

Effect of oxides on binder burnout during ceramics processing

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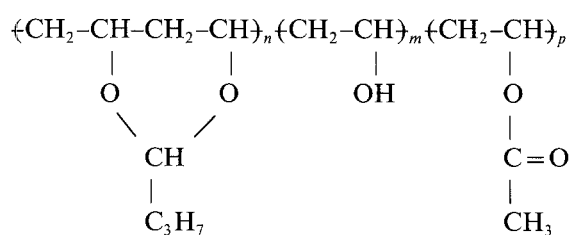
The burnout of poly(vinyl butyral) from green bodies of oxide ceramics was studied by thermogravimetric analysis and infrared spectroscopy. The decomposition of the polymer to release butyraldehyde, in air or in argon, was enhanced by the presence of the oxide powders. The degree of enhancement was much greater in the presence of oxygen. Ceria gave rise to a separate oxidation process at lower temperatures. The concentration of carbon remaining after treatment to 1000° C was correlated with surface activity.

1. Introduction

In processes such as the tape-casting or moulding of ceramics, it is very important to control the burnout of the organic binders, both to prevent the development of flaws and to minimize carbon residues that may inhibit sintering. The minimization of carbon residues is particularly important when the ceramic is co-fired with an oxidizable metal such as copper, since the reducing conditions aggravate carbon formation.

Poly(vinyl butyral) (PVB) is widely used as a binder in tape-cast electronic ceramics for substrates and for multilayer technology [1]. The effect of PVB burnout on the quality of the final ceramic tape has recently been studied by Otasuka and Ogihara [2]. In a normal formulation, the polymer is heavily plasticized and may contain residual solvent from the casting process [3]. It is reasonable to assume that these low-molecular-weight species will mainly be lost by vaporization below 200° C, so we can limit our discussion of high-temperature burnout to the polymer.

PVB is prepared by converting poly(vinyl acetate) to poly(vinyl alcohol) and reacting this with butyraldehyde. The process usually leaves a small fraction of the acetate side groups ($p \approx 2$ wt %) and up to 20% of the alcohol groups ($m < 20\%$) originally present. The hydroxyl and acetate groups promote adhesion of the polymer to ceramic surfaces and thus may be important for the mechanical properties of the green tape. The PVB structure is given below:



The decomposition of PVB in a vacuum at 250° C has been studied by Bakht [4], who observed the

elimination of water and butyraldehyde. The water is believed to arise from dehydration of vinyl alcohol units, and Bakht proposes both a free-radical mechanism and an intramolecular elimination as the source of butyraldehyde. Sacks and co-workers [5, 6] have recently completed similar studies on the decomposition chemistry of ceramic green bodies containing PVB. Decomposition of the related polymer poly(vinyl formal) has been studied by Beachell *et al.* [7], who found that formaldehyde production was responsible for about 25% of the weight loss at 150° C. They proposed an oxidative mechanism for the formation of formaldehyde. Changes observed in the infrared spectrum of the polymer included loss of the formal and C-H bands, an early increase in the intensity of the carbonyl band, and the subsequent formation of C=C bands at 1612 and 910 cm^{-1} .

For a number of reasons, the decomposition of binder in a green ceramic body is more complex than the decomposition of a thin polymer film. Transport rates modify the reaction kinetics; both the diffusion rate of oxygen into the polymer and the flow of decomposition products out. As in the case of a pure polymer, it must also be borne in mind that the primary decomposition products themselves may undergo further reaction in the gas phase. The ceramic powder also plays a role in the reactions and may catalyse the decomposition or react directly with the polymer.

A complete understanding of the mechanisms of polymer decomposition in ceramics is not to be expected. Analyses of the decomposition of pure polymers without any particles present [8, 9] are generally only satisfactory for the initial stages of degradation. Studies of the decomposition of simple hydrocarbons on surfaces only allow detailed interpretation in the case of very clean, well-characterized surfaces at low pressures.

