LEAD INDUSTRIES ASSOCIATION
60 EAST 42ND STREET
NEW YORK 17, N. Y.

August 21, 1959

SUBJECT: SUPPLEMENTS TO "LEAD IN THE CERAMIC INDUSTRIES"

To the Members of the Lead Industries Association:

Enclosed are the third and fourth supplements to our technical data book, "Lead in the Ceramic Industries," issued in December 1956.

The third supplement, to be added to the "Glazes" section of the book, is titled "Use of Lead in Coatings for Ceramic Dielectric Bodies."

The fourth supplement, to be added to the "Bodies" section, is titled "Use of Lead in Ceramic Bodies."

These two supplements are being mailed to more than 6,000 people connected with the ceramic industries who have already received the book, and will also be included with future copies of the book sent out in answer to requests for it.

These will be followed by other supplements from time to time.

Very truly yours,

Secretary

Enc.

April 1961

USE OF LEAD IN COATINGS FOR CERAMIC DIELECTRIC BODIES*

The need for coatings or glazes for low dielectric loss ceramics, which possessed and maintained high surface resistivity under high humidity environments, has been recognized for some time. Such a coated ceramic must be of an equal grade to the uncoated ceramic (JAN-I-10 specifications) and must be capable of easy fabrication by conventional methods.

Some types of organic coatings, e.g., silicones, may provide for temporary benefits. However, it is generally held that to attain the desired permanence, inorganic coatings are a prerequisite.

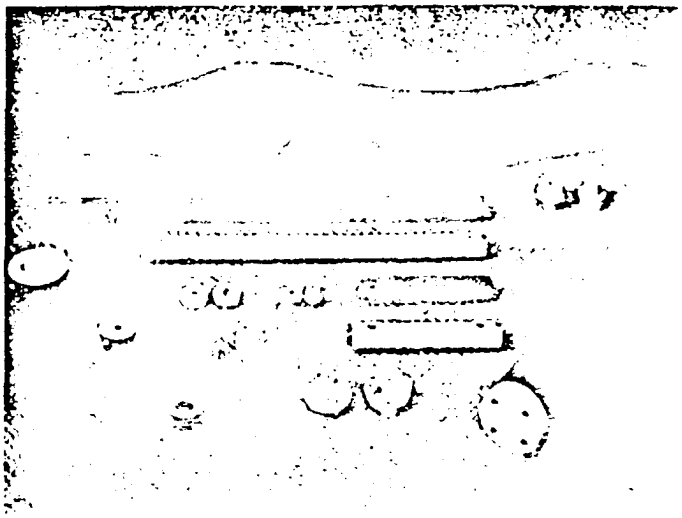
On the basis of extensive evaluation of many different glaze compositions, high lead glazes were found to be superior. Lead monosilicate and lead bisilicate were established as the best coatings in terms of water run-off and electrical resistivity under humidity cycling.

The objective in the research referred to above was to develop a ceramic coating whose surface resistivity would not be less than 7.5×10^{7} megohms under 95 percent relative humidity. The approach to this problem was to study typical glazes, incorporating compositional changes to determine those compositions with the highest electrical surface resistivity. Although the literature provides very limited information concerning the surface resistivity of glazes a number of references pertaining to glass surfaces are noted. The problem involves two mechanisms, conductivity in the coating and conductivity over the surface of the coating. Solubility of the glaze in water is of concern, e.g., alkalies may be leached from the surface when the glass is exposed to high humidities resulting in increased surface conductivity. A lead glaze, though containing alkali, may result in a tight or more stable structure which restricts the motion of alkali ions. The moisture layer may be continuous or discontinuous, depending on solubility, structural groupings and the water layer itself. Lead, as an ingredient of the coating is effective in reducing water solubility and thus promoting non-wetting on the surface and concurrent high surface resistivity.

The measurement of electrical resistivity under high humidity conditions was carried out in a cabinet in which the relative humidity and temperature could be maintained constant. Any value above 10^{12} ohms, as measured, was reported as infinite resistance.

The early work eliminated many leadless and low lead compositions and indicated the need for a high lead content in these coatings. The compositions based on lead borate and lead monosilicate exhibited

*This resume, prepared by John H. Koenig, Edward J. Smoke, and S. DiVita involves results of research at the School of Ceramics, Rutgers, the State University, under the sponsorship of the U. S. Army Research and Development Laboratories.

