“Formulation and processing of screen-printing vehicles for sacrificial layers on thick-film and LTCC substrates

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***Abstract**: Ceramic technologies such as thick-film and LTCC (Low Temperature Cofired Ceramic) are excellent platforms for the fabrication of mesoscale devices such as sensors, actuators, microreactors and MEMS packaging. This work presents two alternative screen-printing vehicles for the processing of sacrificial materials and low-firing thick films: 1) a non-aggressive glycol-based vehicle for screen printing thick sacrificial layers onto thin LTCC, and 2) a "high non-evaporables" vehicle for mineral / carbon sacrificial materials allowing subsequent overprinting in the dried state. Their formulation, processing and applications are discussed with regard to the physical and chemical properties of the solvents, plasticisers and binders.*

1. INTRODUCTION

The inroads of thick-film and LTCC technologies into applications such as sensors, actuators and microfluidic devices have raised the need for convenient and reliable structuration techniques for these materials [1-9].

Structuration of thick-film devices using sacrificial materials is a surprisingly old technique, having been published by Stecher et al. [2] more than 20 years ago, mainly with carbon-based materials, although they had already envisioned mineral or metal-based materials. Their technique was somewhat cumbersome, requiring a sequence of firing steps in variable atmospheres in order to avoid prematurely oxidising the sacrificial carbon layers, which would lead to sagging of the overlying structures

1.1. Carbon sacrificial layers

In LTCC technology, where the sacrificial layer is printed and laminated between tapes [6], sagging can be prevented if the LTCC layers are relatively thick compared to the span of the gaps one wishes to create. Alternatively, in closed structures such as membranes, the gases generated by the burnout of the carbon may be used to suppress sagging, although this requires tight process control [7]. Nevertheless, thin and open structures cannot simply use carbon layers and air firing. For these cases, mineral sacrificial pastes, which survive the air firing step and are later removed by a simple etching step, constitute a much more straightforward solution [8-11].

1.2. Mineral sacrificial layers

Sacrificial layers based on $SrCO_3$ [8], recently introduced in classical thick-film technology, are quite convenient because this material has low reactivity and hygroscopicity, does not significantly decompose (to SrO + CO_2) at normal thick-film firing temperatures (≤900°C), and yet easily dissolves in relatively weak acid solutions. The lack of cohesion and large porosity in the fired states facilitates etching, but requires co-firing with the overlying structure layer. To avoid porosity in the dried state, which would "steal" solvent from overprinted layers, epoxy resin was chosen as the binder, fully plugging the interparticle space in the sacrificial material. However, epoxy requires handling and cleaning separate from standard pastes, which is cumbersome. Also, the need to burn away large amounts of resin can be a quality issue in large production: a more classical binder system would be preferable.

Similar systems were introduced on LTCC and classical thick-film substrates [6, 9-11], with three differences to the aforementioned work: 1) use of CaO or $CaCO_3$ instead of $SrCO_3$, 2) use of a glassy binder such as B_2O_3 or a B_2O_3 / borax ($Na_2B_4O_7$) to give some cohesion to the sacrificial layer, and 3) addition, on LTCC, of graphite to the mineral phase to lower reactivity and increase burnout shrinkage.

1) **CaO / $CaCO_3$**. Some decomposition, which happens for $CaCO_3 \rightarrow CaO + CO_2$, can be desirable in LTCC, as it is a way to somewhat follow the LTCC shrinkage. However, CaO was found to be far too hygroscopic, rapidly hydrating to $Ca(OH)_2$, with the assorted expansion potentially destroying the structures. $SrCO_3$ is therefore more adequate. If CO_2 gas generation during acid etching is a problem, one can probably substitute other materials such as Mg / Ca borates, MgO, etc. In fact, MgO is a "standard" sacrificial material for this purpose in thin-film technology [12].
2) **B_2O_3 / borax**. A small amount (ca. 10-20%) of glassy binder mechanically stabilises the sacrificial layer, allowing more reproducible structure and better dimensional control. However, porosity must be maintained to enable easy etching and excessive levels of Na^+ (from borax) must be avoided, as Na^+ strongly reacts with and destabilises glassy layers, affecting reliability [10]. On classical thick-film, the necessary conservation of porosity requires co-firing the sacrificial layer with the overlying layer, with the aforementioned requirements.
3) **Graphite**. The burnout of graphite contributes to the shrinkage of the mineral sacrificial paste and thereby better matching to that of the LTCC, and can be used to reduce materials interactions [11]. To introduce shrinkage, it is much preferable to $CaCO_3$ (see above).