This paper is the first of a series dealing with the

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TABLE I Materials used

Material	Manufacturer	Type
PVB	Monsanto Plastics (St. Louis, Missouri)	Butvar™ B-76
Al ₂ O ₃	Sumitomo Chemical Co. (Tokyo, Japan)	AKP-HP
TiO ₂	TAM Ceramics, Inc. (Niagara Falls, New York)	0.3 to 1.0 μm
Cr ₂ O ₃	Matheson, Coleman, and Bell (Norwood, Ohio)	CX1600
ZrO ₂	Toyo Soda (Tokyo, Japan)	TSK Z0040794
SiO ₂	City Chemical Corporation (New York)	18M119
CeO ₂	Alfa Products (Farmingham, Massachusetts)	REO # 21109
Toluene*	Mallinckrodt (New York)	-

*Dried with a molecular sieve.

effect of oxides on the burnout of binders. Here we show that oxides have a strong catalytic effect and that the magnitude of the effect on decomposition rate and on carbon residue is very dependent on the chemistry of the oxide surface.

2. Experimental procedure

The PVB used here included up to 10% vinyl alcohol groups and 2% acetate groups in addition to the butyral groups. This PVB and the ceramic powders employed were dried in a vacuum oven at 100°C until used. The materials used are listed in Table I.

PVB-ceramic oxide films were produced under a nitrogen atmosphere in a glove box (to reduce the effects of atmospheric water and oxygen). PVB (0.6 g) was dissolved in 69.6 g toluene, and the solution was stirred for 30 min, after which time 30 g of a ceramic powder was slowly added.

The slurry was then stirred for 1 h, covered, transferred to an ultrasonic bath for 1 h, and returned to the glove box. An eyedropper was used to transfer the slurry to a microscope slide until the slide was completely wet. The slide was left to dry in the glove box for 12 h, then transferred to a desiccator. After drying, the film contained 2 wt % PVB and 98 wt % ceramic powder, as confirmed by thermogravimetric analysis (TGA). The slides were then placed in a vacuum oven at 100°C for 24 h, and finally transferred in a portable

desiccator (to prevent moisture adsorption) to the Perkin-Elmer TAS7 thermogravimetric analyser (Hartford, Connecticut), where they were heated in argon (60 p.p.m. O₂) or air at 5°C min⁻¹ to various temperatures.

For studies on pure polymer it is desirable to have the same thermal mass as the composite films; this sample consisted of PVB and a fused quartz disc which was not in contact with the polymer.

TGA-infrared spectrometry experiments were used to analyse the gases that emerged as the composite films were heated in argon (60 p.p.m. O₂) or air to various temperatures at a rate of 5°C min⁻¹ in a DuPont (Wilmington, Delaware) thermogravimetric analyser. The gases released were passed through a heated transfer line (250°C) and into either a Harrick Scientific (Ossining, New York) TGC-S10 gas cell with double windows (outer KBr window, inner ZnSe window) having a gas path length of 3 mm and a volume of 2 ml, or into an Accuspec (London, UK) Model 36 gas cell with a path length of 3 mm and a volume of 0.4 ml. The same results were obtained using both cells in an IBM-85 Fourier transform infrared spectrometer (FTIR) (Danbury, Connecticut).

Carbon combustion analysis using a Leco (St. Joseph, Michigan) combustion analyser was performed to determine the carbon-residue concentration after firing each film at selected temperatures under different firing conditions. The isoelectric point (IEP) of each of the powders was determined using an HVB-77 Zeta Meter (Zeta Meter, Inc., New York); all measured IEPs agreed with published values [10].

3. Results

The TGA plots show that PVB decomposes in three stages when heated at 5°C min⁻¹ in argon (Fig. 1) or in air. FTIR spectra (Fig. 2) of the gas evolved from heating PVB in argon at 5°C min⁻¹ show that at 250°C (Stage 1, Fig. 2a) the major product was water, with broad bands at 3250 and 1650 cm⁻¹. This presumably included both moisture trapped within the sample and water released by dehydration of vinyl alcohol units (-CH₂-CHOH-) to leave -CH=CH-.

On heating to 350°C (Stage 2, Fig. 2b), the evolved gas shows major bands appearing at 2958, 2806, 2230 and 1744 cm⁻¹. The band at 2230 cm⁻¹ is due to CO₂, showing that some oxidation was occurring. Most of