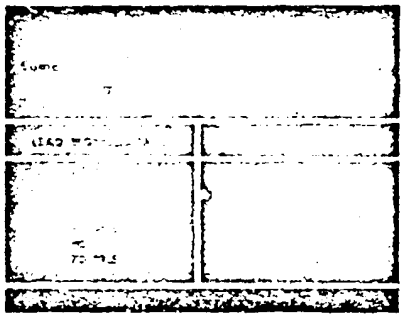


Electrical insulators coated with glazes containing lead bisilicate. Both brown and clear glazes are available and are fired to approximately cone 05.

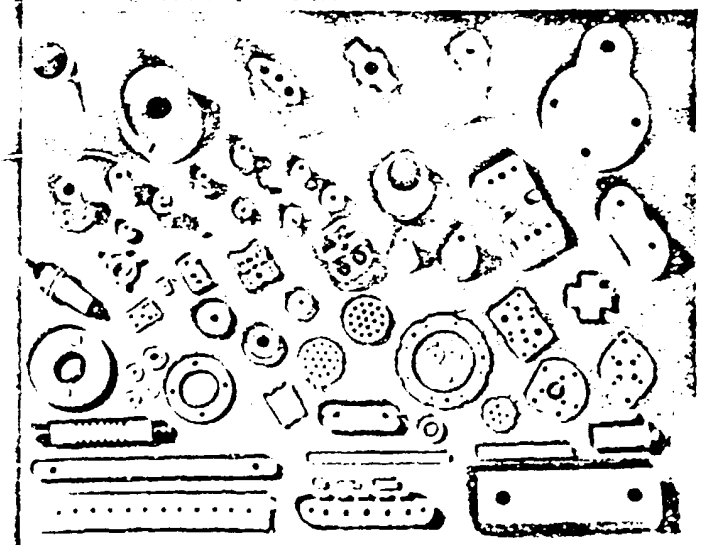
the best water run-off and electrical surface resistivity. The lead borate base coatings appeared to possess a higher degree of non-wetting characteristics but the lead silicate base glazes maintained their initially high resistivity throughout the test (60 days).

The lead borate and lead monosilicate glazes provided clear, smooth glazes. Various additives producing other textures (mat and semi-mat) had little effect on non-wetting and electrical resistivity properties of the base glazes. Numerous test data showed that lead monosilicate was the component necessary in the coating to meet the requirements. Some of the more interesting lead monosilicate coatings are given in Table 3-3. These provided the greatest reproducibility in infinite surface resistivity under high humidity conditions.

There were also a number of other more complex coatings involving the use of small amounts of BeO, alkaline earth oxides, alkaline earth zirconium silicates, etc., which also exhibited infinite surface resistivity in the tests. The lead bisilicate and lead aluminosilicate (bisilicate) base coatings are equally promising and superior where acid resistance is also of concern.



Of interest also is the self glaze formed on the lead aluminosilicate low shrinkage type ceramic at 1950 F. This self glaze coating has practical importance since it possesses high water repellency and has high resistivity under high humidity as characteristic of lead glazes.



Relatively high lead bearing glazes are used on alumina, steatite and forsterite insulator bodies. The lead is important in providing high resistance to the formation of a moisture film on the surface thus assuring high surface resistivity.

USE OF LEAD IN CERAMIC BODIES*

As noted previously in this section, lead oxide has a number of interesting and increasingly important uses in ceramic bodies. This resume concerns primarily the lead fluxed electronic ceramic bodies. The unique properties developed and discussed herein may likely result in other than dielectric uses. Lead oxide has found increasing use also in other electronic ceramics, e.g., high dielectric constant, ferromagnetic, ferroelectric, piezoelectric and semiconducting ceramics.

For example, lead titanate may be added to barium titanate to increase the Curie temperature. Mixtures of lead titanate and lead zirconate have found use because of their excellent electromechanical properties over a wide temperature range. However, the importance of lead in these other electronic ceramics will be covered in later supplements to this Manual.

The ceramics covered in this paper are discussed in the following order:

A. Ultra Low Loss Ceramic Dielectrics
B. Low or Zero Shrinkage Ceramics
C. Other Low Temperature Bodies

*This resume, prepared by John H. Koenig, Edward J. Smoke, and S. DiVita involves results of research at the School of Ceramics, Rutgers, the State University, under the sponsorship of the U. S. Army Research and Development Laboratories.

