMF as solvent
became a hard solid mass in less than 20 hours, if carefully prepared. This meant that if reaction temperature was not controlled, or \( \text{Al(OH)}_3 \) was added too fast, or mixing was not satisfactory, then the reaction mixture would solidify even before \( \text{Al(OH)}_3 \) had been added completely. On the other hand, materials synthesized in DMF retained workable viscosity for more than three months, and products could be made without carefully controlling the reaction temperature. Less mixing was also required. The increase in the working pot life by DMF was probably because the hydrogen bonding of monoaluminum phosphate in the reaction mixture was reduced in DMF. In the preparation of solid samples for analysis, it was of interest to note that products made in DMF were in some ways like a thermoplastic material at temperatures below 95 °C at which most of the solvent was not evaporated and acted as a plasticizer.

As mentioned above, the porosities were formed in the product because of the elimination of water molecules from the hard solid mass. If water could be evaporated from the reaction mixture when it was in a flowing state, then the structure would be less porous. The boiling
point of DMF was 153 °C, hence during cure most of the water molecules were eliminated before DMF was evaporated, and reaction continued with releasing of more water from the still flowing reaction mixture. This led to a less porous structure in the reacted matrix. It was found that the degree of porosity in DMF synthesized product depended upon the amount of solvent used. The amount of porosity increased as the amount of DMF decreased. Also, it had been shown by x-ray analysis that increasing the amount of DMF increased the amount of unreacted aluminum hydroxide. Hence an optimum amount of DMF should be used to obtain the best properties.

In some of the kinetic studies, water was used as one of the solvents. After 3 hours of reaction, the products were saved and retained for analysis. It was observed that two phases formed in the material after about 10 days. The upper layer was a gel-like transparent phase, while the bottom layer was a white opaque solid material. These two phases could be separated and air dried. Rickles\(^{(37)}\) reported that the products of the reaction of aluminum hydroxide and phosphoric acid were a gel-like amorphous material, i.e., monoaluminum phosphate, and a crystalline solid material of the form
3Al$_2$O$_3$·2P$_2$O$_5$·6H$_2$O. X-Ray studies of these two phases indicated that the gel-like material was essentially monoaluminum phosphate; it was amorphous at room temperature and the crystallinities were improved as temperature increased. The white opaque solid was also an amorphous material with some unreacted aluminum hydroxide. No evidences could prove the existence of 3Al$_2$O$_3$·2P$_2$O$_5$·6H$_2$O; however, compounds of xAl$_2$O$_3$·yP$_2$O$_5$·zH$_2$O compositions were possibly formed. It was found that the relative amount of two phases was not influenced by the reaction temperature.

A boundary also formed in the DMF synthesized product, but took almost 10 days and was much less definitive than the water product. No analysis was made for each phase, but it was of interest to note that the relative amount of the two phases seemed to depend on the reaction temperatures. The amount of gel-like material in the upper phase was decreased as reaction temperature increased. This also could be due to the acid addition rates since different acid rates might change the reaction mechanism.

As the molar ratio of Al/P decreased more gel-like materials were formed. At the molar ratio of 0.33:1 an
essentially transparent gel-like material was obtained. This material became thicker and thicker when made in DME. On the other hand, when no solvent was used, it crystallized out after 3 weeks. Further studies on these phenomena are recommended.

It is also recommended that further studies be made on the processing of monoaluminum phosphate. Spinning might be possible.

**Recommendations**

During the course of this investigation, several areas for possible improvement in experimental techniques and for future research became apparent. These recommended areas for additional work are discussed in the following paragraphs.

1. The difference in thermal expansion characteristics between aluminum phosphate and the materials to be laminated will affect the strength of the composite. It is recommended that the phase transition of aluminum phosphate be studied further to higher temperature regions by differential thermal analysis technique and also by studying the weight loss versus temperature with a constant heating rate.
2. No mechanical and electric properties were tested for the phosphates synthesized in DMF. Hence no comparisons could be made. It is recommended that the amount of DMF used be studied further to obtain a workable viscosity and ease of evaporation of solvent. It is also recommended that the solvent effects be studied with regard to physical properties of products, including the investigation of solvents other than DMF.

