Three Roll Mills and Thick Film Paste

1. Introduction

Thick Film Materials is ink paste produced through mixing, kneading, and dispersing of metal powders, glass powders, and inorganic oxides with organic solvent in a three-roll mill. The thick film pastes are screen-printed on ceramic boards or green sheets as circuit patterns and then burned. They are mainly used for various electronic components such as multilayer chip capacitors, chip resistors, etc. These components are used in volume in personal computers, mobile phones, etc. Depending on the application, the paste can act as conductive materials, resistor materials and insulate materials. In conductor compositions, the conductive phase is generally a precious metal or mixture of precious metals. In resistor compositions, the conductive phase is generally a metallic oxide. In dielectric compositions, the functional phase is generally a glass or ceramic.

2. Ingredients of Thick Film Paste

A thick film ink comprises main functional powder, glass frit, transitional metal oxide, dispersing agent, and organic medium, which is typically solvent and organic binder. It serves as a vehicle to disperse the main functional powder.

There are three critical parameters of the paste that related to screen printing: (1) the ratio of the solid contents, (2) the particle size distribution, and (3) viscosity.
The solids content (active element and adhesion element) as a ratio of the total weight of the paste will dramatically affect the ability of the paste to be screened, as well as the density of the fired film. If the solids content is high, the fired film will be dense, but it will also be difficult to screen. A typical value for thick-film conductors is 85-92%.

The particle size distribution of a thick film paste is a compromise between screenability and the properties of the fired film. For screenability, it is desirable to have very small particles, but very small particle size in thick film resistors produce parameters that are skewed and not suitable for most circuit applications. Larger particles will obviously be more difficult to screen and may actually block one or more screen opening. Particle size distribution may be measure in a manufacturing environment by the use of a fineness-of-grind (FOG) gauge.

Viscosity is related to the molecular attraction within the body of the liquid and is the ratio of the shear rate of the fluid (in sec-1) to the shear stress (in force per unit area). The viscosity measurement is usually employed by spindle method.

2.1 Functional Ingredients

2.1.1 Conductive Compositions

Any of the noble metals, their alloys or mixture may be used as the conductive phase. Noble metals such as Ag, Pt, and Pb can be used and their alloys can be Pt/Au, Pd/Ag, Pd/Au and Ag/Pt/Pd. The particle size of conductive phase should be in the range 0.5-1.0 µm and a surface area of 1-12 m2/g. The more preferable amount is 50-75 wt % of the compositions, excluding the organic medium.

2.1.2 Resistor Compositions

The thick film resistor composites generally comprise a mixture of electrically conductive materials finely dispersed in an insulative glassy phase matrix. The compositions should provide a wide range of sheet resistance (0.5 Ω/□ and higher than 1×109 Ω/□ and any intermediate resistance value)

The viscosity will be in the range of about 15-50 pascal-seconds (Brookfield RVT, 10 rpm, #5 spindle)

2.1.3 Dielectric Composition

The main functional phase of the dielectric paste is ceramic compositions from Al_2O_3, SiO_2, CaO and MgO or the mixtures.

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2.2 Glass Frit

The glass frit powder is essential to the composition to promote adhesion to the substrate and densification of the composition upon processing. The glass frit should be 3 to 4 wt% of the whole ink amount. The glass frits most preferably used are the borosilicate frits, such as lead borosilicate frit, bismuth, cadmium, barium, calcium or other alkaline earth borosilicate frits. The preparation of such glass frits is well-known and consists in melting together the constituents, and pouring such molten composition into water to form the frit. The main materials are the transition metal oxide generally comprising zinc oxide, titanium oxide, chromium (III) oxide, cadmium oxide and nickel (II) oxide. To obtain the above desired oxide, the bath ingredients could be any compounds that yield the desired oxides under the usual condition of frit production. For example, boric oxide will be obtained form boric acid, silicon dioxide will be produced from flint, barium oxide will be produced from barium carbonate, etc. The desirable amount is from 0.5 to 2.0 wt%.

