

Chapter 1

Overview

For the friendly and comfortable human-based electronic produces, the flexible electronics devices are required. In order to meet this requirement, process and design technologies such as device-structure designs, flexibility materials application and new materials development become challenged. Furthermore, for the requirements of high performance, multiple functions and high production efficiency, efforts to decrease the processing temperature and processing time and retain the desired functional properties are essential for the development of flexible electronics.

Good conductors, such as gold, silver, copper, nickel and aluminum etc., are extensively applied in electronic devices. Due to the high conductivity requirement, no other material can replace their position for practical applications. In order to be process compatible with the flexible polymer substrate, development of the low-curing-temperature metal paste becomes a great challenge.

1-1 General Background

Metals account for about two thirds of all the elements and about 24% of the mass of the planet. They are all around us in such forms as steel structures, copper wires, aluminum foil, and gold jewelry. Metals are widely used because of their properties: high strength and ductility, high melting point, high thermal and electrical conductivity, and good toughness. Metal conductors (gold, silver,

copper, nickel and aluminum) have good conductivity with excellent electron transmission ability for electronics industry. Electrical conductivities and thermal conductivities of high-purity metals are shown in **Table 1-1**. Most metals are transition element and possess metal bonding. They have valence electrons in *d* or *f* orbital. Due to the low electronegativity, the valence electrons are weakly bonded, which allows the outermost electrons to be shared by the surrounding atoms. This results in positive ions (cations) surrounded by a sea of electrons (sometimes referred to as an electron cloud). Because these valence electrons are shared by all the atoms, they are not considered to be associated with any one atom. This is very different from ionic or covalent bonds, where electrons are held by one or two atoms. The metallic bond is therefore strong and uniform. Since electrons are attracted to many atoms, they have considerable mobility that allows for the good heat and electrical conductivity seen in metals. Above their melting point, metals are liquids, and their atoms are randomly arranged and relatively free to move. However, when cooled below their melting point, metals rearrange to form ordered, crystalline structures.

The excellent electrical conductivity of conductor can be used for electron transmission of electronics devices, such as metal circuit, antenna pattern, inner interconnect, terminal electrode of passive component and transmission line. Common applications for the metal conductors are inner electrodes and terminal electrodes of capacitors, inductors and ceramic modules, surface circuits of IC, and circuit pattern of antenna.

In few years, flexible electronics become the new devices tendency and direction. Products which can be flexibility for collection and application can promote a convenient life handling. Flexible full color display, polysilicon thin film transistor, organic field effect transistors, organic light emitting diodes,

amorphous silicon solar cell, and ultra-low-cost radio frequency identification (RFID) are the typical flexible products. For flexible electronics, there is a tremendous interest to use all-printed electronics as a means of achieving ultra-low-cost electronic circuits in displays and disposable electronics such as RFID tags.

In recent years, low-cost RFID tags are considered to be a compelling application, since they may be used to replace UPC barcodes on consumer products, ushering in an era of enhanced consumer convenience and warehousing efficiency, though a realization of real-time price and product controls, automated inventory processes, and automated checked [1]. RFID is hitting the mainstream now for a number of reasons. There are three parts of the RFID system. The tag is affixed to the item being tracked. The reader is the device that reads the tag. The third part of the system is the antennas, an important of communication between the tag and reader [2]. The system figure was shown at **Figure 1-1**. For 13.56MHz frequency application, the antenna is typically a loop as shown in the figure. Among other materials, the tag's substrate can be paper, PVC, or PET (Teflon). The antenna can be made from copper, aluminum, or conductive ink or paint. RFID tags will be used for comparison with current methodologies to elucidate the advantage of high speed roll to roll printing presses in the manufacture of electrical interconnects [3].

In general, three main approaches are currently pursued to realize item-level RFID. In the most conventional approach, low-cost silicon RFID tags are used. The cost of silicon itself is miniscule, since typical tags are less than 1 mm on one side [4]. Additionally, to realize low silicon cost while maximizing range, manufacturers are pushing toward higher operating frequencies (900 MHz and 2.4GHz) to drive down the size of the chip and increase antenna Q. At

13.56MHz, this is used for providing power to the tag via inductive coupling, besides serving its primary role in RF communication which most certainly have to support bidirectional communication, since this will probably be required to realize the anti-collision algorithms used to enable a reader to talk to a large number of tags in its read-field. In particular, given the large size of the inductor, Q of the tag is usually limited by series resistance. So realization of a roll-to-roll compatible low-resistance printed metallization technology is crucial. The electrical performance of a coil is determined by the following equation:

$$Q = \frac{L\omega}{R} \quad 1.1$$

Q: Quality factor: measure of coil efficiency which influences the working distance of coil; L: Inductance: determined by number of loops and dimensions; ω : Omega: frequency $\times 2\pi$; and R: Resistance: determined by resistivity of material and length, thickness and width of coil. In applications functioning at the 13.56MHz frequency the Q factor should be higher than 30.