ULTRA LOW LOSS CERAMIC DIELECTRICS

Ceramic dielectric bodies generally contain a glass and one or more crystalline phases. The dielectric loss is largely due to the dielectric loss of the component phases and in varying extent also to the elastic loss of the ceramic body. Therefore, in designing a low loss body the dielectric losses of the various phases and also the loss due to elastic causes should be minimized. The glass phase should contain ions, such as lead, with high valency and large electronic polarizability. The crystalline phase should not be piezoelectric. The proper amount of glass phase should be employed and good fabrication techniques to provide for a dense, void-free structure to prevent conversion of electrical to mechanical energy. The dielectric constants of the crystalline phase(s) and glass should be nearly the same. The ceramic body should be cooled slowly to provide for a more stable configuration of the networks and ions.

Early work showed wollastonite to be an excellent crystalline phase. This type of wollastonite ceramic, such as referred to briefly on page 2 of this Section, has provided for the lowest loss characteristics yet noted for any glass fluxed crystalline ceramic.

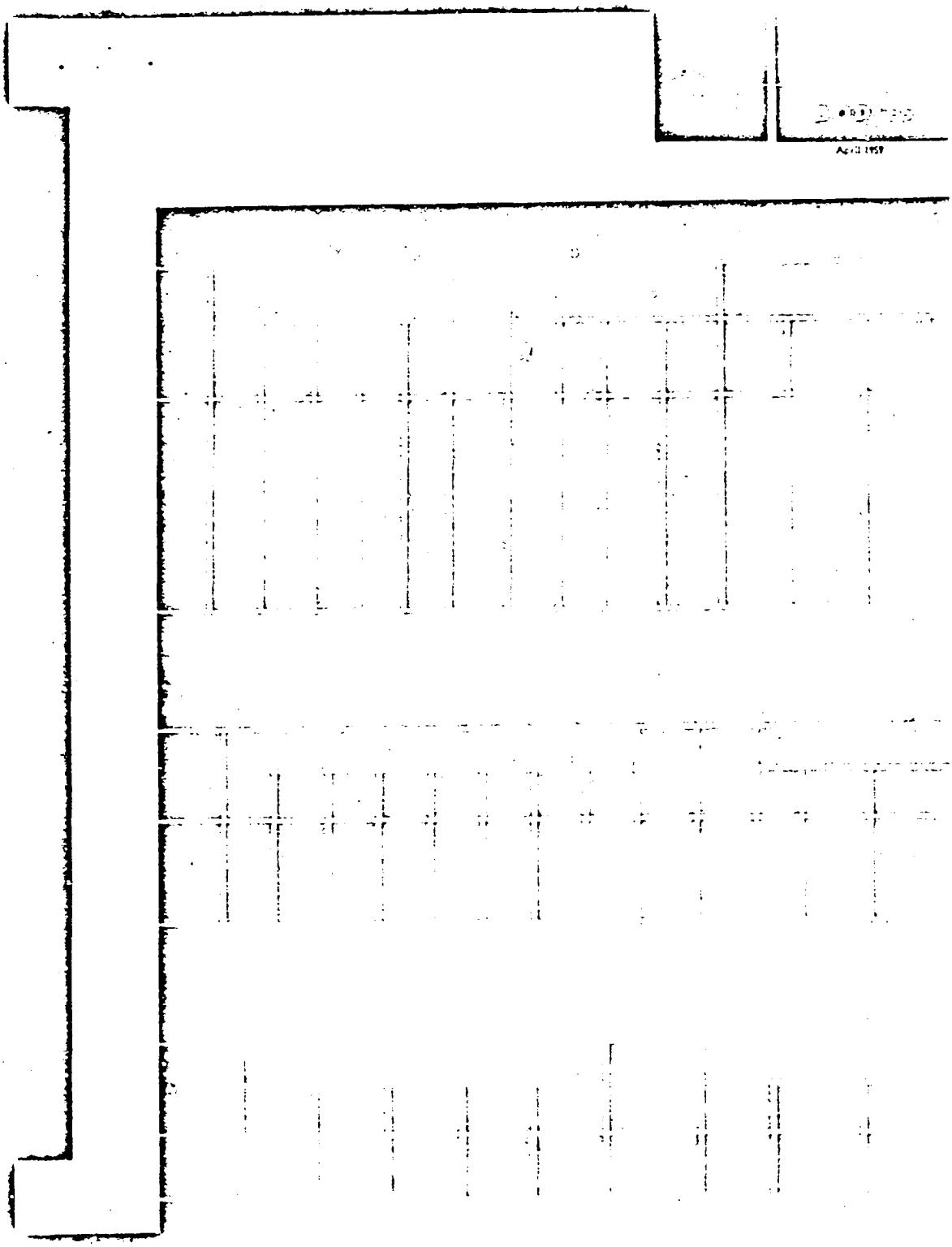
Table 7-1 shows the use of various amounts of lead fluxes (lead borate and lead bisilicate) in a wollastonite type ceramic. Table 7-2 shows the effects