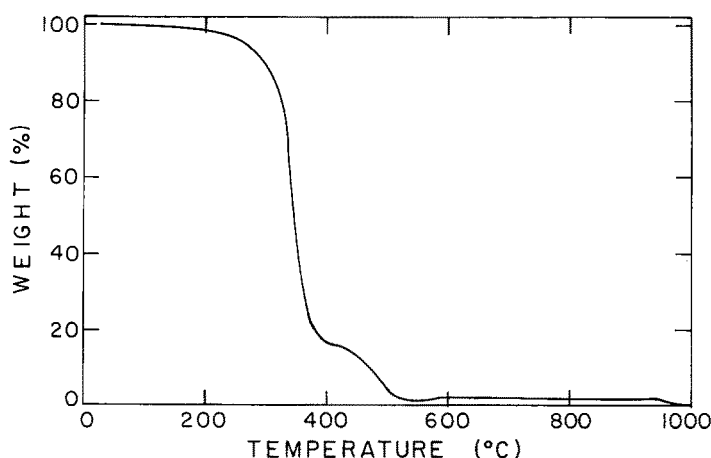


Figure 1 TGA plot of PVB decomposed in argon at 5°C min⁻¹.

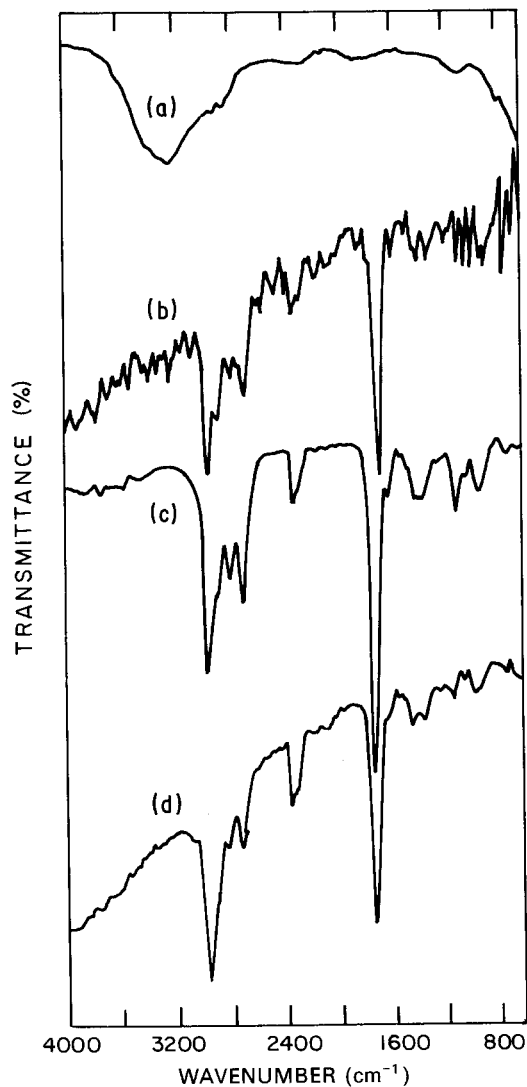


Figure 2 FTIR spectra of gases evolved from PVB when heated at $5^{\circ}\text{C min}^{-1}$ in argon (60 p.p.m. oxygen) to (a) 250°C , (b) 350°C , (c) 420°C , (d) 500°C .

the remainder of the spectrum can be accounted for by butyraldehyde. The spectra for products evolved at 420 and 500°C (Figs 2c and d) are similar, except for changes in the relative intensities in the C-H region around 3000 cm^{-1} . A small peak at about 1640 cm^{-1} and a splitting of the carbonyl peak suggest that some crotonaldehyde also formed. A peak at 1602 cm^{-1} also indicates unsaturated products.

Heating the PVB in air at 180°C caused an increase in carbonyl content and a decrease in C-H and C-C