Some investigations based on metallic nanoparticles have been performed. Small-diameter nanoparticles have reduced melting points relative to their bulk material counterparts. Another approach based on polymer additions have also been studied. Using polymer with low curing temperature to consolidate the structure and flake metal powder to connect each other result in good electrical conductivity and flexibility. DuPont developed the polymeric thin film (PTF) coil for RFID tags and Smart Labels applications. The paste has been particularly developed for the coil printing in the applications of RFID tags and contactless smart cards. It possesses the following key properties: sheet resistivity of 10-20 m Ω /sq at 25mm after drying and 4-8 m Ω /sq at 25 μ m after lamination. The substrate is compatible with polyester, ABS, polycarbonate, and

paper [5].

The functionality of an RFID tag is determined by its design and the materials it is made from. The frequency at which the tag will operate is determined by several factors. One is number of turns in the coil, coil design, and the conductivity of the coil. The former is an exercise in print capability and resolution in most cases. Specially, silver, one of the most conductive metals available, is chosen almost exclusively as the conductive pigment in the majority of electrically conductive inks. In common industry practices to circumvent this problem include overprinting multiple passes of silver resulting in printed silver traces 25-75 microns thick and high temperature sintering [8]. Another conductive process way, punched aluminum offers a cheaper alternative but as it is a subtractive process it is only possible to maintain the high level of waste by the relatively low cost of aluminum. And aluminum does not offer the same conductivity as silver and products made by this technique offer inferior performance.

For standard roll-to-roll printing presses are typically capable of :

- High speed (typically 150-1000 Feet/min)
- Good dimensional control compared to rotary screen.
- Low cost per sheet (low ink volume/substrate).
- Widespread availability of necessary production facilities.

However, development of high conductivity metal ink with low temperature process was an important factor for low-cost roll-to-roll process. Parelec Inc [6,7] developed an innovative process which provides a two-step process (printing and curing) with high yield. This system is adaptable to sheet fed or roll-to-roll printing processes. The materials are comprised of metal

particles and a reactive organic medium (MOD) that volatilizes during the heating process and can be cured very quickly to give a very thin highly conductive film. The films can be cured in 25 seconds to 5 minutes at temperature as low as 135°C in a box oven or roll-to-roll continuous print and cure production line, as shown at **Figure 1-2**.

So technology advances in the fields of materials, printing, and electronics have led to the evolution of the field of printable electronics. Direct printing of electronic features may eliminate complex procedures employed in traditional electronics manufacturing, leading to low-cost devices.



1-2 Silver paste

Metal pastes are currently used for various electrical and electronic components such as solar cells, multilayer ceramic capacitors, single and multichip modules and hybrids for the automotive and aerospace industries. All these applications require finely structured conductive layers, which are usually produced with screen printing technologies, using metal powders containing print paste.

Generally the conductive pastes consist of metal powders, such as Ag, Au, Pd, Pt, Cu and Ni., the glass frit and the organic vehicle. Sometime the conductive paste of Ag system has the addition of Pd, in order to lessen the solder foods crack at the time of soldering of the terminal electrode of the printing ceramic condenser. The purity of metals powders that is now typically required for the production of metal pastes is not at all well-defined. In most cases, only the main metal content is analyzed, whereas the presence of trace elements is normally neglected. But trace element content, in particular, can significantly influence rheological properties and long-term storage stability of pastes. For metal powder, some parameters must be selected for different applications, such as, particles size distribution, tap density, surface area, ignition loss, degree of deagglomerated, and powder shape etc,. All of the foregoing parameters can effects the paste rheology during printing and subsequently the microstructural evolution and physical characteristic of the films after sintering.

The typical pastes used today are based on organic solvents, like as, butyl carbitol acetates, terpeneol, hydrated castor oils in combination with rheological

additives, like as, pine or fish oils. Most experts agree that in the long-term use of such solvents is inconsistent with aims to protect the environment and with the concept that ecological aspects should be integrated into production procedures. Some solvent used today are based on water solvents, but general were used at low temperature or quickly curing paste, some low viscosity paste application and requirement of environmental.

