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INVESTIGATIONS INTO THE BURNING-OUT OF ORGANIC SUBSTANCES IN THE CERAMIC BODY

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16. Abstract  Pressed compacts were made of spray-dried alumina containing water-soluble polyvinylalcohol or cellulose derivative binder. The burning out of organic binder on gradual heating was investigated by visual and microscopic observations of the cross section and by thermogravimetry. Burning out proceeds inward from the peripheries, gradually reducing the size of the black core, which first consists of a dark boundary layer and later turns uniformly black with a sharp boundary. A detailed mechanism of the burning-out process between and within the spray-dried granules can be observed under the microscope. Oxygen atmosphere accelerates the burning-out process. pp. 6			
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INVESTIGATIONS INTO THE BURNING-OUT OF  
ORGANIC SUBSTANCES IN THE CERAMIC BODY

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The process of burning off organic substances at various temperatures is demonstrated with the aid of investigations of body structure. These results are augmented by thermo-gravimetric investigations. The comparative discussion forms a contribution to the understanding of the possible formation of "black cores".

1. Introduction

The production process of ceramic articles often requires the addition of organic substances to the raw material, which must again be driven out of the molding in the subsequent burn. These additives are basically required by the chosen shaping process, which sometimes is only possible (e.g. injection molding) or becomes optimized and rationalized through such additives.

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Thus, for example in the production of slips, organic additives are used that extensively influence the liquefaction properties, formation and strength of the body, and the shaping properties. Binders are added in spray drying in order to enhance the strength of the granules and the green product. Waxes are rather often used as lubricants, which for example reduce the friction between the die wall and also between the primary particles in molding and thereby lead to a more uniform density of the green product. In this manner it is attempted to reduce the density gradients in the body in order to obtain a homogeneous texture.

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\* Numbers in the margin indicate pagination in the foreign text.

These organic additives must be uniform driven out of the body as soon as possible during the burn, as they may hinder the sintering.

Thus the burnout process, as well as the method of the burn, acquires an important influence on the properties of the end product.

The burn out of organic additives can be initially described in three simplified stages:

- thermal decomposition of the organic additives (e.g. Moviol, tylose).
- diffusion of gases through the available porosity into the furnace space.
- oxidation of these gases in the furnace space and in the ceramic body in dependence on the available pore space.

Depending on the type of organic component, the thermal decomposition takes place at various temperatures and can begin as early as 200°C. Thus the burnout process falls within the heat-up phase of the burn, which generally may take place quickly (fast burn over). The completeness of the burnout largely depends on the diffusion resistance of the molding and the available time. As the burn proceeds, the porosity diminishes and the pores become smaller. Thus, with increasing temperature, an increasing resistance is offered to the diffusion of gas.

If molded ceramic objects with large green density are being burned, it is possible that the pore channels necessary for the diffusion processes have already been closed before the burnout is finished. The application of a glaze to the green body intensifies this process, so that swelling and cracks can result from

the buildup of gas pressure. If the burnout process is only incomplete, so-called "black cores" remain in the fired structure.

## 2. Investigations

The formation of black cores in ceramic bodies was investigated by the example of uniaxial-molded, spray-dried alumina (Table 1). Small cylindrical specimens ( $d = 20$  mm,  $h = 7.5$  mm) of sample 1 were heated in a Simon-Müller furnace and taken out at different temperatures. After cooling to room temperature, the objects were embedded in synthetic resin, cut out, and photographed.

Table 1. Investigated samples (alumina: Alcoa Al6)

Specimen	Percentage of Binder (Moviol, tylose) %	Moisture Content %	Bulk Density, $g/cm^3$
1	3	$\approx 1.2$	1.38
2	5	$\approx 1.2$	1.05

In parallel a thermogravimetric investigation was made on an additional specimen. Fig. 1 shows the burnout of the binder as a function of the temperature. In this figure the curve has been supplemented with macro-photographs of the sectioned specimen.

At about  $200^\circ C$  the curve displays a sharp inflection. We may conclude from this that the removal of the residual humidity of 1-1.2% is complete and that the burnout of the binder now begins.

