

# Ethyl Silicate Bonded Alumina as a Ceramic Binder

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## Abstract

Ethyl silicate was used as organic binder for alumina refractories. In the present work only 15% of the water required for complete hydrolysis of ethyl silicate was initially added. The balance was provided from the atmosphere under controlled conditions of temperature and rh. The purpose of detailing the possible binder problem areas is more to indicate that the binder can have an effect on ceramic operations.

**Key Words** : ethyl silicate, organic binder, alumina refractory, hydrolysis, ceramic operation

## 1. Introduction

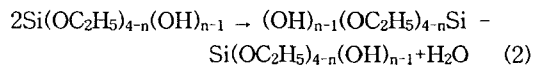
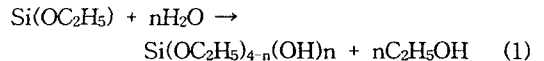
Organic binders were used in the ceramic industry as a processing aid before spray drying began to replace older method of granule preparation. In many respects, the organic binder performs similar functions for the spray dried granule and for other granulation methods. Spray drying is another means of granulation which can produce in one step what may take several steps by other methods.

The selection of a binder is based on four criteria:

1. Economics - the process and end product should be able to afford its cost.
2. The properties required in the various manufacturing steps, that is, the binder should do what it is supposed to do.
3. Absence of undesirable qualities in the various manufacturing steps, that is, the binder should not hinder any step.
4. If necessary, the capability of enhancing desirable properties and/or suppressing undesirable properties by various means.

Ethyl silicate has been used as a binder specialty refractors with varying degress. Processing variables have not always been completely defined and day to day atmospheric variations have been blamed for losses. This paper is intended as a contribution to the knowledge extant on the use of ethyl silicate as a ceramic binder.

The formation of SiO<sub>2</sub> gel that is deposited from an ethyl silicate solution depends on (1) the successful hydrolysis of the ethyl silicate, and (2) the subsequent polycondensation of the ethyl silicate molecules which proceed according to the following general equations:



The water added in Eq. (1) is usually added as aqueous alcohol due to the immiscibility of ethyl silicate and water. However, it has been shown [1-2] that if sufficient water to complete the reaction is added to the initial solution, the strength of the bonded aggregate will be reduced. It has also been shown [3-4] that by

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keeping the initial water content low, sufficient water can be absorbed from the atmosphere to complete the reaction and develop adequate bond strength.

In the present work only 15% of the water required for complete hydrolysis of ethyl silicate was initially added. The balance was provided from the atmosphere under controlled conditions of temperature and rh.

## 2. Sample Preparation

A model refractory system of -325 mesh A-10  $Al_2O_3$  was used. The binder solution consisted of the following volume mixture:

Ethyl silicate (40 wt % $SiO_2$ )	78 %
Dicyclohexylamine 33 1/3 (vol %)	
Piperidine 33 1/3 (vol %)	2 %
Distilled water 33 1/3 (vol %)	
Ethyl alcohol 89.5 (vol %)	20 %
Distilled water 10.5 (vol %)	100 %

*Casting:* A slurry containing 29 wt.% binder solution was mixed by hand and immediately cast into metal molds and vibrated for 1 min. Polyethylene glycol was used as a mold release agent. Setting time was 10 min. The mold was removed after an additional 10 min.

*Curing:* After removal from the mold and preparation for the intended test the specimens were immediately placed in a controlled atmosphere with a dry bulb temperature of 85°C and an Rh of 30, 40, 50, 60 or 80%. Specimens were withdrawn for analyses after 24h.

## 3. Specimen testing

*Thermogravimetric analysis:* The specimens were divided into quarters before curing, thereby the same specimens could be tested at different curing times. After curing, the specimens were ground to pass a 100-mesh sieve. Weight loss was run at a heating rate of 5°C/min with airflow of 0.2 l/min through the specimen chamber.