Glass or metallic oxides frits are the important elements for paste system of metals. By adding a specific metallic oxide to the conductive paste of the conventional metal paste as a constituent were maintained the stability of the product of a ceramic condenser, highly efficient nature, high-reliability, etc., and it sets at the time of a manufacture of a ceramic condenser. The knowledge of decreasing the crack generated in change of composition by the dielectric at the time of baking and the reaction of an electrode material and the dielectric layer at the time of baking as such as possible, and improving remarkably problems, such as the stability of properties, such as a dielectric constant dielectric loss, insulation resistance, and isolation voltage, a performance, and a process, was carried out. Wetting and dispersing agent adjusted to meet the demands of each application, synthetic rheological additives and in terms of purity and morphology, tailor-made metal powders made it possible to develop these innovative paste systems for metallization purposes.

Nowadays, polymer-metallic type pastes are used in electronics. The compositions of polymer-metallic pastes included the diluents, curing agent, resin and metal powder as conductive grain, and are well mixed. Conductive film is formed after printing and curing process. The curing reaction is dependent on the resin cross-link due to temperature effect or solvent evaporation. This is completely different from the high-temperature metal paste

which densifies as a result of metal sintering and glass softening. These polymer-metallic pastes were designed to be compatible with the printed wiring board industry and can be printed on any material that can withstand 150°C for two or three hours. The polymer-metallic type pastes have two basic types. The first is the thermoplastic type where the paste is kept in liquid form by a solvent. These materials soften on heating and have a lower operating temperature. Curing is normally caused by solvent evaporation at 70°C - 125°C under infrared heating. The other type is the thermosetting paste. These pastes are thermally fired at 150°C - 180°C for typically 2-3hours. Increasing the curing temperature is possible to reduce the soaking time. The pastes viscosity is controlled by either a solvent or a functional dilutant which is often the additive that decides the paste function. The solvent is evaporated during curing, whereas the monomer becomes part of the polymer during cross-linking by heating or UV light. The advantages of the thermosetting pastes include low current noise, high wear resistance and low costs.

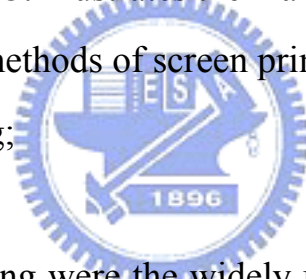
1-3 Printing Method

1-3-1 Screen Printing

Screen printing is the basic technology for thick-film microcircuit. The screen printing process is unique in its ability to place thick deposits of ink or paste precisely while maintaining extremely good volume control and line definition. In ideal screen printing process, the objective is to fill the pattern on the screen completely with the ink or paste during the squeegee pass and leave all the ink or paste on the substrate in the exact pattern as on the screen after the squeegee passes. **Figure 1-3.** illustrates the manufacturing of the screen printing.

There are two basic methods of screen printing:

- 1) off-contact printing;
- 2) contact printing.



The off-contact printing were the widely used method, only one section of the screen, the section directly under the squeegee, is in contact with the substrate during the printing process. In contact printing, the entire screen is in contact with the substrate during the complete pass of the squeegee [11].

There are many variables that affect the quality of the screen printed pattern in the screen printing process. There can be classified into five basic categories:

- 1) the rheological properties of the ink or paste;
- 2) the setting of the screen printer;
- 3) the geometry of the pattern on the screen;
- 4) the screen;
- 5) the substrate.

For the rheological properties of the ink or paste, the viscosity of the ink or paste determines to a large extent the quality of the printed pattern. In general, the shear thinning flow which illustrates at **Figure 1-4**. were agreed with screen printed application. The shear-thinning behavior means the shear viscosity is dependent on the degree of shear load. The terms shear-thinning is sometimes also used to describe the time-dependent flow behavior under constant shear load. The other important rheological properties are flow thixotropy. The line or pattern resolution or leveling characteristic of screen printed are depended on flow thixotropy properties of rheology. Thixotropic behavior means the reduction in structural strength during the shear load phase and the more or less rapid, but complete structural regeneration during the subsequent rest phase. The thixotropy is measured from area of thixotropic loop in the shear rate v.s. shear stress curve. The area is equal to $\tau \times \gamma$, and is equal to $\text{N/m}^2 \times 1/\text{s}$ to $\text{N}\cdot\text{m/s} \times 1/\text{s}$, so is equal to energy / volume.

In general, low viscosity ink or paste results in a thinner printed pattern. Thinners may be used to change the yield point of the ink or paste without changing the shape of the viscosity curve. However, it is very difficult to return back to its original consistency, after the thinner is added. Usually, high thixotropy inks or paste are used to meet the demand of high printing resolution [12].