LTCC dissolution by ink solvents

Another potential problem faced with LTCC is attack of the tape by the solvents in the ink. This is due to the Hansen solubility parameters [13] δ_d, δ_p and δ_h of commonly used solvents such as terpineol lying close to that of the acrylate (e.g. PMMA, polymethyl methacrylate) and polyvinyl butyral (PVB) binders [14] used in LTCC tapes (table 1). In practice, destruction of the LTCC tape is a potential issue on thin tapes (≤100 µm) when using thick sacrificial layers.

Purpose of this work

The object of this work was therefore to improve the existing ink vehicle systems. Specifically, our aims were twofold:

1) **For sacrificial pastes on LTCC**, develop a vehicle system that does not attack LTCC.
2) **For sacrificial pastes on classical thick-film,** develop a standard vehicle (not epoxy) with a high non-evaporable content and clean burnout, to fill the porosity in the dried state and thus allow reliable overprinting.

2. NON-AGGRESSIVE VEHICLE FOR LTCC

To allow printing of thick sacrificial layers onto thin LTCC tape, the ink solvent must not dissolve the LTCC binder. This can be evaluated through solubility parameters, of which the most common description is from Hansen [13, 15]. In this framework, the total (Hildebrand) solubility parameter δ of a solvent, plasticiser or polymer is decomposed in three components: 1) non polar "dispersive" (δ_d), 2) polar aprotic (δ_p) and 3) polar hydrogen-bonding (δ_h). Solubility / compatibility is evaluated in terms of "like dissolves like", i.e. a polymer is expected to be dissolved by solvents with solubility parameters close to its own.

From Table 1, it can be easily seen that the ethylcellulose binder used in standard inks lies very close in terms of solubility parameters to PMMA or PVB, the commonly used binders in LTCC. Therefore, a compatible ink system will be more easily developed with another binder.

A rough compatibility test of commercial LTCC tapes with common solvents was first carried out. Solvents were purchased from Sigma-Aldrich, and LTCC was obtained from the corresponding manufacturers. The results of dispensing large drops of solvent on the LTCC sheets are given in Table 2. Most common solvents will rapidly soften the LTCC. As expected, terpineol, whose solubility parameters lie close to that of the binders, is especially aggressive, while propylene glycol (PG), glycerol (G) and water (H_2O), whose solubility parameters lie very far from those of PMMA and PVB, show no attack.

Property **Solvent / polymer**	**Melting point [°C]**	**Boiling point [°C]**	**ER***	δ_d [MPa]$^{0.5}$	δ_p [MPa]$^{0.5}$	δ_h [MPa]$^{0.5}$
Terpineol		217	0.01	13.9	8.0	10.3
Dibutyl carbitol (DBC)	–60	256	<	16.2	2.3†	6.9†
Diglyme	–64	162	0.15	15.8	6.2	9.2
Triglyme	–40	220	<	15.8	2.3	8.2
Tetraglyme	–30	275	<	15.8	2.1	8.2
Tracetin (TA)	+3	258	<	16.5	4.5	9.1
Propylene glycol (PG)	–60	187	0.01	16.8	9.3	23.3
Glycerol / glycerine (G)	+18	290	<	17.4	12.1	29.3
Triethylene glycol bis 2-ethylhexanoate (TEG-EH)	-50	344	<			
Propylene carbonate (PC)	–55	242	<	20.0	18.0	4.1
N-methyl-2-pyrrolidone (NMP)	–15	205	0.03	18.4	12.3	7.2
Water (H_2O)	0	100	0.36	15.5	16.0	42.3
Polyvinyl alcohol (PVA)				16.4	14.7	24.2
Ethylcellulose (EC)				17.1	7.3	9.7
Polymethyl methacrylate (PMMA)				18.6	10.5	7.5
Polyvinyl butyral (PVB)				18.6	4.4	13.0

Tab. 1. Solvent, plasticiser and binder properties [13, 15-17].
* Evaporation rate relative to n-butyl acetate; "<" = significantly below 0.01
δ_d, δ_p & δ_h : Hansen dispersive, polar and hydrogen solubility parameters (see text)
† Calculated from total polar contribution, assuming $\delta_h \approx 3\,\delta_p$ by analogy with similar compounds.