of quartz and alumina additions to this type body. Table 7-3 presents properties of lead fluxed wollastonite bodies containing alkaline earths and other additives. Table 7-4 shows the composition of three lead fluxed wollastonite bodies, the dielectric properties being measured at 1, 8(00), and 25,000 megacycles. In the absence of lead the loss factor falls off to L-3 at 25,000 megacycles (See loss factors corresponding to JAN-I-10 L grades in note under Table 7-1). The best body, fluxed with lead bisilicate, remains L-5 at 25,000 megacycles. Table 7-5 provides some summary data in terms of specific compositions and includes strength values. Table 7-6 shows the effect of lead fluxes on a typical steatite body. These examples of ultra low loss dielectric bodies are dependent upon the lead flux to supply the glass phase.

LOW OR ZERO SHRINKAGE CERAMICS

The objective in designing low or zero shrinkage bodies is to provide for easier fabrication of parts where extremely small tolerances are a prerequisite. Obviously, the most desirable shrinkage would be zero.

The normal firing shrinkage which occurs in a



April 1959

ceramic is the result of mechanically and chemically combined water being driven off, evolution of gases due to dissociation of raw materials, formation of glasses and or crystalline phases of higher specific gravity, and filling of voids to produce a matured ceramic (zero moisture absorption). These mechanisms can result in firing shrinkage up to 30 percent. The principle involved in developing a dense ceramic of zero firing shrinkage consists of incorporating into the ceramic composite a predominance of a crystalline phase and or a glassy phase which upon firing will irreversibly invert to a phase of lower specific gravity; thus, this phenomenon compensates for the inherent firing shrinkage present in the body.

Research led to two types of ceramic bodies possessing zero firing shrinkage, a spodumene type and a lead aluminosilicate type composition. The spodumene type is not a true non-shrinking body but rather undergoes a relatively large firing expansion reaching a maximum of 10 percent at 1700 F and then gradually

shrinks to the zero shrinkage reference line at approximately 2000 F, see figure 7-1. Of the two compositions, the lead aluminosilicate body more closely approaches the characteristics of a true non-shrinking type ceramic. The firing shrinkage steadily increases to a maximum of about 2 percent at 1600 F and then gradually expands up to the zero shrinkage value at 2000 F, as shown in Figure 7-1. However, this type body had to be fabricated at relatively high pressure.

It was later found that additions of clay to the spodumene composition produced zero firing shrinkage at moderate fabrication pressures. Then, it was considered that perhaps similar additions of clay as well as other conventional ceramic materials to the lead aluminosilicate body might prove promising and in fact, led to low or even zero firing shrinkage ceramics fabricated at moderate pressures. Therefore, the lead aluminosilicate composition was chosen as the base formula for this new approach to the problem.

The lead aluminosilicate diagram, see Section II, Page 1, shows several binary and ternary compounds. Some of these were prepared as bodies and are plotted on Figure 7-2; the areas of crystallization are also shown. Table 7-7 shows the properties of some of these lead aluminosilicate bodies. The most promising body is the P-2 composition. Table 7-8 shows properties for P-2 and small modifications of this composition in its further development.

This is truly more of a non-shrinking body since it shrinks only about 2½ percent, then expands and comes back to the original size at maturity due to the development of a new crystalline phase (49.98 percent PbO, 20.05 percent Al_2O_3, and 29.97 percent SiO_2). See Figure 7-1. These bodies have not only low maturing temperatures but also long firing ranges and good dielectric properties.

Over the range 1700° to 2000 F the P-2 body showed water absorption values of 0.05 percent or less. Once vitrified as the temperature is increased, the glass starts to bleed out resulting in self-glazing. This self-glaze, being a lead aluminosilicate glass, does not detract from the good dielectric properties. Coatings of this type are highly desirable in maintaining high resistivity under extreme conditions of humidity for prolonged periods of time.

Table 7-9 presents summary data for the two approaches for the low shrinkage body.

Systematic addition of pyrophyllite, clay, zircon, petalite, wollastonite and alumina were made respectively to this lead aluminosilicate base body in 5 per-

cent increments up to 60 percent additions in some cases. These specimens were pressed using 8 percent moisture content (semi-dry pressing) and fired. The shrinkage data as presented in Figure 7-3 show the range possible from an expansion of 1.3 percent to shrinkage greater than 3 percent. The moisture content required for the type forming operation influences the firing shrinkage. The P-2 type body plus an additive (which would compensate for the shrinkage) was evaluated for extrusion, plastic pressing, dry pressing, and casting. Table 7-10 shows low shrinkage compositions as designed for the various fabricating techniques.