3. Heat and free energy of formation of many phosphorus compounds had been reported; however, no data for aluminum phosphate could be found in the general literature. Further work in the field of kinetics and thermochemistry is recommended.

4. Aluminum phosphate is mainly used as a binder. It is recommended that other applications be studied further. Spinning processing seems to be possible.
Limitations

The experimental limitations on this investigation are given in the following paragraphs.

**Kinetic Studies.** The investigation was confined to the system aluminum hydroxide-phosphoric acid, carried out in DMF and in water using a 1:1 molar ratio of Al/P under adiabatic conditions. The apparent rate constants were determined at 30-70 °C for the DMF system, and at 30-40 °C for the water system.

**Differential Thermal Analysis.** The thermograms of the products studied were obtained in a 30-50 °C temperature range. The accuracy of the temperature readings was about 5-10 °C. Products were made using 1:1, 0.75:1, 0.5:1, and 0.33:1 molar ratios in DMF and in the absence of solvent.

**X-Ray Studies.** The x-ray diffraction patterns were made for both products made in DMF and in the absence of solvent. Specimens were prepared at room temperature, also heat-treated at 95 and 170 °C.

**Infrared Spectra.** The study of the spectra of the products was limited to the 4000-400 cm⁻¹ range. Samples made using four different molar ratios in DMF and in the absence of solvent were heat-treated at 100, 170, 270, 400, 800, and 1000 °C.
V. CONCLUSIONS

The present investigation was undertaken to study fundamentally the difference in structure between aluminum phosphate synthesized in various mediums. The conclusions reached were as follows:

1. Studies were made on the phase transformations of products formed from the reaction of phosphoric acid and aluminum hydroxide in various mediums. Molar ratios of Al₂O₃/P₂O₅ of 1, 0.75, 0.50, and 0.33 were studied. Products were cured at temperatures ranging from room temperature to 1000 °C. A number of compounds were found in the products. These included monoaluminum phosphate Al(H₂PO₄)₃, metaphosphate Al(PO₃)₃, cyclic metaphosphate Al₄(P₄O₁₂)₃, orthophosphate AlPO₄, and possibly compounds of the form xAl₂O₃·yP₂O₅·zH₂O.

2. A considerable amount of linear metaphosphate was found to form near 175-240 °C, while cyclic metaphosphate and orthophosphate were generally formed near 800-1000 °C.

3. The largest amounts of unreacted Al(OH)₃ were found in products for a 1:1 molar ratio of Al₂O₃/P₂O₅. The amount of this material decreased as the molar ratio decreased.
4. The amount of $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ increased with increasing molar ratios of $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$. At higher temperatures, more $\text{AlPO}_4$ was formed in the products synthesized in DMF. This indicated that probably more $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ was initially formed.

5. Energies of activation of pseudo first order reaction of aluminum hydroxide and phosphoric acid were determined. A value of 8-12 kilocalories per mole was found for reactions carried out in DMF, while 12-16 kilocalories per mole was determined for the reactions carried out in water.

6. The rate of reaction was found to be faster in DMF.

7. Decreasing the amount of DMF reduced the amount of unreacted $\text{Al(OH)}_3$ but increased the porosity of the product.

8. DMF gave the reaction mixture a workable viscosity and increased the pot life of the product.

9. The bonding mechanism of the hydroxyl groups was quite different for the DMF synthesized product with reduced hydrogen bonding.
10. Products synthesized using only Al(OH)$_3$ and H$_3$PO$_4$ (i.e., the absence of water and DMF), became a hard solid mass long before reactions were completed.

11. Products synthesized using water as a reaction medium separated into two phases: a gel-like phase containing essentially monoaluminum phosphate, and a solid opaque phase that contained unreacted Al(OH)$_3$ and possibly $x$Al$_2$O$_3$·$y$P$_2$O$_5$·$z$H$_2$O.
VI. SUMMARY

The purpose of this investigation was to study fundamentally the difference in structure of aluminum phosphates synthesized in various mediums.