It becomes evident that the burnout of the binder proceeds

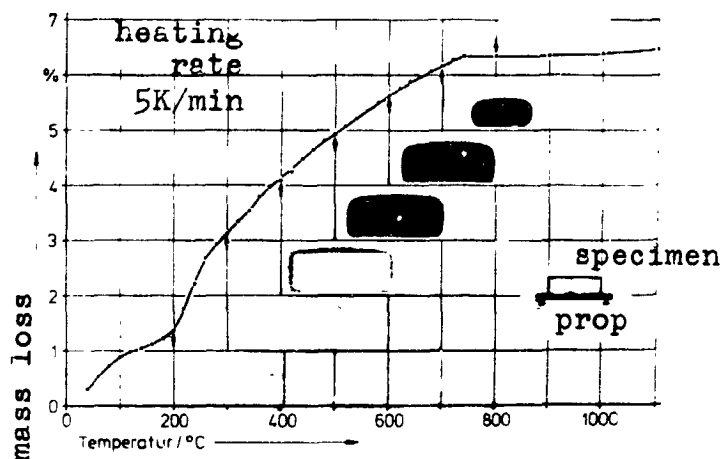


Fig. 1. Thermogravimetric analysis of specimen 1, showing the specimen cross sections.

from the outer toward the inner margin. As the bottom edge of the specimen is little exposed to convection on account of the necessary backing, the burnout is impeded at that place and is only incomplete at first. Under closer consideration it appears that the core of the specimen is separated by a dark ring from the outer rim of the body, which is already burned white. We shall discuss this phenomenon further below.

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The observations allow the following initial conclusions. The organic components decompose into gases, as mentioned. With rising temperature, pure amorphous carbon splits off and can result in formation of black cores, so that it must be oxidized by inward-diffusing oxygen. It can then leave the body as CO and CO<sub>2</sub>. This has been described by Otto in similar form [1]. The formation of black cores thus depends significantly on the partial oxygen pressure of the furnace atmosphere.

### 2.1. Experimental Firing with Nitrogen and Oxygen Injection

If the formation of black cores is to be attributed, as assumed, to the deposition of carbon, i.e. an incomplete oxida-

tion of this carbon, the entire body would therefore be uniformly black in color during a firing under protective gas.

Specimens heated to various temperatures in a silit tube furnace with  $N_2$  spray revealed a uniform black coloration. On the contrary, during a firing with oxygen spray no formation of black cores was observed. This also shows that the deposits are in fact attributable to carbon. Oxygen injection is therefore a prospect for avoiding the formation of black cores. The slow and early burnout of the binder at low temperature is a more interesting and economical possibility for the practical prevention of deposits of organic additives.

#### 2.2. The Burnout of Binder at Low Temperature with Lengthy Holding Time (Specimen 1)

In the Simon-Müller oven, six molded objects of alumina No. 1 were heated to  $270^\circ C$  and taken out after various holding times. In parallel, the loss in mass was measured on a thermal balance for one specimen (Fig. 2). After a holding time of 67 h, the specimen was again heated. At  $1000^\circ C$  no further mass loss could be detected.

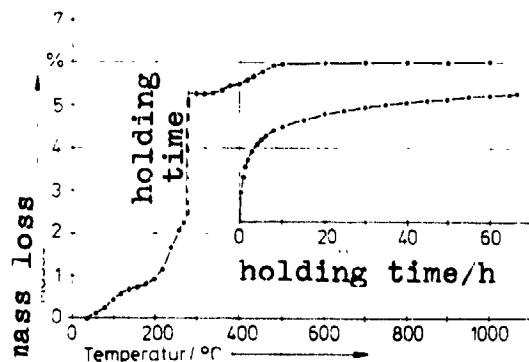


Fig. 2. Thermogravimetric analysis of specimen 1. Holding time 67 h at  $270^\circ C$ .

The specimens taken out after various holding times show that no black core was formed. Except for a minor blackening at the outer margin, the binder is quite uniformly burned out in this case. After a holding time of 5 h, the majority of the binder is already burned out.

This investigation shows that even at relatively low temperature the majority of the binder can be burned out.

### 2.3. Burnout of Binder and Observation of Black Cores in Specimen 2

Similar studies were done on specimen 2 as well. For this, five specimens were prepared and fired in the Simon-Müller furnace. At 200°C and thereafter, a sample was taken for every 100 K, vacuum-impregnated after cooling, and prepared for study by light microscope [2]. The macro-photographs are shown in Fig. 3. For the sample taken at 400°C, an enlarged section under the reflected light microscope was also prepared. This is shown by Fig. 4.



Fig. 3. Section of specimen 2:  
a - 200°C; b - 300°C; c - 400°C;  
d - 500°C; e - 600°C.