1-3-2 Ink-Jet Printing

Ink-jet printing is a non-impact dot-matrix printing technology in which droplets of ink are jetted from a small aperture directly to a specified position on a media to create an image. The ink-jet printing has been implemented in many different designs and has a wide range of potential applications. A basic map of the ink-jet technologies is shown in **Figure 1-5** [13]. Today the ink-jet technologies most active in laboratories and in the market are the thermal and piezoelectric drop-on-demand ink-jet method. The thermal ink-jet printing method was commercialized by Hewlett-Packard. The thermal ink-jet printing solved the reliability problem of ink-jet technology by throwing away the printhead at the end of its useful life. Depending on its configuration, a thermal ink-jet can be a roof-shooter which shown at **Figure 1-6(a)**. with an orifice located on top of the heater, or a side-shooter which shown at **Figure 1-6(b)**. with an orifice on a side located nearby the heater. In the piezoelectric ink-jet, depending on the piezoceramic deformation mode shown at **Figure 1-7.**, the technology can be classified into four main types: squeeze, bend, push, and shear.

The most critical component of ink-jet printing is probably the ink. Ink chemistry and formulations not only dictate the quality of the printed image, but they also determine the drop ejection characteristics and the reliability of the printing system. In which, aqueous or water base inks are commonly used in ink-jet printing system. Typical composition of a water base ink for ink-jet printing is presented in **Table 1-2**. Viscosity of water-based ink-jet inks range from 2 to 8 cps.

1-3-3 Gravure Printing

Traditionally, particulate inks have been screen-printed, but the method is limited due to line resolution, speed and cost. Direct gravure printing methods have also been developed previously where the paste is first doctored to the grooves of the gravure and then printed directly onto a substrate. In this methods, a release layer between the gravure and the paste or ink has been used, and the paste is hardened by means of drying, UV-light, or freezing to allow complete transfer of the paste or ink from the grooves to the substrate. The charts of gravure printing were shown at **Figure 1-8**. The printing mechanism of gravure printing were described as below: The flexible substrate to send and pass through the gap between two roller by substrate roller were printing pattern which form screen pattern to soak and pass through from ink trough on the printing roller. The gravure printing can be extended to roll-to-roll printing. The roll-to-roll printing method needs flexible substrates, such as paper or plastic films. These substrates offer a much less expensive solution than the subtractive method and the method is much more environment friendly [14].

Control of gravure printing machines is basically composed of tension control and register control [15]. Tension control is a prerequisite for accurate register control to obtain high printing machine is too high, several problems occur such as large register error, rewinder wrinkling, web tearing, and plastic deformation of the web. On other hand, if web tension is too small, then problems occur such as web oscillations, loose rewinding and web surface damages. The real actual gravure printing machine is shown at **Figure 1-9**.

1-3-4 Flexo Printing

Flexography is the major process used to print packaging materials. Flexography is the fastest growing conventional printing process, especially in packaging such as corrugated containers and flexible films. This printing method is the suitable printed method for RFID tag process with low cost requirement. The flexography is used to print corrugated containers, folding cartons, multiwall sacks, paper sacks, plastic bags, milk and beverage cartons, disposable cups and containers, labels, adhesive tapes, envelopes, newspapers, and wrappers. In the typical flexo printing sequence, the substrate is fed into the press from a roll, and the chart is shown at **Figure 1-10**. The image is printing as substrate is pulled through a series of stations, or print units. Each print unit is printing a single color for color printing. Flexographic and letterpress plates are made using the same basic technologies utilizing a relief type plate. Both technologies employ plates with raised images and only the raised images come in contact with the substrate during printing. Flexographic plates are made of a flexible material, such as plastic, rubber or UV sensitive polymer, so that it can be attached to a roller or cylinder for ink application.

The flexographic inks are very similar to packaging gravure printing inks in that they are first drying and have a low viscosity. The inks are formulated to lie on the surface of nonabsorbent substrates and solidify when solvents are removed. Solvents are removed with heat, unless UV curable inks are used. After printing the substrate may run through a number of operations to be “finished” and ready for shipment to the customer. The finishing may include operations such as coating cutting, folding and binding.

1-4 Thermal and Rheometer Analyses and Measurement Techniques

1-4-1 Thermogravimetric analysis, TGA[12]

Thermogravimetric analysis (TGA) was the study of weight changes of a specimen as a function of temperature. The technique is useful strictly for transformations involving the absorption or evolution of gases from a specimen consisting of a condensed phase. Typical TG specimen powder or liquid was placed on a refractory pan, often porcelain or platinum. The pan, in the hot zone of the furnace, is suspended from a high precision balance. A thermocouple is in close proximity to the specimen but not to interface with the free float of the balance. The balance was electronically compensated so that the specimen pan does not move when the specimen gain or loss weight.