The kinetics of aluminum hydroxide-phosphoric acid reaction in varied mediums were studied by measuring the temperature change during reaction at different acid rates. Apparent reaction rate constants at different temperatures were calculated from temperature versus time data and activation energies were obtained from the Arrhenius plot. The results compared favorably to estimated values for a pseudo first order reaction. These data also indicated that reaction was more rapid in dimethylformamide than other mediums.

The structure of products were studied at various molar ratios of reactants and for different heat-treatments up to 1000 °C. The structures were determined using differential thermal analysis, x-ray, and infrared techniques. It was found that:

1. A number of compounds were found in the products at temperatures ranging from room temperature to 1000 °C. These were: monoaluminum phosphate, metaphosphate,
cyclic metaphosphate, orthophosphate, and possibly compounds of the form $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$.

2. A considerable amount of linear metaphosphate was found to form near $175-240$ °C, while cyclic metaphosphate and orthophosphate were generally formed near $800-1000$ °C.

3. The largest amounts of unreacted $\text{Al(OH)}_3$ were found in products for a $1:1$ molar ratio of $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$. The amount of this material decreased as the molar ratio decreased.

4. The amount of $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ increased with increasing molar ratios of $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$. At higher temperatures, more $\text{AlPO}_3$ was formed in the products synthesized in dimethylformamide. This indicated that probably more $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ initially formed.

5. Energies of activation of pseudo first order reaction of aluminum hydroxide and phosphoric acid were determined. A value of $8-12$ kilocalories per mole was found for reactions carried out in dimethylformamide, while $12-16$ kilocalories per mole was determined for the reactions carried out in water.

6. The rate of reaction was found to be faster in dimethylformamide.
7. Decreasing the amount of dimethylformamide reduced the amount of unreacted \( \text{Al(OH)}_3 \) but increased the porosity of the product.

8. Dimethylformamide gave the reaction mixture a workable viscosity and increased the pot life of the product.

9. The bonding mechanism of hydroxyl groups was quite different for dimethylformamide synthesized products with reduced hydrogen bonding.

10. Products synthesized using only \( \text{Al(OH)}_3 \) and \( \text{H}_3\text{PO}_4 \) (i.e., absence of water and dimethylformamide) became a hard solid mass long before reactions were completed.

11. Products synthesized using water as a reaction medium separated into two phases: a gel-like phase containing essentially monoaluminum phosphate and a solid opaque phase that contained unreacted \( \text{Al(OH)}_3 \) and possibly \( x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O} \).
VII. BIBLIOGRAPHY


VIII. ACKNOWLEDGMENTS

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The author especially wishes to thank the Brunswick Corporation for providing financial assistance and Mr. V. A. Chase and Mr. R. L. Copeland, who suggested the topic and provided advice throughout the course of the investigation.
The author was born August 14, 1940, in Taiwan, China. He graduated from Taipei Chun Kon High School, in Taipei, Taiwan, in June of 1959. In September of that same year, he enrolled at the National Taiwan University as a Chemical Engineering student.
The author received a Bachelor of Science Degree in Chemical Engineering in June of 1963. After one year of military service in the Chinese Army, he attended Virginia Polytechnic Institute and received the degree of Master of Science in Chemical Engineering in July, 1966. He is a member of the Chinese Chemical Engineering Society and Phi Lambda Upsilon Honor Society.

Perry H. Lin
X. APPENDIX

APPENDIX I

Materials
Materials

**Aluminum Foil.** Pure cooking aluminum foil. Obtained from Reynolds Metals Co., Richmond, Va. Used as reference material and sample dish in DTA technique.


**Hydrated Alumina.** Reagent grade, catalog RN-730. Obtained from Reynolds Metals Co., Bauxite, Ark. Used as one of the reactants.

**Ice.** Obtained from refrigeration of tap water. Used to provide a cooling medium for thermocouple cold junction.

**di-Phenyl Benzidine.** Reagent grade, catalog D-84. Obtained from Fisher Scientific Co., Fair Lawn, N. J. Used to check the temperatures of the DTA unit.


