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Conference Director

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A Message from the Technical Forum Chairman

We were delighted to have again this year more than 200 technical representatives in attendance at our annual PEI Technical Forum on the campus of The Ohio State University. It proved to be a particularly effective Forum with excellent papers and fine participation in the discussions following each one and in the informal gatherings during the meeting.

As is the case every year, a large number of people contribute to the success of this year's meeting. The committee, the Forum speakers, all those connected with the host University, the panel participants and an active and interested audience all played an important part in the success of the meeting.

As you know, plans for an annual technical meeting such as this begin almost immediately on completion of the previous year's session. Then, in the spring of the year, a hardworking Technical Forum Committee meets and begins to assemble candidate topics for presentation. After careful study, some 30 papers and panel presentations are agreed upon, participants lined up and papers are prepared for the Forum audience.

This year's Technical Forum began with the A.I. Andrews Memorial Lecture presented by Dr. Dale E. Niesz of Battelle Columbus Laboratories. He discussed some of the advancements being made in powder processing technology. Following his lecture, several papers devoted to advances in processing methods were presented with technology from overseas being introduced. Then, a series of papers dealing with developments in porcelain enamel powder applications followed. During the first afternoon session, attention was given to personnel and health aspects. These were followed by several papers on various phases of metal preparation. The day's sessions concluded with papers dealing with special markets for porcelain enamel and a report on a series of industry projects.

On Thursday, papers relating to firing and drying received attention. Then, several papers directed at environmental considerations followed. An important session was devoted to reports on the latest effluent regulations as they stood following the PEI-led litigation with the Environmental Protection Agency. A highlight of the last afternoon was an active Question and Answer session, and this was followed by papers reporting on laboratory investigations and a discussion of the latest in equipment development.

As I conclude my two years as chairman of the PEI Technical Forum Committee, I want to express my appreciation for the support of the officers and staff of the Porcelain Enamel Institute. Also, I want to especially thank the many individuals associated with our host Universities at Ohio State and Illinois, particularly Dennis Readey and Clifton Bergeron; they have done
many things to make us feel welcome and have contributed significantly to
the success of the meeting. Finally, I want to again thank members of the
committee, the speakers and the session chairmen for all of their efforts. We
look forward to seeing all of you at next year’s Technical Forum which will
be held again at Ohio State University on October 2 and 3, 1984.

James F. Quigley, Chairman
1983 Technical Forum Committee
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Ceramic powder preparation techniques are reviewed with an emphasis on new technology. Powder characterization technology is discussed with an emphasis on physical characteristics and their influence on microstructural development in powder compacts. The relationship between the physical characteristics of powders and the microstructural uniformity of sintered powder compacts is shown. The characteristics desired in a powder for advanced powder processing are reviewed.

Introduction

Ceramic powder processing is a very old technology. Ancient pottery-making involved ceramic powder processing. The powders used in early ceramic powder processing were natural minerals, such as clays, silica, and feldspar. Most powders used today in advanced ceramic powder processing are synthetic powders. Early investigators studied the relationships between raw materials and end properties. Microstructure is now viewed as an intermediate link between powder characteristics, chemistry and processing parameters, on the one hand, and properties on the other. In the 60's and 70's a lot of research on the relationships of powder processing parameters and powder characteristics to microstructure was not considered good research at that time by many investigators. In the 70's powder processing research began to be recognized as critical to achieving advanced properties. Today, powder processing is one of the key areas of ceramic research.

Of course, the key is the powder. A good job of powder processing with a bad powder will result in a bad material, and so will a bad job of processing with a good powder. Both a good powder and good powder processing are required to obtain a high quality materials. Ceramic technology is often paced by the quality of available powders. The prime example is alumina ceramics. The lack of high quality powders is a key limitation in the development of most of the advanced ceramics today.1,2

What characteristics are generally sought in the advanced powders for processing of advanced materials? Four of the key characteristics are particle
size, degree and strength of agglomerates in the powder, purity, and batch-
to-batch consistency. The desired particle size is usually between 0.1 μm and 1
μm. Above 1 μm a lot of reactivity is lost, and processing becomes much more
difficult below 0.1 μm because of inherent aggomeration due to van der
Waals forces. A uniform particle size is also desirable, since large grains
often act as strength limiting flaws and lead to discontinuous grain growth
during sintering. The powder should not be agglomerated. If a powder is ag-
gglomerated, the agglomerates should be weak so that they are easily reduced
to their ultimate particles. High purity and batch-to-batch consistency are
also important. In many developmental powders, "tramp" material and a
lack of batch-to-batch consistency are major problems.