If reactive gases are passed through the specimen chamber or gases are released by the specimen, the chamber containing the balance is often maintained at a slightly more positive pressure via compressed air or inert gas; this is in order to protect the balance chamber and its associated electronic components from exposure to corrosive gases.

Sometime were shown the figure is the numerical derivative TG trace (DTG), which is a smoothed plot of the instantaneous slope of the specimen mass with respect to time. DTG does not contain any new information, however it clearly identifies the temperature at which mass loss is at maximum “ the DTG peak”. Superimposed transformations, which are seen only as subtle slope changes in a TG trace appear more clearly shown as DTG peaks. Comparison of

DTG data with DTA data of the same material shows striking similarity for those transformations with an associated weight change. Thus, combining DTA and DTG traces is useful for differentiating the types of transformations depicted by the DTA trace.

Thermogravimetric analysis that provide for a spell of constant temperature of a specimen once the non-steady heating is over give the most correct results. They are used to determine key physical and chemical properties of individual substances. The percentage difference was calculated as:

$$p = [(T_f - T_{sp}) / T_f] \cdot 100\% \quad 1.2$$

The results of thermogravimetric analysis cast doubts over the validity of a number of experimental investigations in which the reference temperature for the data obtained was that of the furnace space rather than the specimen temperature. Note than an intensification of heating did not lead to a proportional increase in the temperature of specimens T_{sp} which leveled out at an ultimate value peculiar to every substance.

Dynamic thermal analysis of thermal decomposition was investigated by thermogravimetric analysis. Depending on the importance and goals of investigation, one may call upon various types of heaters: convective heaters, lasers, plasma gun and a whole range of burners and furnaces. The derivatographs manufactured produce TG and DTG curves, which make it possible to determine the thermal effects of decomposition, complete with the decomposition rate records $\dot{\omega} = \omega(t)$.

The most common approach to describing the kinetics of isothermal decomposition is to consider it as a homogeneous one-stage chemical reaction:

$$\frac{d\omega}{dt} = -k\omega^n \quad 1.3$$

Where, n is the reaction order; w is the weight per unit of a reacting substance; k is reaction rate constant at a given temperature; $w=M/M_0$. By integrating blow equation one can obtain an analytical expression describing the kinetic curves of decomposition. At $n = 1$:

$$\omega = \omega_0 \exp^{-(kt)} \quad 1.4$$

The constant of integration, w_0 , is determined by the initial condition, $\omega|_{t=0} = \omega_0$. It is not much more difficult to obtain solutions at $n \neq 1$.

One-stage chemical reaction between gases and solutions sometimes follow fairly well the empirical Arrhenius equation in relatively narrow ranges of temperature:

$$k = k_0 \exp^{(-E/RT)} \quad 1.5$$

Where, k_0 is pre-exponential factor; E is activation energy.

The equation includes the Boltzmann constant $e^{-E/RT}$ which has a physical meaning in rate calculations for gas-phase reactions, according to the theonection that a more elaborate temperature dependence of the rate of chemical reactions was derived from this theory [9]:

$$k = (k_B T / h) k_0 \exp^{(-E/RT)} \quad 1.6$$

Where, the k_0 coefficient takes account of changes in entropy and in the number of particles produced when an activated complex is being formed which has great bearing on polymer systems.

The physical irrelevance of apparent characteristics is evident in activation energy changing with temperature and depending on the extent of conversion, pre-exponential factor is, in turn, often time-dependent and differeing from its theoretical value of 10^{12} s^{-1} .

The theory of absolute rates of chemical reactions forms the groundwork of the equation within the strict framework of rigorous limitations the most important of which are:

1. the reaction should be homogenous and occur in a gas medium;
2. the starting compound should be in equilibrium with its activated complex;
3. temperature and all other parameters are constant;
4. the reaction does not alter the Maxwell-Boltzmann equilibrium distribution;

Non-isothermal decomposition of solid substances fails to meet these requirements to a lesser or greater extent. It is a heterogeneous process developing at phase boundaries. This equilibrium between an initial substance and its activated complex is broken by the loss of vibration stability of oscillators in three-dimensional and linear crystals. Kinetic equations of heterogeneous decomposition of solids were shown at **Table 1-3**. The equations cited may describe intricate kinetic curves more than exponential equations, yet they fall short of taking into account certain factors of nonisothermal heating such as homogeneous nucleation. The thermodynamic feasibility of such nucleation is well established and experimentally verified for metastable liquids [10].