*Differential thermal analysis:* Some of the powders prepared for the TGA were also used for DTA. Thermograms were run at a heating rate of 5 °C/min in a static atmosphere against calcined  $Al_2O_3$  as a reference.

*Thermal dilatometric analysis:* Dilatometer specimens 0.5 x 0.5 x 5.0 cm were cut from cast cylinders for irreversible thermal expansion measurements.

*Bio<sub>2</sub> analysis:* Specimens were analyzed for  $SiO_2$  content, both immediately after curing and after firing to 1000°C. Analysis was performed by standard gravimetric methods.

*Infrared spectroscopic analysis:* Specimens were heated to 275°C, and vapors released were collected, both as a gas and as a liquid condensed in a ice bath, for IR spectroscopic analysis.

*Compressive strength:* Specimens were 5.0 cm cubes cured, then cooled for 1 h at ambient conditions before measurements were made.

## 4. Results and Discussion

The large weight loss in the 200°C to 300°C range shown in Fig.1 in the specimens cured at low humidity corresponds to the negative thermal expansion exhibited by the specimen cured at 30% Rh in this range in Fig. 2. The shrinkage is believed to be due to the replacement of remaining ethoxy groups by hydroxyl groups and their subsequent polycondensation as well as a reaction of the following type:

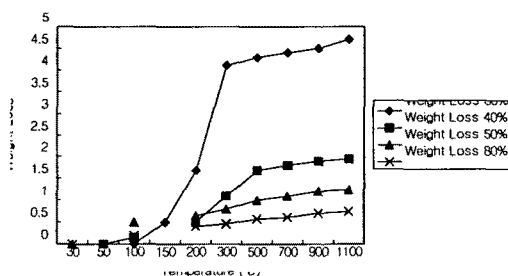
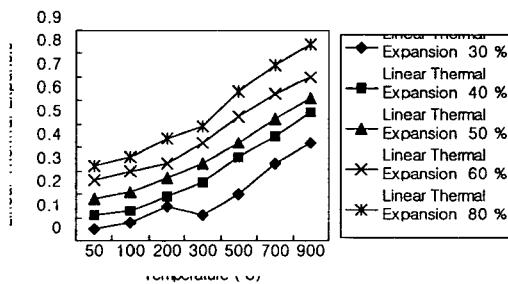


Fig. 1. TG of ethyl - silicated bon  $Al_2O_3$  cured at 85°C for 24h at varying relative

humidities (1-Weight loss 30%;  
2-Weight loss 40%; 3-Weight loss 50%;  
4-Weight loss 80%)

As the larger ethoxy groups replaced by smaller hydroxyl groups with subsequent polycondensation, the gel network contracts resulting in the observed shrinkage. The IR spectroscopy analysis performed in this study showed that in specimens cured at the lowest humidity, alcohol was present in the vapor given off in the 200°C to 300°C range; therefore, it follows that the foregoing reactions are possible and likely.



**Fig. 2.** Irreversible thermal expansion behavior of ethyl silicate bonded  $Al_2O_3$  cured 85°C for 24h at varying relative humidities

The weight loss in the 200°C to 300°C range is related to the vaporization of the hydroproducts of the reactions and unpolymerized or small chain length polymers of the ethyl silicate. Ethyl alcohol is expected to vaporize readily at these temperatures.

Evidence of ethyl silicate vaporization was obtained using IR analysis. Ethyl silicate was identified by IR absorption spectroscopy in a condensate which was derived from a specimen cured at the lowest humidity by heating it to 275°C. Additionally chemical analyses (Table 1) showed that the  $SiO_2$  content of fired specimens was lower for those cured at low humidities than for those cured at high humidities. This indicates that unreacted ethyl silicate vaporizes from the specimens during firing. The characteristic weight loss and shrinkage of the

specimens cured at the low humidity were not observed in those cured at higher humidities. This is because the water vapor available at the higher humidities penetrated the body to hydrolyze many of the unreacted ethoxy groups during the 24 hour curing, allowing the gel to more closely approach completion. This would explain the lower weight loss and the absence of the shrinkage in the 200°C to 300°C range for these specimens because the liberated ethoxy groups would be expected to leave as the reactions took place. Analysis of the  $SiO_2$  content after 24 h curing substantiates the assumption that more unreacted ethoxy groups remain in specimens cured at the low humidity than in those cured at the high humidities. It was found (Table 1) that the  $SiO_2$  content after 24 h of curing was greater for specimens cured at high humidity.