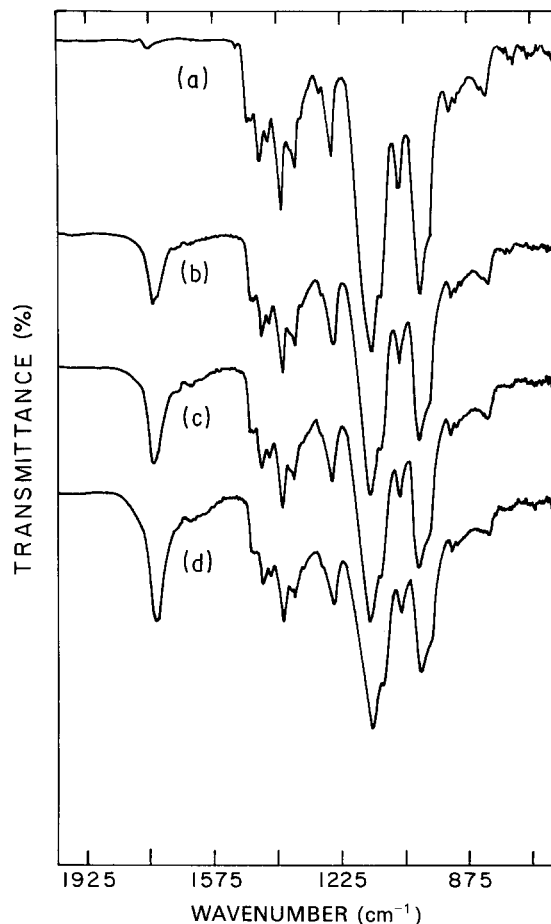


Figure 3 FTIR spectra of PVB residue heated at 180°C in air and held for (a) 5 min, (b) 10 min, (c) 40 min, (d) 60 min.

absorption bands, as would be expected both from oxidation of the polymer and from the slow release of butyraldehyde (Fig. 3).

In the presence of each oxide, the three decomposition stages of PVB in air were shifted to lower temperatures (Fig. 4); up to 1% of the polymer remained as a residue, however, which burned out as a fourth stage above 700°C (Fig. 5). All the oxides except CeO_2 and ZrO_2 reduced the temperature of maximum weight loss by about 100°C with respect to pure PVB. ZrO_2 reduced the initial burnout temperature by only 40°C (to 280°C), but CeO_2 reduced the initial burnout temperature by almost 200°C . The CeO_2 powders also showed the highest catalytic activity; burnout was almost complete by 165°C

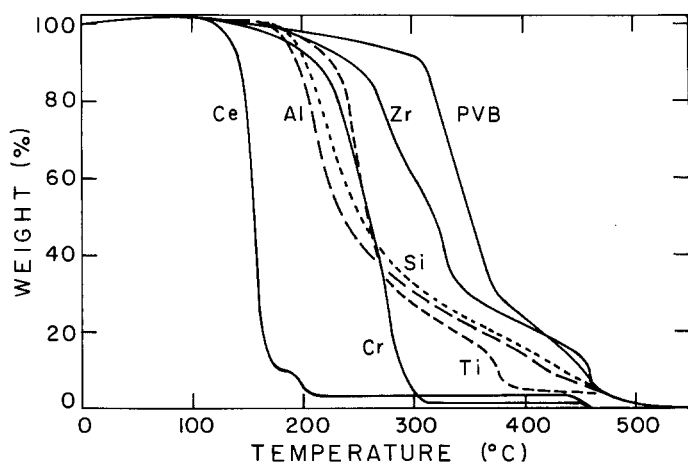


Figure 4 TGA plots of PVB decomposition from films containing 2 wt % PVB and 98 wt % of various oxides and heated in air at $5^{\circ}\text{C min}^{-1}$.

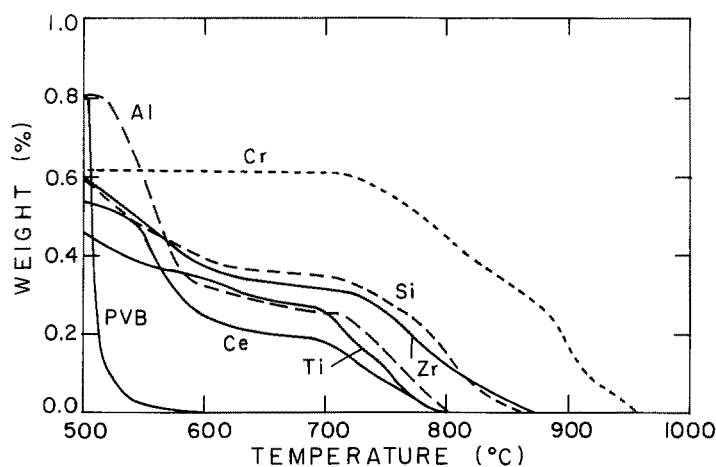


Figure 5 Carbon residue elimination from oxide films originally containing 2 wt% PVB, and containing 0.8 wt% or less of original PVB weight at 500°C when heated in air at 5°C min⁻¹.

(Fig. 4), and the remaining polymer residue was decomposed below 700°C.

On heating PVB in air with any of the oxides, the amount of carbon residue at 600°C was in the range of 0.2 to 0.4 wt% of the original PVB; pure PVB left essentially no carbon residue. Thermogravimetric analysis shows that CeO₂, TiO₂, and Al₂O₃ (Fig. 5) were most effective in subsequently removing the carbon residue on heating above 600°C in air. Cr₂O₃ apparently does not allow carbon residue removal below 900°C.