Responding to the practical need to have simple analytical relationships for TG curves, many researchers are determined to apply equations derived for isothermal conditions to the kinetics of decomposition during monotonic heating. The KEKAM equation, which incorporated the Arrhenius law, will then become:

$$\frac{d\alpha}{dt} = nk_0^{1/n} \exp(-E/nRT)(1-\alpha)[1 - \ln(1-\alpha)^{1-1/n}] \quad 1.7$$

At constant heating rate:

$$[-\ln(1-\alpha)]^{1/n} \cong [nk_0^{1/n} RT^2 / bE] \exp(-E/nRT) \quad 1.8$$

To describe the non-isothermal kinetics of decomposition of condensed substances, many also adopt the One-stage chemical reaction equation:

$$\frac{d\omega}{dT} = (-k_0/b)\exp(-E/RT)\omega^n \quad 1.9$$

The TG curves of linear polymers while quantitatively different from calculated curves are qualitatively the same at low heating rates. More complex substances such as coals and thermosets do not evince even a qualitative agreement with calculated plots at high heating rates.



1-3-2 Differential thermal analysis, DTA[12]

Differential Thermal Analysis DTA, can provide the some material information during thermal processing. The temperatures of transformations as well as the thermodynamics and kinetics of a process may be determined using DTA. The DTA information of material were glass transition, crystallization temperature, melting temperature, and any reaction about exothermic and endothermic during thermal processing.

The Differential Thermal Analysis DTA, measures the difference in temperature between a sample and reference which are exposed to the same heating schedule via symmetric placement with respect to the furnace. The reference material is any substance, with about the same thermal mass as the sample, which undergoes no transformations in the temperature range of interest. The temperature difference between sample and reference is measured by the differential thermocouple in which one junction is in contact with the underside of the reference crucible. The sample temperature is measured via the voltage across the appropriate screw terminals and similarly for the reference temperature; generally only one or the other is recorded.

The material sample undergoes a transformation, the single will either absorb, means endothermic, or release, means exothermic, heat. Usually the melting of solid material will absorb heat, where that thermal energy is used to promote the phase transformation. The DTA will detect that the sample is cooler than the reference, and will indicate the transformation as the endothermic on the plot of differential temperature (ΔT) versus time.

In order to analyze the differential heating curve, it is convenient to write down a formal expression for the rate at which heat is transferred into and out of

the sample or reference cell.

$$\frac{dq_s}{dt} = K_s(T_w - T_s) + \sigma(T_r - T_s) + \alpha(T_0 - T_s) \quad 1.10$$

$$\frac{dq_r}{dt} = K_r(T_w - T_r) + \sigma(T_s - T_r) + \alpha_r(T_0 - T_r) \quad 1.11$$

Here dq/dt is the rate at which heat is received by the reference material and sample material, respectively. K_r and K_s are heat transfer coefficients between the materials and the furnace wall. They are made as nearly identical as possible by choice of reference material and design of cell and furnace. Sigma is the heat transfer coefficient between the cells, and alpha is the heat loss to the outside environment. T_w , T_r , T_s and T_0 are the temperature of the furnace wall, reference and sample materials, and external environment, respectively.

Next use can be made of the identity

$$\frac{dq}{dt} = \frac{dH}{dt} = \frac{dH}{dT} \frac{dT}{dt} \quad 1.12$$

For the sample it is convenient to segregate the portion of the increased heat content arising from phase change, writing

$$\frac{dq_s}{dt} = C_s \frac{dT_s}{dt} + \Delta H \frac{df}{dt} \quad 1.13$$

Here C_s is the heat capacity of the cell plus its contents, while ΔH is the heat of the transformation and df/dt is its time rate of occurrence under the conditions of the experiment, f being the fraction of the sample transformed at any time t .

For reaction kinetics in DTA, the temperature distribution in the differential thermal analysis specimen holders obeys the general heat flow equation.

$$\frac{\partial T}{\partial t} - \frac{k}{\rho c} \nabla^2 T = \frac{1}{\rho c} \frac{dq}{dt} \quad 1.14$$

Where T is the temperature, t the time, k the thermal conductivity, ρ the density, c the specific heat, and dq/dt the rate of heat generation due to a

chemical reaction per unit volume of sample. No heat effects occur in the reference sample, so the temperature distribution in the reference is given by:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c} \nabla^2 T \quad 1.15$$

The differential temperature is the difference in temperature of the centers of the two samples. The differential temperature, θ , is then given by

$$\theta = f\left(\frac{dq}{dt}\right)_{\text{sample}} - \left(\frac{\phi \rho c a^2}{4k}\right)_{\text{reference}} \quad 1.16$$

This equation it is seen that when d^2q/dt^2 , the derivative of the rate of heat absorption, is zero, $d\theta/dt$ is also zero. Since the rate of heat absorption is proportional to the rate of reaction, the equation states that the peak differential deflection occurs when the reaction rate is a maximum. So the results of the differential thermal study agree with results obtained isothermally except in some specific cases.