**Table 1.** Gravimetric Chemical Analysis for  $SiO_2$  Content of Unfired and Fired Specimens of Ethyl Silicate Bonded  $Al_2O_3$ .

% rh	Unfired		Fired	
	Avg% $SiO_2$ (+0.1%)	No. of specimens	Avg% $SiO_2$ (+0.1%)	No. of specimens
80	8.75	2	8.45	1
60	8.82	2	8.27	1
50	8.37	2	8.22	2
40	8.00	3	7.95	3
30	7.28	3	6.94	3

*All specimens cured for 24h at 85°C.*

This would be expected if the heavier ethoxy groups had been replaced by lighter hydroxyls or siloxane oxygens. Also, in the specimens cured at high humidity there is no evidence of loss of  $SiO_2$  due to vaporization of unreacted ethyl silicate because sufficient vapor was not given off in the specimen cured at high humidity to permit analysis by IR spectroscopy.

In the exothermic reaction which was observed in the 250°C to 400°C range has been noted phenomena attributed in to the burning of alcohol and another, unknown, coincidental

reaction. This explanation appears to be satisfactory as the product to the reaction occurring between 200°C and 300°C is alcohol. It was noted that this reaction was much more pronounced in the specimens cured at low humidity than in those cured at high humidity. This would be expected because those cured at low humidity have a reaction which liberates volatiles just previous to the observed exotherm. On the other hand, the specimens cured high humidity have liberated these volatiles by the appropriate reactions during the cure; therefore, the volatiles most likely left the specimens by evaporation as they were produced during the cure.

Comparison of the green compressive strength of specimens cured at different humidities (Table 2) shows that those cured at 80% rh were 55% longer than those cured at 30% Rh.

**Table 2.** Compressive Strength of Unfired Ethyl Silicate Bonded Al<sub>2</sub>O<sub>3</sub>.

% Rh	Avg strength MPa	No. of specimens	Standard deviation
80	4.9	36	34
60	5.0	36	41
50	4.5	36	126
40	3.8	36	76
30	3.1	36	41

*All specimens cured for 24h at 85°C.*

The low humidity cured gel has a higher ethoxy group content; therefore, it must have less polymerization and crosslinking of polymers. It is this lack of ultimate bonding within the gel structure that is responsible for its weakness. Specimens subjected to the same atmospheric conditions up to four days did not show any appreciable change.

## 5. Conclusions

It can be concluded that close control of atmospheric conditions during curing is necessary to assure complete gel formation in

ethyl silicate binders. At 85°C it is noted that relative humidities of > 50% are required to achieve the best bond development. This was determined on the basis that these humidities give the highest green strength and do not show the contraction that begins at 250°C. Curing at 30% rh is undesirable because of the low strength and other indications of incomplete gel formation. From TGA and TDA data it was concluded that 40% Rh is an intermediate situation which allows a significantly greater total weight loss than the highest humidities but fails to show the characteristic period of shrinkage of the lower humidity. Samples cured in a 50% rh gave strengths closely approaching those obtained from the higher humidity curves and also do not show the contraction.

While it was shown that increasing the amount of water added during mixing is deleterious to the gel strength, it is essential that the water needed to replace the ethoxy groups be subsequently provided to properly cure the gel. This work has shown that at least a 50% Rh atmosphere is needed at 85°C to provide this moisture while curing.

The purpose of detailing the possible binder problem areas is more to indicate that the binder can have an effect on ceramic operations and, when problems do occur in the process line, the action of binders should be considered.

## Acknowledgement

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