**Powder Preparation Techniques**

**Categories**

Powder preparation techniques can be divided into six categories. These are:
- Comminution
- Calcination
- Precipitation
- Freeze-Drying
- Vapor Phase Reaction
- Sol-Gel.

**Comminution**

Comminution, or grinding of various kinds, has been a standard tech-
nique for powder preparation since its use in reducing raw materials such as
clay, flint, and feldspar to powders. Ball milling is the most common type of
comminution, but many other techniques such as vibratory ball mills, rod
mills, attritor mills, fluid energy mills, and shear mills are used. Comminu-
tion is also a standard technique of pretreatment for reducing the particle size
of powders prepared by calcination or other techniques.

**Calcination**

Calcination is a standard technique for preparing mixed oxide powders
from physical mixtures of single oxides or salts such as carbonates. Many
electronic oxides such as barium titanate and PBT (solid solutions of lead and
zirconium titanate) are conventionally prepared by this technique. Structural ceramic powders such as silicon carbide can be prepared by calcining
mixtures of silica and carbon. The nitridation of silicon by reaction with a
nitrogen-containing vapor phase at high temperature to form silicon nitride
can also be considered a form of calcination.

**Precipitation**

Precipitation is the most common technique for preparation of synthetic
powders and is usually used in conjunction with calcination and comminu-
tion to prepare a powder for green forming. Most aluminum oxide powders
are prepared by precipitation, and the development of alumina ceramics was
paced by the development and control of the precipitation process. In nonox-
ide ceramics one of the major barriers is the lack of high quality, reproduc-
ible powders. If ceramic processing technology is to move ahead, process
engineers need to gain control of the powder preparation process. It is difficult to make high quality ceramics without high quality powders. In the 1960's there was a lot of effort devoted to looking at the advantages of using various starting materials such as sulfates, chlorides, and citrates. Much of that work was rather empirical because we lacked knowledge of the relationships between powder characteristics and processing. Today there is a much better basis for understanding these relationships.

Coprecipitation is a technique for preparing precipitates consisting of more than one precipitate. Coprecipitation implies simultaneous precipitation of more than one precipitate. Generally, however, one phase precipitates first and the second phase precipitates around the first. As a result, atomic mixing is not usually achieved, although the mixing is more intimate than can be readily achieved by separate precipitation of the phases followed by calcination and blending by milling techniques.

Another type of precipitation is hydrolytic precipitation. This technique involves addition of water to a solution of organometallics in an organic liquid. Probably the best example of this technique is the development of Zitrite powders by hydrolytic precipitation of yttria-stabilized zirconia from mixed alkoxide solutions. This technique can be used to prepare very high purity powders, since the alkoxide precursors can be purified as organics. The major disadvantage is the cost of the alkoxides.

Hydrothermal precipitation is another precipitation technique that is being applied to the preparation of ceramic powders. This process involves precipitation at elevated temperatures and pressures. Pressures are usually under 10.3 MPa (1500 psi) and temperatures are under 300 °C. The major advantage of hydrothermal precipitation is the ability to form anhydrous oxides directly rather than precipitating a hydroxide or salt, followed by drying and calcination of the precipitate to produce an oxide powder. Hydrothermal precipitation also produces a non-agglomerated powder, thereby eliminating the need for milling. Other advantages include the ability to produce a uniform particle size distribution, the ability to incorporate dopants directly into the powder during precipitation, the ability to prepare high purity powders, and the ability to control particle shape for specific powder applications. The process has been used on a commercial scale to prepare catalysts, pigments and other materials.

Vapor-Phase Reaction

Vapor-phase reaction has been receiving considerable attention in recent years for the preparation of Si₃N₄ and SiC powders. It is a standard technique for preparation of titania pigments. The process used for titania preparation is a chemical vapor-phase reaction in which two or more vapor phases react to form powder particles in the vapor phase. Plasma vapor-phase reaction has been used to prepare Sialon powders, and laser vapor-phase reaction is being studied. Sol-Gel Techniques

Sol-gel technology is also applicable to advanced ceramic powder preparation. This technique involves the preparation of a sol and then conversion to a gel. The gel is dried, calcined and milled to prepare a powder for green forming. The principal advantage of the process is the atomic scale mixing that occurs in the sol particles, which are clusters of atoms over about
5 nm. Because of the atomic mixing, mixed oxide crystalline phases can be formed at considerably lower temperatures than by calcining mixed oxides or salts by coprecipitation.

**Powder Characteristics**

For convenience, powder characteristics can be divided into chemical, physical, and structural characteristics. Chemical characteristics include the concentration of major and minor elements as well as their distribution in the powder. The advances in analytical tools for chemical analysis have greatly improved the ability to characterize the chemistry of powders.