Fig. 6 shows the decomposition of PVB when mixed with oxide powders and heated in argon. All the oxides reduced the initial PVB decomposition temperature by 30 to 50°C. After heating in argon, the amount of carbon residue at 650°C was in the range of 0.5 to 1.0 wt% of the original PVB in the presence of all the oxides. Again, pure PVB left essentially no residue.

When Al₂O₃-PVB films were heated in argon at 5°C min⁻¹, the FTIR indicated a similar pattern of evolved gas to pure PVB, with the presence of water at 180°C, and butyraldehyde and some unsaturated products at 250°C and above. A coke residue remained at 540°C. Another FTIR spectrum showed a coke residue on the Al₂O₃ surface after heating at 700°C in argon (Fig. 7).

For a CeO₂-PVB film fired in argon, the picture is similar to that for the decomposition of PVB alone except for the fact that CeO₂ caused PVB to oxidize, as shown by the intense CO₂ peak present in Fig. 8 at 2200 cm⁻¹ throughout PVB decomposition, and

the fact that only highly oxidized products formed at high temperatures. This CO₂ absorption band also appeared during the decomposition of TiO₂-PVB films.

Carbon analysis of the Al₂O₃-PVB samples heated in air and argon to various temperatures showed 260 p.p.m. carbon residue when the composite was fired in air at 5°C min⁻¹ to 700°C. The carbon concentration was reduced at higher temperatures; the powder contained 80 p.p.m. residue when heating to 1000°C. Table II shows the amount of carbon residue left after various oxide-PVB films were heated in air and in argon at 5°C min⁻¹ to selected temperatures. Under these conditions, TiO₂ and CeO₂ exhibited the least amount of carbon residue.

4. Discussion

Most polymers oxidize by a free-radical mechanism when heated in air. One characteristic of this process is an increasing carbonyl content which is detected by infrared spectroscopy. A free-radical mechanism for the oxidation of poly(vinyl formal) has been proposed by Beachell *et al.* [7]. PVB can also decompose by a cyclic-elimination mechanism to release butyraldehyde, with associated chain breakage to leave aldehyde and unsaturated end-groups (Fig. 9) [4]. In the late stages of this process, various products including crotonaldehyde and unsaturated hydrocarbons form by breakage at adjacent sites. Such a mechanism is consistent with the second stage of the decomposition process in which 73% of the weight is lost. Butyraldehyde corresponds to 52% of the nominal composition. We would

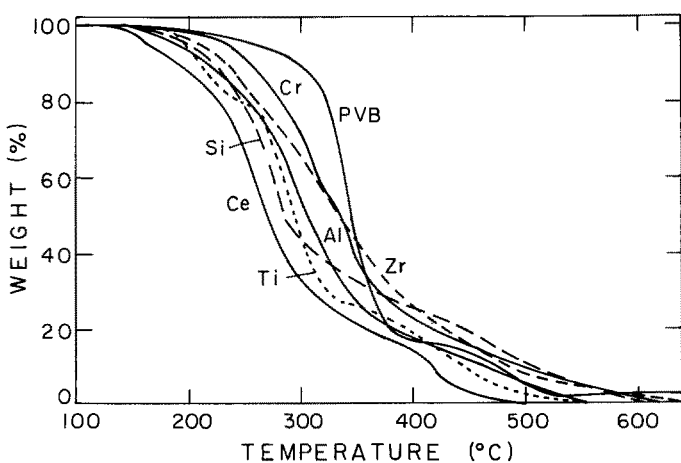


Figure 6 TGA plots of PVB decomposition from films containing 2 wt% PVB with various oxides heated at 5°C min⁻¹ in argon (60 p.p.m. oxygen).