OTHER LOW TEMPERATURE BODIES

Lead frits were used in fluxing a large number of other low temperature bodies where the crystalline portion contained one or more of the following: alumina, clay, kyanite, spodumene, talc, wollastonite, zircon, and zirconates. A number of highly interesting bodies were developed maturing at low temperatures.

An example of the type of exploratory work carried out is given in Table 7-11. Zircon and several double silicates were used as the crystalline phases in two lead fluxed bodies; the 10 percent clay being added for workability. It will be noted that all these bodies mature at relatively low temperatures. For example, the zircon body A fluxed with 21 percent of lead borate and 10 percent clay has zero absorption at 1800 F. This is a grade L-4 body.

The following data show titania fluxed with lead borate to provide bodies of higher dielectric constant.

Titania	69%	66%
Lead Borate	21%	24%
Ball Clay	10%	10%
K	44	51
P.E.	0.00415	0.00092
Moisture Absorption (%) (1800-1900 F)	<0.05	<0.05

These bodies matured nicely in the range of 1800°F to 1900 F.

In the following data, calcined kyanite was the principal phase, the lead borate flux being held constant at 23 percent, and clay increasing at the expense of kyanite.

Calc. Kyanite	62%	57%	52%
Lead Borate	23%	23%	23%
Ball Clay	15%	20%	25%
K	6.01	5.31	6.08
P.E.	0.00110	0.00110	0.00111
L.F.	0.00661	0.00585	0.00675
Moisture Absorption (%) (1800-1900 F)	0.05	0.05	0.05

These provided nicely matured bodies in the range of 1800 F to 1900 F, which were L-5 bodies.

The controlled Ajax kaolins were studied extensively as the principal phases of lead-fluxed bodies. The Ajax P consists of 96 percent kaolinite plates and 4 percent stacks, all less than 2 microns in size. The Ajax S is composed of 30 percent plates and 70 percent stacks larger than 2 microns. Ajax SC has the large stack particles precalcined at 1000°C. These materials, when fluxed with various lead frits, resulted in many interesting bodies. The Ajax P (plates) provides for very smooth surfaces. Some of the results are generalized as follows:

1. Using 10 percent Ajax P, 40-60 percent Ajax S and 30-50 percent of the lead aluminosilicate frit (61.3 percent PbO, 3.1 percent Al_2O_3, 35.6 percent SiO_2), bodies were found to vitrify circa 2200°F for the higher fritted content. These bodies possessed good workability.

2. Using the calcined stacks (Ajax SC) in a similar series, matured bodies were obtained in the range 2100 F to 2200 F for the higher fritted contents (40-50 percent) of the above mentioned lead aluminosilicate frit.

3. In a series where the Ajax kaolins were the principal components, a number of bodies within the composition range shown were grade L-4 at temperatures of 2300 F to 2350 F.

	Composition Range (All Bodies)	*Body No. 38*	*52*
Ajax P	22-35	24	26
Ajax SC	38-60	41	44
$PbO \cdot B_2O_3$	0.20	25	30
$BaCO_3$	0-10	10	—
$CaCO_3$	0-10	—	—
$MgCO_3$	0-10	—	—
Talc	0-10	—	—

Two compositions (38 and 52) when fired at 2350°F were grade L-5. These bodies provide for good strength and relatively low shrinkage, since the stock content is pre-calcined. The use of these controlled materials also provides for very smooth surfaces as well as good dielectric properties.

Some of the lead fluxed wollastonite type bodies have been shown to provide for good impact resistance. A large number of bodies were studied involving 50-70 percent wollastonite, 30-50 percent clay, and 0-20 percent lead bisilicate and other additives. Table 7-12 presents data for one of the best of these bodies (B-32) in comparison with some high alumina bodies, the latter requiring considerably higher maturing temperatures. The addition of lead flux to the wollastonite bodies generally improved their impact resistance. The lead fluxed B-32 body, matured at 2080°F, had higher impact resistance (Charpy test) than a 90 percent Al_2O_3 body fired to 2970°F or approximately 900°F higher.

The foregoing examples show the use of lead fluxes in bodies to provide such properties as high strength, impact resistance, very smooth surfaces, good dielectric properties, etc., at relatively low temperatures.