Structural characteristics include the phase composition of the powder and atomic scale defects. One important area in which analytical ability limits powder characterization is in identifying and quantitatively analyzing minor phases and the degree of inhomogeneity they give the powder and, ultimately, the degree of inhomogeniety they impress on the microstructure.

Some physical characteristics of powders are shown in Table I. Many physical characteristics of a powder are dominated by the agglomerate structure of the powder. As a result, powder processing parameters, microstructure, and bulk properties are often dominated by the structure and properties of the agglomerates in a powder. Some physical characteristics of agglomerates are shown in Table II.

Since the term “agglomerate” does not connote a consistent meaning among ceramic scientists, the following definition clarifies its use in this paper. An agglomerate is an assemblage of ultimate powder particles or crystallites which are held together by diffusion bonds, surface charges, van der Waals forces, and/or cementitious materials such as hydrates or organic binders.

The most common type of agglomerate in a commercial ceramic powder is one bonded by a diffusion bond formed during calcination. The structure and properties of agglomerates of this type vary widely depending on the precursor, preparation parameters, and calcination parameters. Such agglomerates are strong enough to retain their identity during green-forming. In a powder with a fine ultimate particle size, the agglomerates are often quite porous. This leads to a low powder bulk density and a nonuniform green compact, as will be shown later.

The agglomerates in calcined powders normally are broken down to their ultimate particles by ball milling in a water medium followed by spray drying. The resulting powder is composed of weak, spherical agglomerates or granules. Control of the characteristics of the spray-dried powder is a key element in many ceramic powder processes. The agglomerates in a spray-dried powder are held together by organic binders, plastic materials such as clay or talc, and by decomposed gels or hydrates precipitated from solution during drying. Agglomerates in calcined powders can also be broken down by dry milling. The resulting powder is composed of weak, dense agglomerates.

A type of agglomerate that is not widely recognized is one bonded by decomposed gels or hydrates. Such agglomerates form by precipitation of cations from solution when water slurries are dried. Some bonding may also occur between the hydrated surface layers of the powder particles. The strength of the resulting agglomerate depends on the percentage of bond phase. For high surface area powders, this type of bonding can produce strong agglomerates as will be discussed later.
Most active powders contain agglomerates of some kind. To fully characterize the physical properties of the powder, the influence of agglomerate character must be taken into account. The first step in evaluating a powder and its agglomerate structure is microscopic evaluation to obtain a physical picture of the powder and its agglomerates. This provides a basis on which to interpret the results of other characterization techniques. Characterization of agglomerate strength is a good illustration of the importance of a physical picture to interpretation of characterization data.

### Agglomerate Strength

The strength of the agglomerates in a powder can be determined from powder compaction data. By this technique, the relative strength of the agglomerates in a powder is related to a break in the compaction curve when the logarithm of pressure is plotted against percentage of theoretical density.

The compaction data for an alumina powder in the as-calcined, wet-milled, and dry-milled conditions is shown in Fig. 1. Data for an aluminum powder are also shown. The data are plotted as the logarithm of pressure versus percentage of theoretical density. The break in the curve for alumina indicates the pressure at which plastic deformation of the powder particles at their contact points begins to control the compaction behavior.

Alumina I in the unmilled, calcined condition contains two distinct types of agglomerates. An electron micrograph of this powder is shown in Fig. 2. The break in the curve at 2.07 MPa (300 psi) for this powder indicates the pressure at which crushing of the contact points of the porous agglomerates begins to control the compaction behavior. Thus, the strength of the agglomerates composed of 10 to 20 nm ultimate particles is indicated by this break point.

The curve for Alumina I after milling in water for 20 h shows a break point at approximately 20.7 MPa (3000 psi). This indicates the presence of strong agglomerates. Figure 3 shows an electron micrograph of this powder. The translucent web-like material that can be seen around the edges of the agglomerates has been identified as aluminum monohydrate by thermogravimetric analysis. This hydrate acts as a cement which bonds the agglomerate particles together.

The curve for Alumina I after dry milling for 20 h does not exhibit any breaks between 0.07 and 689 MPa (10 and 100,000 psi). The only agglomerates in this powder are those held together by the small amount of dry-milling aid. These are so weak that their presence is undetectable by this technique.

The strength of agglomerates or granules in spray-dried powders can also be determined from compaction data. This technique is quite sensitive to variations in the strength of spray-dried granules, and it can be used as an effective quality control technique. Compaction data can also be used to determine the pressing pressure required to close the voids between spray-dried granules.

There is an upper limit of agglomerate strength that can be evaluated by this technique, and the presence of such agglomerates must be determined microscopically. The coarse-particle agglomerates in Alumina I shown in Fig. 2 is an example of an agglomerate whose strength cannot be determined by this technique at pressures below 689 MPa (100,000 psi).