2.2 Organic Medium

Organic medium is the solution of organic binder solved into the solvent. The organic solvent amount composing the vehicle should be 0.04 to 0.18 by weight to the whole powder amount.

The solvent system is required to primarily dissolve the polymeric resin system (i.e. organic binder) as well as adequately wet the substrate during the screen-printing operation.

The solvent usually boils within the range of 130-350 ℃. Suitable solvents include kerosene, mineral spirits, dibutylphthalate, butyl carbitol, butyl carbitol acetate, hexylene glycol and high-boiling alcohols and alcohol esters. Various combinations of these and other solvents are formulated to obtain the desired viscosity, volatility, and compatibility with dielectric tape.

The primary function of organic binder is to bind together the main functional materials, such as conductive particles or resistor particles. In general, these consist of polyesters, acrylics, vinyl, or polyurethane polymers, and they may be combined to obtain optimum properties.

The most common resin is ethyl cellulose. However, resins such as ethylhydroxyethyl cellulose, wood rosin, mixtures of ethyl cellulose and phenolic resins, polymerthacrylates of lower alcohols, and monobutyl ether or ethylene glycol monoacetate can also be used. The weight-average molecular weight of the organic binder is preferably 100,000 to 1,300. The content of the organic binder is preferably 2 to 15 wt% in the whole ink.

In addition, the thixotropic agents and wetting agents are added into the solvent. Thixiotropic agents are commonly hydrogenated castor oil, and its derivatives are and ethyl cellulose. Of course, it is not always necessary to incorporate a thixotropic agent since the solvent/resin properties couple with the shear thinning inherent in any suspension may alone be suitable in this regard. The wetting agents include phosphate esters and soy lecithin.

2.3 Other Additives
Additives may also be employed to fine-tune viscosity for good screen-printing characteristics enabling accurate and reproducible production, or to modify the binder system acting as, for example, a plasticizer to enhance flex properties. The additives account for 0.05 to 5.0 wt% in the whole ink.

3. Process Thick Film Paste
The ingredients (the particulate inorganic solids and the organic medium) of the paste are first weighed together in a container. The components are then vigorously mixed to form a uniform blend, and are then passed through three-roll mill to achieve a good dispersion of particles. A three roll mill is composed of three horizontally positioned rolls rotating at opposite directions and different speeds (Fig. 1). When material is passed through the first nip, between the feed roll and the center oil, it is subjected to high shear force resulting in mixing, refining, dispersing and/or homogenizing of the material. When the material passed through the second nip, between the center roll and the discharge roll, it is again subjected to high shear force resulting in further mixing, refining, dispersing and/or homogenizing of the material. Milled material is removed from the apron roll by a knife that runs against the roll. The cycle can be repeated to improve dispersion until equilibrium is reached. A Hegman gauge is used to determine the state of dispersion of the particles in the paste. **The satisfactory dispersion will give a fourth scratch point of 10-18 µm.** The viscosity of the paste is typically within the following ranges when measured at room temperature on Brookfield viscometers at low, moderate and high shear rates (showed in Table 1).

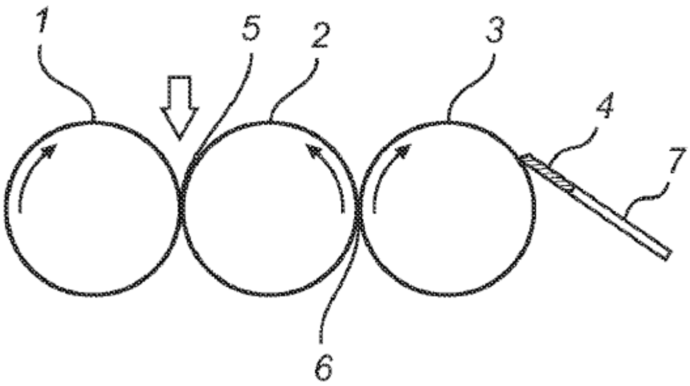

Figure 1. *Schematic drawing of three-roll mill: (1) feed roll, (2) center roll, (3) discharge roll, (4) discharge blade, (5) first nip, (6) second nip, and (7) apron*

Table 1. *Typical viscosity range of thick film paste*

Shear Rate (Sec-1)	Viscosity (Pa.s)	
0.2	100-5000	-
	300-2000	Preferred
	600-1500	Most preferred
4	40-400	-
	100-250	Preferred
	140-200	Most preferred
384	7-40	-
	10-25	Preferred
	12-18	Most preferred

4. Examples

4.1 Conductive Paste

Examples are showed in Table 2-4 [1].