LTCC **Solvent**	**DuPont DP 951** Acrylic [14, 18]	**CeramTec CeramTape GC** ?	**Heraeus HL2000** PVB (?) [19]	**Heraeus CT700** PVB [14]	**Heraeus CT800** PVB [14]
Terpineol	X	X	X	X	X
Dibutyl carbitol (DBC)	X	X	X	X	X
Diglyme	X	X	X	X	X
Triglyme	X	X	X	X	X
Tetraglyme	X	X	X	X	X
Tracetin (TA)	X	OK	X	OK	X
Propylene glycol (PG)	OK	OK	OK	OK	OK
Glycerol / glycerine (G)	OK	OK	OK	OK	OK
Propylene carbonate (PC)	X				
N-methyl-2-pyrrolidone (NMP)	X				
Water (H_2O)	OK	OK	OK	OK	OK

Tab. 1. LTCC (with binder type) - solvent empiric compatibility table.
X = degraded; OK = not affected

Some results were less expected. For instance, triacetin was found to be well compatible with CeramTape GC and Heraeus CT700, while unacceptably softening the other tapes, without correlation with tape binder type or solubility parameters. It must be noted, though, that LTCC tapes contain other substances besides the binder, such as solvent residues and plasticisers, which may affect these results. Unfortunately, the details of the organic systems used in commercial LTCC tapes are proprietary, and published information [14, 18, 19] is relatively scarce and sometimes inconclusive.

Based on our results, PG, G and H_2O, which did not attack the LTCC tapes, were envisioned for the solvent system. Polyvinyl alcohol (PVA, Mowiol® 4-88 and 40-88, Sigma-Aldrich), a well-known water-soluble polymer with solubility parameters close to PG and G, was chosen as a binder. The numbers 4 and 40 denote the viscosity (here determined from the polymer chain length) and 88 is the percentage of hydrolysis of the initial polyvinyl acetate polymer. Therefore, our "PVA-4-88" and "PVA-40-88" are actually copolymers with 12% remaining acetate groups.

For the solvent, water is not favourable as a basis, as it is far too volatile, and also dissolves commonly used screen-printing screen fillers (which are based on PVA). G, on the other hand, has a too high boiling point (290°C), but is useful as a plasticiser for PVA [17]. Therefore, PG, with a desirable boiling point around 190°C, was selected as basis for the solvent system.

First tests showed that although PVA dissolves rapidly in PG and G above ca. 100°C, the solutions were found to gel upon cooling, for weight loadings of < 5%. Adding a small amount of water, however, strongly stabilised these solutions. Therefore, a systematic investigation was carried out for a reasonable loading of 10% PVA by weight for 100% total solvent, with the aim of achieving stable solutions with reasonable viscosity, minimal water content and good dried properties. A more limited series of concentrations were also explored for 20% PVA.

The results are given in Figures 1 and 2. Three main features stand out:

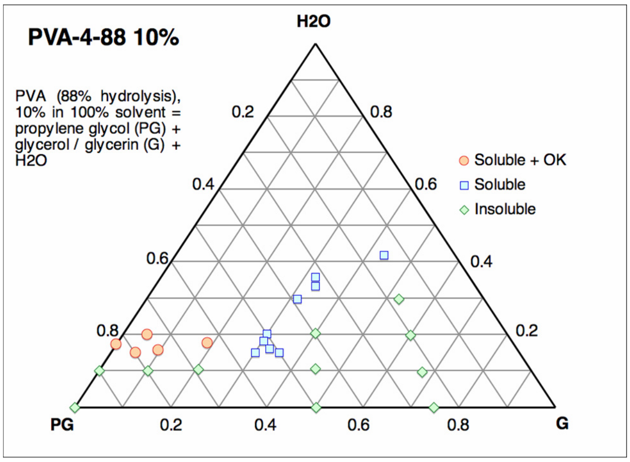

Fig. 1. PVA-4-88 10% in 100% PG+G+H_2O.

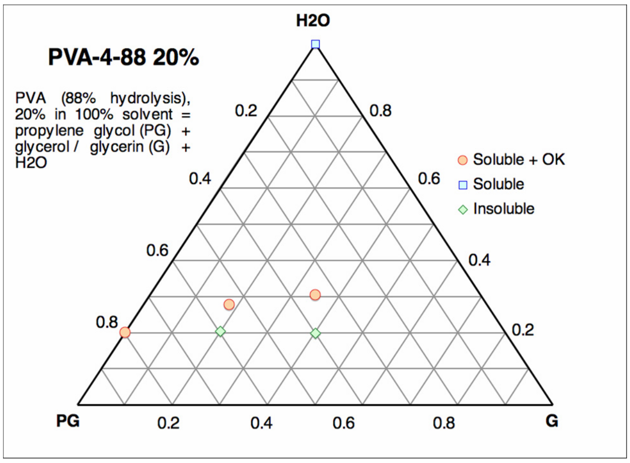

Fig. 2. PVA-4-88 20% in 100% PG+G+H_2O.