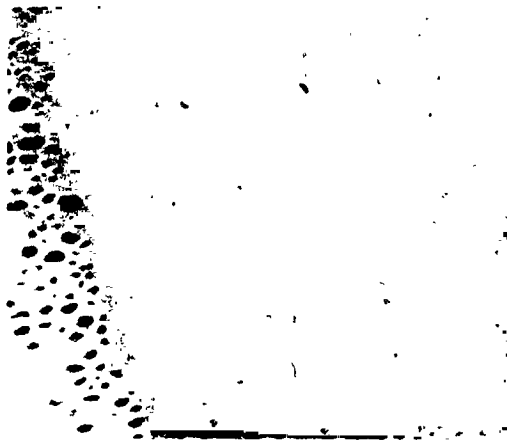


Fig. 4. Detail magnification of  
Fig. 3c.

The burnout of binder begins at the granule margins, which become visible to the naked eye by deposition of carbon. This picture (Fig. 4) of the granulates in the green texture further allows an assessment of its deformation and orientation during the compaction process [3]. At a further temperature rise to 300°C the formation of a dark ring becomes clear, as also observed in the study of specimen 1. At a temperature of 400°C, completely black granules with white border precipitate in the outer rim of the body, which is already burned white. This is especially clear in the magnified section of Fig. 4.

These pictures allow a more extensive interpretation of the burnout process. For this, the properties of the granules must be especially consulted. In the interpretation of the findings given here it became evident that it is necessary to examine more closely the influence of oxygen on the decomposition reaction. Therefore, a further thermogravimetric investigation was made.

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#### 2.4. Investigation of the Oxygen Influence

The aim of this investigation was to prove that the oxygen produces a pre-oxidation of the binder and that this decomposes

more easily as a result of the consequent instability.

Two thermogravimetric investigations of alumina No. 1 were done on the thermal balance. The specimens weighed 50 mg and were heated as loose powder in a platinum crucible. The heating rate was 5 K/min and the gas sweep was 2.5 dm<sup>3</sup>/min.

Specimen "a" was heated to 200°C under oxygen sweeping and then held at this temperature for 65 min. Then, at the same temperature, a switch was made to nitrogen sweeping with holding for an additional 45 min. After this, it was again heated to 1500°C. Specimen "b" was processed under nitrogen alone as a reference sample. The TGA curve (thermogravimetric analysis) and the respective temperature curve are shown in Fig. 5 and 6.

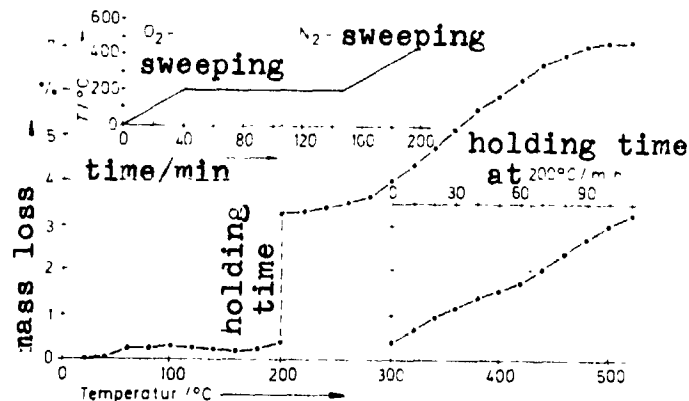


Fig. 5. Thermogravimetric analysis and temperature curve of specimen "a".

The heating to 200°C under nitrogen results in a mass loss of 1.2%, which can be explained by the evaporation of the residual moisture. A similar heating to 200°C under oxygen produces a lesser mass loss of only 0.6%. Since we must assume that a residual moisture of 1.2% is also evaporated in this case, the measurement finding can only be explained by an accumulation of oxygen.

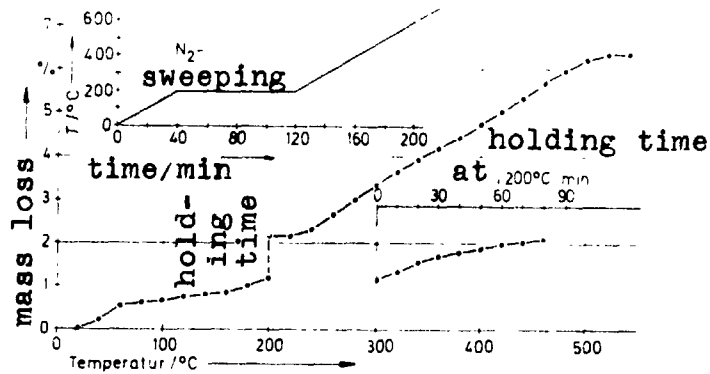


Fig. 6. Thermogravimetric analysis and temperature curve of specimen "b".