Table 2. *Copper ink*

Copper (mean particle size 1.0 μm)	79 (parts by weight)
Glass frit (Nippon Electric Glass Co. GA-9 which has the composition PbO.B2O3.SiO2)	3
ZnO (Kanto Chemical Co.)	1
i-BMA, α-MeSt resin (Sekisui Chemical Inc. IBS-6) Weight average molecular weight 4750	10
solvent (Kanto Chemical Co., butylcarbitol acetate)	6.6
Dispersing agent (alkyl-substituted polyoxyethylene phosphate or alkylallyl-substituted polyoxyethylene phosphate	0.4

Table 3. *Gold ink*

Gold (mean particle size 1.0 μm)	79 (parts by weight)
Glass frit (Nippon Electric Glass Co. GA-9 which has the composition PbO.B2O3, SiO2)	3
ZnO (Kanto Chemical Co.)	1
i-BMA, α-MeSt resin (Sekisui Chemical Inc. IBS-6) Weight average molecular weight 1360	9
solvent (Kanto Chemical Co., butylcarbitol acetate)	7.6
Dispersing agent (alkyl-substituted polyoxyethylene phosphate or alkylallyl-substituted polyoxyethylene phosphate	0.4

Table 4. *Silver ink*

Silver (mean particle size 2.0 μm)	79 (parts by weight)
Glass frit (Nippon Electric Glass Co. GA-9)	3
ZnO (Kanto Chemical Co.)	1
i-BMA, α-MeSt resin (Sekisui Chemical Inc. IBS-6) Weight average molecular weight 32060	10
solvent (Kanto Chemical Co., butylcarbitol acetate)	6.6
Dispersing agent (alkyl-substituted polyoxyethylene phosphate or alkylallyl-substituted polyoxyethylene phosphate	0.4

4.2 Resistor Paste

Table 5. *Example of resistor paste [2]*

	Example 1	Example 2
TiSi2	29.2%	12%
Ti5Si3	0%	18%
Al2O3	2.6%	0%
Glass I	68.2%	35%
Glass II	0%	35%

The first glass: 5-10% SiO2, 30-50% BaO, 40-60% B2O3 and 1 to 5% CuO
The Second glass" 50 to 70% B2O3, 25 to 40% SrO, and 2 to 10% SiO2

4.3 Dielectric Paste

Table 6. *Example of dielectric paste [3]*

	Compositions						
	SiO2	B2O3	Al2O3	BaO	Na2O	K2O	Li2O
Glass 1	60	30	5	3	1	0.6	0.4
	Al2O3	SiO2	CaO	MgO			
Ceramic 1	100	0	0	0			
Ceramic 2	95	5	0	0			
Note: Sample 1 is ceramic 1 + glass 1 with ration of 50/50, Sample 2 is ceramic 2 + glass 2 with ration of 50/50							

Conclusion

The three-roll mill has been used in thick film materials manufactures. The mills with different sizes are good for laboratories and small production runs to large batch production. Our products [4] provide a great deal of flexibility in designing a machine that best meets the customers' specific application. We pursue our products to reach the most precise requirements for dispersing, refining, shearing, particle size reduction, homogenizing, blending, mixing and de-aearting. We continue to seek out unique applications with our high quality product and service.

References:

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2. Charles C. Y. Kuo, Thick film Resistive Paint and Resistors made therefrom, 1985, US Patent 4639391
3. Satorn Yuhaku, Seiichi Nakatani, Tsutomu Nishimura, and Toru Ishida, Dielectric paste and method of manufacturing the paste, 1986 US Patent 4812422
4. http://www.threerollmill.com