**Phosphoric Acid.** Food grade, 85%. Obtained from Monsanto Company, St. Louis, Mo. Used as one of the reactants.

APPENDIX II

Apparatus
Apparatus


**Potentiometer.** Model 759-6, 115 v, 60 cp, 30 w. Manufactured by Magnetic Instruments Co., Thornwood, N. Y. Used to measure voltage of thermocouple in reactor.

**Powerstat.** Variable transformer, type 3PN116, 115 v, 50/60 cy, output range 0 to 140 v, 7-1/2 amp maximum. Manufactured by Superior Electric Co., Bristol, Conn. Used to control the stirring speed in kinetics study and to synthesize materials.

**Press.** Laboratory use, capacity 20,000 psi, model B, serial 7670-10. Manufactured by Fred S. Carver, Inc., Summit, N. J. Used to prepare pellet sample in infrared test.

**Recorder.** Temperature, two points, 115 v, 60 cy, ac. Manufactured by Texas Instruments, Inc., Houston, Tex. Used to record temperature of reaction mixture.


**Spectrophotometer.** Model 337, double beam, range 2.5-25.0 u. Manufactured by Perkin-Elmer Co., Norwalk, Conn. Used as infrared instrument.

Thermometer. Mercury in glass, range -10 to 150 °C, 1.0 °C subdivision, catalog 8315. Obtained from Ace Glass Corp., Vineland, N. J. Used to calibrate the reading of thermocouple.


Vacuum Oven. Capacity 30 in. Hg; series number and other information not available. Purchased from Will Corp., Rochester, N. Y. Used to dry samples below 100 °C.


APPENDIX III

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APPENDIX IV

X-Ray Diffraction Patterns
FIG. 21 X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIZED USING A 0.5:1 MOLAR RATIO IN ABSENCE OF SOLVENT.
FIG. 22 X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIZED USING A 0.5:1 MOLAR RATIO IN DMF.
FIG. 23. X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIZED USING MORE DMF.
FIG. 24 X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIZED USING LESS DMF.
FIG. 25 X-RAY DIFFRACTION PATTERN OF PRODUCT SYNTHESIED USING A 1:1 MOLAR RATIO IN DMF.
FIG. 26  X-RAY DIFFRACTION PATTERN OF WHITE SOLID MATERIAL IN WATER SYNTHESIZED PRODUCT.
FIG. 27 X-RAY DIFFRACTION PATTERN OF GEL-LIKE MATERIAL SYNTHESIZED IN WATER.
APPENDIX V

Infrared Spectra
FIG. 28. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 0.75:1 MOLAR RATIO, IN ABSENCE OF SOLVENT.
FIG. 29. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 0.5:1 MOLAR RATIO IN ABSENCE OF SOLVENT.
FIG. 30. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 0.75:1 MOLAR RATIO IN DMF.
FIG. 31. INFRARED SPECTRA OF PRODUCT SYNTHESIZED USING A 0.5:1 MOLAR RATIO IN DMF.
FIG. 32. INFRARED SPECTRA OF PRODUCTS AT 100°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 33. INFRARED SPECTRA OF PRODUCTS AT 170°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 34. INFRARED SPECTRA OF PRODUCTS AT 170°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 35. INFRARED SPECTRA OF PRODUCTS AT 270°C SYNTHESIZED USING A 1:1 MOLAR RATIO
FIG. 36. INFRARED SPECTRA OF PRODUCTS AT 270°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
**FIG. 37.** INFRARED SPECTRA OF PRODUCTS AT 400°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 38. INFRARED SPECTRA OF PRODUCTS AT 800°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 39. INFRARED SPECTRA OF PRODUCTS AT 1000°C SYNTHESIZED USING A 1:1 MOLAR RATIO.
FIG. 40. INFRARED SPECTRA OF PRODUCTS AT 270°C SYNTHESIZED USING A 0.5:1 MOLAR RATIO.
FIG. 41. INFRARED SPECTRA OF PRODUCTS AT 400°C SYNTHESIZED USING A 0.5:1 MOLAR RATIO.
FIG. 42. INFRARED SPECTRA OF PRODUCTS AT 800°C SYNTHESIZED USING A 0.5:1 MOLAR RATIO.
FIG. 43. INFRARED SPECTRA OF PRODUCTS AT 1000°C SYNTHESIZED USING A 0.5:1 MOLAR RATIO.
FIG. 44. INFRARED SPECTRA OF GEL-LIKE MATERIAL / FROM ROOM TEMPERATURE TO 400°C SYNTHESIZED USING A 1:1 MOLAR RATIO IN WATER.
FIG. 45. INFRARED SPECTRA OF GEL-LIKE MATERIAL 400°-1000°C SYNTHESIZED USING A 1:1 MOLAR RATIO IN WATER
Fig. 46. Infrared spectra of white solid material synthesized using a 1:1 molar ratio in water.
FIG. 47. INFRARED SPECTRA OF PRODUCTS SYNTHESIZED USING DIFFERENT MOLAR RATIO OF $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5$ IN ABSENCE OF SOLVENT.
A FUNDAMENTAL STUDY OF ALUMINUM PHOSPHATE SYNTHESIZED IN VARIOUS REACTION MEDIUMS