1-3-3 Differential Scanning Calorimeter[11]

In differential scanning calorimetry, the recorded parameter is the flow of heat supplied to the specimen and registered by the calorimeter. Thermodynamic constants, such as the heat released or absorbed in a phase transformation, may be determined by DSC. DSC plot of dQ/dt versus temperature may be translated to a plot of dQ/dt versus time, using the heating rate. The heat released/absorbed in a reaction is simply the area under the peak:

$$Q = \int_{-\infty}^{\infty} \left(\frac{dQ}{dt}\right) dt \quad 1.17$$

Ideally, there is no harm in integrating from such broad extremes, since there is no accumulated area except where the peak lies. For energy function, the enthalpy has been constructed for these conditions, which is defined as:

$$H = U + pV \quad 1.18$$

The total differential of this function has the form:

$$dH = dU + pdV + Vdp \quad 1.19$$

Inserting the expression for dU :

$$dH = dQ - pdV + pdV + Vdp = dQ + Vdp \quad 1.20$$

Thus under the conditions of constant pressure, $dH = dQ$ or $\Delta H = Q$. Since enthalpy is the sum of state functions, it too is a state function. As a short aside, we can use the above equation to define heat capacity, the ability of a substance to hold thermal energy. The constant volume heat capacity is defined:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dQ_V}{dT} \quad 1.21$$

The constant pressure heat capacity is defined:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{dQ_P}{dT} \quad 1.22$$

The importance of heat capacity will become apparent throughout the discussion of these instruments.

Irreversible transformations are those in which reactants do not reform from products upon cooling. Generally one of the reactants is in a metastable state, and only requires thermal agitation or the presence of a catalyst to initiate the transformation. As glass devitrification proceeds, for example, heat released at the glass-crystal interface raises the temperature of the sample. The rates of such transformations generally have an exponential temperature dependence, causing them to proceed more quickly, which in turn causes a more rapid temperature rise, and so on. As a result, these “self-feeding” reactions will show irregular temperature/time profiles when externally heated at a constant rate. A heat-flux DSC simply measures the temperature difference between sample and reference and makes no effort to maintain the sample temperature at the setpoint value. However, a precise value of sample temperature, or a linear sample heating rate, is necessary to fit these transformation data to kinetic equations in order to determine the activation energy of the transformation. Under slower heating rates in heat-flux DSC, the deviation of sample temperature from the setpoint during a self-feeding reaction may be maintained adequately small so as to be neglected.

Powder-compensated DSC has the advantage that it measures the transformation by maintaining a null balance, while also maintaining the sample and reference temperatures at the setpoint. To maintain the sample at the setpoint temperature during a self-feeding reaction in a power-compensated DSC, small sample mass $< 10\text{mg}$ and excellent thermal contact between the sample and its container, as well as the container and the chamber, are required.

1-3-4 Stress and Strain Rheometers[13]

Rheology is the science of deformation and flow. It is a branch of physics since the most important variables come from the field of mechanics: forces, deflections and velocities. All forms of shear behavior, which can be described rheologically in a scientific way, can be viewed as lying in between two extremes: the flow of ideal viscous liquids on one hand and the deformation of ideal elastic solids on the other. The behavior of all real materials is based on the combination of both the viscous and the elastic portion and therefore, it is called *viselastic*.

Rheometry is the measuring technology used to determine rheological data. The emphasis here is on measuring system, instruments and analysis methods. Both liquids and solids can be investigated using rotational and oscillatory rheometers. Viscosity curves are usually plotted with $\dot{\gamma}$ on the x-axis and η on the y-axis. When measuring at shear rates $\dot{\gamma} < 1$ 1/s, it is important to ensure that the measuring point duration is long enough. This is especially true for high-viscosity samples which are tested at very low shear rates. Otherwise start effects or time-dependent transition effects are obtained, this means the transient viscosity instead of the desired steady-state viscosity is measured. When $\dot{\gamma} > 1$ 1/s, transient effects only influence samples with pronounced viscoelastic properties. Therefore, for liquids with low or medium viscosities the duration of $t=5$ s is sufficient in most cases for each measuring point. However, transient effects should always be expected for polymers at shear rates $\dot{\gamma} < 1$ 1/s.