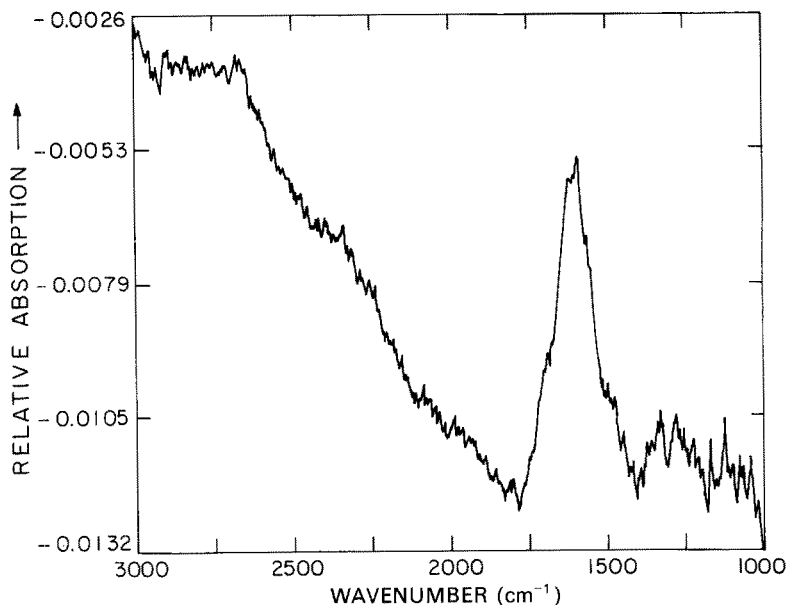


Figure 7 FTIR spectra of PVB residue on alumina after heating to 700°C at 5°C min⁻¹ in argon.

expect that the elimination might be sensitive to acidic or basic catalysis, whereas the oxidation reaction might be analysed by transition-metal oxides.

In general terms, the effect of a catalyst on a reaction can be characterized as a reduction in activation energy. Hence we would expect the catalysed reaction to show a slower rate of change with temperature than

the uncatalysed reaction, reflecting the lower activation energy. This is observed in Fig. 4. The actual rate of the catalysed process is a function of the activation energy and the number of active sites, a product of the surface site density and the powder surface area.

On heating PVB with an oxide powder in argon, the release of butyraldehyde moves to a lower temperature and broadens in range, when compared to pure PVB. This is expected from a catalytic effect, which can be related to the acidity of the particle surfaces.

While the decomposition of pure PVB at these high heating rates is not greatly affected by the presence of air, the decomposition rate of PVB with an oxide powder is affected by air. The ceria and titania curves also become noticeably steeper, suggesting that an oxidative mechanism for decomposition may be becoming dominant, at least for these oxides. Apparently ceria acts as a strong catalyst for oxidation. This oxide also gives rise to much more carbon dioxide in the decomposition products. The effect is catalytic rather than simple oxidation by the ceria, since it is much reduced in argon with a low oxygen level. Ceria has been shown to be very active in the oxidation of polybutadiene [11] and butane [12]. For the other oxides we have discovered no clear correlation between the oxide properties and the PVB decomposition kinetics.

The formation of carbonaceous residues is also a very complicated process and is a minor side-reaction to the main oxidation. PVB itself leaves no residue. The residue which is present on the oxide at 700°C

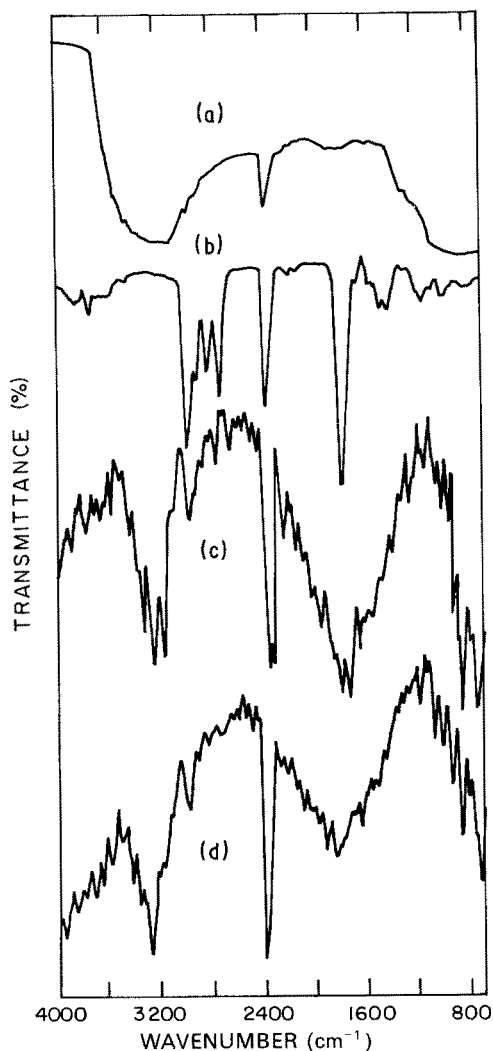


Figure 8 FTIR spectra of gases evolved from a CeO₂-2 wt % PVB film when heated at 5°C in argon (60 p.p.m. oxygen) to (a) 150°C, (b) 220°C, (c) 350°C, (d) 450°C.