by

Perry Han-cheng Lin

Candidate for Degree of Master of Science in Chemical Engineering

July, 1966

ABSTRACT

The purpose of this investigation was to study fundamentally the difference in structure of aluminum phosphates synthesized in various mediums.

The kinetics of aluminum hydroxide-phosphoric acid reaction in varied mediums were studied by measuring the temperature change during reaction at different acid rates. Apparent reaction rate constants at different temperatures were calculated from temperature versus time data and activation energies were obtained from the Arrhenius plot. The results compared favorably to
estimated values for a pseudo first order reaction. These data also indicated that reaction was more rapid in dimethylformamide than other mediums.

The structure of products were studied at various molar ratios of reactants and for different heat-treatments up to 1000 °C. The structures were determined using differential thermal analysis, x-ray, and infrared techniques. It was found that:

1. A number of compounds were found in the products at temperatures ranging from room temperature to 1000 °C. These were: monoaluminum phosphate, metaphosphate, cyclic metaphosphate, orthophosphate, and possibly compounds of the form $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$.

2. A considerable amount of linear metaphosphate was found to form near 175-240 °C, while cyclic metaphosphate and orthophosphate were generally formed near 800-1000 °C.

3. The largest amounts of unreacted $\text{Al(OH)}_3$ were found in products for a 1:1 molar ratio of $\text{Al}_2\text{O}_3 / \text{P}_2\text{O}_5$. The amount of this material decreased as the molar ratio decreased.

4. The amount of $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ increased with increasing molar ratios of $\text{Al}_2\text{O}_3 / \text{P}_2\text{O}_5$. At higher
temperatures, more $\text{AlPO}_3$ was formed in the products synthesized in dimethylformamide. This indicated that probably more $x\text{Al}_2\text{O}_3 \cdot y\text{P}_2\text{O}_5 \cdot z\text{H}_2\text{O}$ initially formed.

5. Energies of activation of pseudo first order reaction of aluminum hydroxide and phosphoric acid were determined. A value of 8-12 kilocalories per mole was found for reactions carried out in dimethylformamide, while 12-16 kilocalories per mole was determined for the reactions carried out in water.

6. The rate of reaction was found to be faster in dimethylformamide.

7. Decreasing the amount of dimethylformamide reduced the amount of unreacted $\text{Al(OH)}_3$ but increased the porosity of the product.

8. Dimethylformamide gave the reaction mixture a workable viscosity and increased the pot life of the product.

9. The bonding mechanism for hydroxyl groups was quite different for dimethylformamide synthesized products with reduced hydrogen bonding.

10. Products synthesized using only $\text{Al(OH)}_3$ and $\text{H}_3\text{PO}_4$ (i.e., absence of water and dimethylformamide)
became a hard solid mass long before reactions were completed.

11. Products synthesized using water as a reaction medium separated into two phases: a gel-like phase containing essentially monoaluminmum phosphate and a solid opaque phase that contained unreacted Al(OH)$_3$ and possibly xAl$_2$O$_3$·yP$_2$O$_5$·zH$_2$O.