1. The minimal amount of **H_2O** for a stable solution is ca. equivalent (in mass) to the mass of PVA. In practice, some more must be incorporated to have reliable results, e.g. 15% H_2O is a good value for 10% PVA.
2. **Glycerol** plasticises the PVA and reduces H_2O+PG evaporation. The maximum value before the film becomes too soft is ca. 2x PVA (in mass), but 0.5…1x is preferred.
3. **Processing**. PVA dissolution is very sluggish in the PG+G+H_2O mix around 90°C, and further heating evaporates water, which must be compensated. A better method is to first dissolve PVA in PG+G around 150°C, let the mix cool to <100°C, then add the water.

Based on these results, the following "standard" formulation was established (in mass):

Binder: 10% PVA-4-88 + 40-88

Solvent: 100% = 80% PG + 5% G + 15% H_2O

Viscosity can easily be adjusted by changing the ratio between PVA-4-88 and PVA-40-88. Test prints made onto 50 µm DuPont 951 LTCC, alone or with carbon powder as filler, confirmed the excellent compatibility of this vehicle.

3. VEHICLE FOR DRY OVERPRINTING

To enable easy processing of mineral sacrificial layers on normal thick-film substrates, the sacrificial layer and overlying layer (dielectric or conductor) must be co-fired, which requires printing this overlying layer onto the dry sacrificial one.

One issue with "on-dry" printing is that the dried layer, when too porous "steals" the solvent from the printed overlayer, prematurely drying it and preventing it from levelling properly. In extreme cases, the currently printed paste is dried on the screen, plugging the mesh apertures and seriously affecting the reliability of the process. Therefore, we aimed in this part to modify a standard vehicle, consisting of ethylcellulose (EC) in Terpineol + Dibutyl carbitol (DBC), by increasing the "non-evaporable" content. This can be done by increasing the EC content and/or by introducing a non-evaporable plasticiser.

First tests showed that binder content was mainly limited by excessive viscosity: we therefore used the EC grade with the smallest available chain length (Sigma-Adrich, "4 cP" & 48% ethoxyl grade). We were able to incorporate 20% (by mass) of this "EC-4-48" binder into 100% solvent, (suitable mix: 50% Terpineol + 50% DBC).

DBC with a relatively high boiling points around 250°C, can be used as a plasticiser with terpineol, but some evaporation will take place over time at the standard 150°C drying temperature. Based on Table 1, we chose to try triethylene glycol bis 2-ethylhexanoate (TEG-EH), whose >300°C boiling makes it essentially non-evaporable at 150°C.

Simply substituting DBC with TEG-EH, however, increases the viscosity considerably. Based on the large ethylhexanoate groups (we were unable to find solubility parameters), it was thought that this was due to the too low polarity of TEG-EH We therefore attempted to correct this by replacing DBC with a more polar solvent such as N-methyl-2-pyrrolidone (NMP), which was successful in restoring a lower viscosity. Tests gave the following vehicle formulation (in mass):

Binder: 20% EC-4-48

Solvent: 100% = 40% Terpineol + 30% NMP
+ 30% TEG-EH

This composition is not as definitive as that of the PVA-based binder developed in section 2 – some fine-tuning is still necessary. Nevertheless, first thick-film dielectric printing tests onto a dried paste (40% volume solids) were encouraging, showing low premature drying by solvent loss into the dried sacrificial layer.

4. CONCLUSIONS AND OUTLOOK

This work aimed at developing screen-printing vehicles to address several processing problems in thick-film and LTCC structuration techniques: an LTCC-compatible vehicle for printing onto thin LTCC sheets and another for printing sacrificial layers that must be overprinted in the dry state, which is more useful for classical thick-film technology.

For printing onto LTCC, a compatible vehicle based on PVA binder in PG solvent (with G added as a plasticiser and water as a solubiliser) was successfully developed. As PG and G are basically non-toxic, this vehicle also has the advantage of intrinsic safety and low environmental concern.

For sacrificial layers that must be overprinted when dry (classical thick-film), a preliminary vehicle based on classical ethylcellulose was developed, with porosity minimised both by increasing the binder content (and choosing a short-chain binder) and by adding a non-evaporable plasticiser.

Future work will concentrate on finalising the 2nd vehicle and then on optimising mineral sacrificial layers for precise thick-film structuration.

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