When 200°C is reached, the binder starts to decompose in both specimens. Under oxygen sweeping the mass loss takes place more quickly than the nitrogen sweeping. After changing from oxygen to nitrogen sweeping in experiment "a", there is a larger rise in the curve, explained by the now-absent overlay caused by the oxygen uptake.

Comparison of both curves shows that in experiment "a" after a holding time of 80 min a larger amount of binder is burned out and the later burnout process takes place more quickly. The 0.5% smaller mass loss of specimen "b" indicates the much more intense deposition of carbon.

The finding is significant for practical purposes, as it shows that a heating under sufficient oxygen excess produces a later accelerated decomposition of binder even at low temperatures. In this manner, formation of black cores can be avoided.

### 3. Summary and Interpretation

The heating of the specimen produces a thermal decomposition of the binder, starting at about 200°C. The liberated gases

diffuse from the specimen into the furnace space. At increasing temperature, carbon is liberated.

A second reaction, having decisive influence on the burnout process, is superimposed on this decomposition when there is sufficient oxygen in the furnace space. Depending on the available partial pressure, oxygen diffuses into the specimen and is deposited on the binder. This reaction begins at quite low temperatures. As a result of this oxygen uptake, the organic chain becomes unstable and breaks down more quickly. It is to be assumed that the decomposition products also take up oxygen and further decompose. The resulting carbon is oxidized to CO and CO<sub>2</sub> and diffuses out of the specimen.

The oxygen diffusing into the body encounters a diffusion resistance that varies in time and space. It is very dependent on the porosity. This can explain why the thermal decomposition is at first more intense at the granule boundaries than in the granules themselves. This was observed with special intensity in the case of specimen 2. The oxygen required for oxidation of the binder can be supplied more quickly across the grain boundaries than from the outer shell into the grain interior. This is explained by the densified porosity between the grains, which can still be detected in part in the fired texture.

Under stronger heating the decomposition and oxidation of the carbon take place more quickly and also extend to the grain interior in the areas of the specimen where the partial oxygen pressure is larger. The oxygen required for these reactions is at first available only in the boundary layer of the body, with the exception of the bottom surface, which is only slightly exposed to convection. The drop in the oxygen pressure in the marginal zone is shown schematically in Fig. 7.

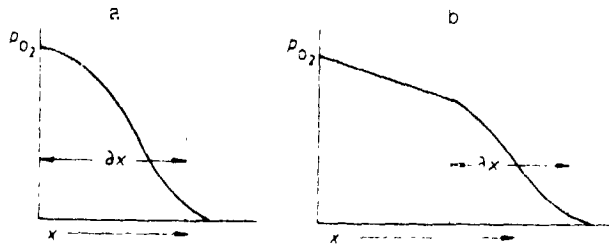


Fig. 7. Schematic representation of the partial oxygen pressure at (a) 300°C and (b) 400°C.

The oxygen is instantly consumed at the outer margin of the specimen. It settles on the binder. Thus, in the oxygen-free boundary zone there is an intensified cracking of the binder and also an intensified deposition of carbon. The oxidation of the carbon also takes place from the margin of the specimen toward the interior, but at low temperatures not to the same extent as the oxidation and decomposition of the binder. Thus, at the margin of the specimen a dark ring is formed.

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After the completed burnout of binder from the marginal zones, the diffusional resistance becomes smaller in that place and the oxygen pressure rises, as there is no more oxidation in this zone. The boundary zone  $\Delta x$  therefore shifts toward the interior of the specimen, as shown in Fig. 7b.

The dark-colored grains, located in the specimens pressed from alumina No. 2 shortly in front of the dark ring in the margin of the body that is already burned white, reflect these processes. If the grain surface is free of carbon, there is an intensified diffusion of oxygen into the core. The binder will now also decompose in the core of the grain, liberating carbon. Due to the improve diffusion pathways along the boundaries of the granulate, the carbon in the interior of large grains is oxidized more slowly, and the dark spots in the picture are formed.

The difference between a diffusion across grain boundaries and into the interior of the grains is the larger as the grains are more dense. A perfect sphere (approximately) only obtains in the case of specimen 2, however, as studies of the grains have shown [4]. Spray-grain No. 1 consists for the most part of open hollow spheres. This is attributable to the larger proportion of binder. For this reason, there is no distinct difference between the margin and interior of the granules in specimen 1. The oxygen is supplied almost equally to both the outer and inner surface of these hollow spheres. Therefore the carbon is burned more uniformly out of the granules.

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