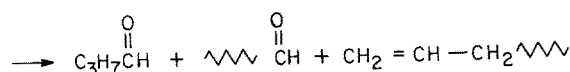
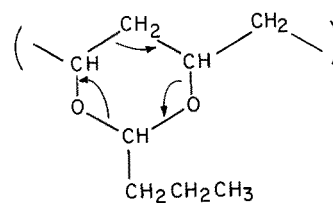


Figure 9 Cyclic-elimination mechanism for butyraldehyde.

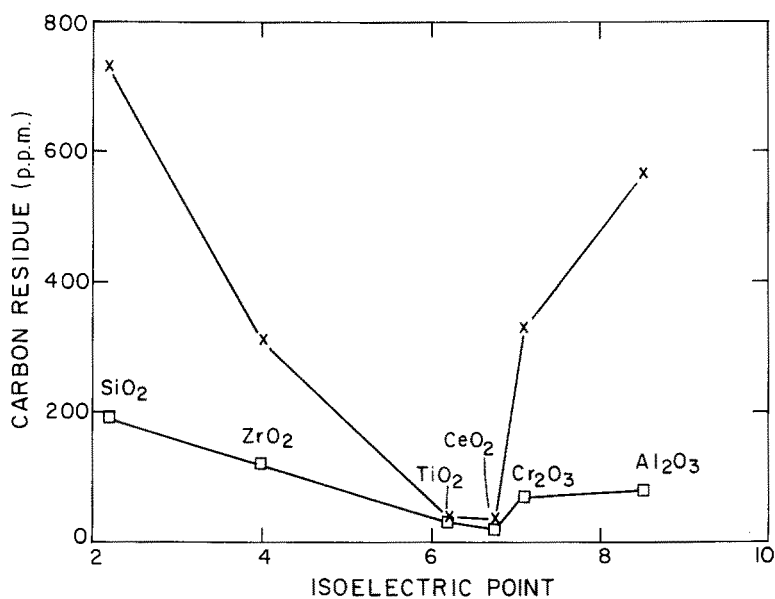


Figure 10 Carbon residue (p.p.m.) left after firing various oxide-PVB films to 1000°C at 5°C min⁻¹ against isoelectric point: (□) air, (x) argon.

presumably arises from dehydration and dehydrogenation reactions giving rise to unsaturation, cross-linking, and polynuclear aromatic compounds. While the material present at 700°C (0.2 to 0.7%) must involve large aromatic structures, that at 1000°C (< 1000 p.p.m.) corresponds to a monolayer or less of carbon on the surface and is presumably bonded to the oxide surface. The formation of such bonds must also depend on the acidic or basic properties of the oxide surface; a correlation with isoelectric point is shown in Fig. 10. Powders with IEPs between 6.4 and 6.9 had a minimum amount of carbon residue, which was expected since highly acidic or basic oxides lead to the formation of carbon double bonds by dehydration.

5. Conclusions

These results show that oxides decrease the initial decomposition temperature of PVB. The effect of oxides on decomposition is much greater in air than in argon containing 60 p.p.m. oxygen. The subsequent stages of PVB decomposition are also moved to lower temperatures, and a fourth decomposition stage is added due to the formation of carbon residue adsorbed on to the ceramic surface. Ceria and titania catalyse PVB oxidation in air, but not under totally oxygen-free conditions.

The results also show a good correlation between weight of carbon residue and IEP. However, surface

chemistry is not the only variable that can influence the surface reaction. The surface structure, number of hydroxyl groups, percentage of free water, amount of oxygen adsorbed on the oxide surface, and surface impurities also affect binder decomposition.

Acknowledgements

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TABLE II Carbon analysis of films containing various oxides and 2 wt % PVB, fired at 5°C min⁻¹ to selected temperatures in air and in argon

Oxide	Carbon content (p.p.m.)			
	700°C air	800°C air	1000°C air	1000°C argon
Al ₂ O ₃	260	90	80	565
CeO ₂	90	80	35	45
TiO ₂	70	60	30	40
ZrO ₂	160	130	120	310
SiO ₂	400	210	190	730
Cr ₂ O ₃	210	160	70	330

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