Rotational tests are performed to characterize viscous behavior and

evaluated viscoelastic behavior, creep tests, relaxation tests and oscillatory tests are performed. In all fluids, there are frictional forces between the molecules and, therefore, they display a certain flow resistance which can be measured as viscosity. The dynamic viscosity is sometimes used for η . However, many rheologists also use this term to describe either the complex viscosity measured in oscillatory tests or the real part of the complex viscosity. The inverse value of viscosity is referred to as fluidity ϕ and following as:

$$\phi[1/\text{pas}] = 1/\eta \quad 1.23$$

For rotational tests, the different types of flow behavior were presented and their rheological background was explained using, for example, Newton's law or other viscosity functions which depend on the structure of the sample. A normal test for shear rate tests, the speed or shear rate is set and controlled. This tests method with controlled shear rate is usually selected when specific flow velocities of technical processes have to be simulated. The viscosity curves are usually plotted with $\dot{\gamma}$ on the x-axis and η on the y-axis.

To know the structure decomposition and regeneration were measured by thixotropy and rheopexy which are shear rate step function test. For measurements like this, three test intervals are preset:

1. Rest phase under low-shear conditions during the time period between t_0 and t_1 . The aim is to achieve a fairly constant η value for the whole first interval, since it is then used as the reference value for the third interval;
2. Load phase under high-shear condition during the time period between t_1 and t_2 in order to decompose the structure of the sample;
3. Phase after removing the load under low-shear conditions during the time

period between t_2 and t_3 , under the same shear conditions as in the first interval to facilitate regeneration of the structure.

The extent of thixotropy is given as the change in viscosity $\Delta\eta$, which is calculated as the difference between the maximum viscosity. Here, η_{\min} is taken at the time point t_2 and η_{\max} at the point t_3 . The formula were $\Delta\eta = \eta_{\max} - \eta_{\min}$. And the total thixotropy time is the time difference between the end of the structural decomposition phase and the time point at which the maximum value η_{\max} is reached after structural regeneration. The total thixotropy time were analyzed as the period of time required for the structure to reach the state of complete regeneration in the third test interval. The testing and analysis method that flow curve with hysteresis area for determining thixotropic and rheopectic behavior were now outdated, although it is still used for QC tests in some industrial laboratories. The hysteresis area was determined by taking the difference between the following two areas: the area between the upward curve and the $\dot{\gamma}$ axis, and the area between the downward curve and the $\dot{\gamma}$ axis. Sample with positive area value were referred to as thixotropic and those with negative values as rheopectic.

For viscoelastic behavior, a viscoelastic material shows viscous and elastic behavior simultaneously. For viscous portion behaves accorded to Newton's law, and elastic portion behaves accorded to Hooke's law. The behavior of viscoelastic liquid can be illustrated using the combination of a spring and a dashpot in serial connection. Both components can be deflected independently of each other. The extent of the reformation represents the elastic portion, and the extent of permanently remaining deformation corresponds to the viscous

portion. So the deformation process is irreversible, as the sample has changed its form at the end of the process because its reformation is not complete. Therefore, the material behaves essentially as a liquid and is referred to as a viscoelastic or Maxwell liquid due to the above-mentioned properties.

For an elastic deformation you apply the Hook's law to rheology:

Shear Stress $\tau = \frac{F}{A}$, and the deformation $\tau = G^* \gamma$. The reasons of viscoelasticity were entanglement in polymers and structure or network of an emulsion. Always used the oscillation test to give the extension of the measuring range, non destructive methode, and analyses data of the material structure and monitoring of time or temperature-depending changes. The oscillation were used the change of direction for input shear stress τ then give the elastic reaction for deformation γ and 0° phase shift for elastic response or 90° viscous response. Separation in elastic and viscous components was:

$$\gamma = \gamma_0 \sin(\omega t - \delta) = \gamma_0 [\sin(\omega t) \cos \delta - \cos(\omega t) \sin \delta] \quad 1.24$$

So to define the complex mouulus:

$$G^* = \frac{\tau}{\gamma} = G' + iG'' \quad 1.25$$

The G' is storage modulus to define:

$$G' = G^* \cos \delta \quad 1.26$$

And G'' is loss modulus to define:

$$G'' = G^* \sin \delta \quad 1.27$$

The oscillatory test included some methods as simple oscillation, time curve for ageing, curing and gelation, and sweep experiment for frequency, amplitude and temperature, and preshear oscillation for structure recovery, and multiwave for monitoring material changes. The stress sweep test was determination of the linear-visco-elastic range for material stability and yield

point. The G' and G'' are independent from stress or deformation. All stress sweeps can be presented either as function of stress or strain. For material stability, the critical stress from the stress sweep is used as characteristic value. The frequency sweep was investigated materials response to impact or gradual load and usually applied at material condition, impact resistance, damping properties and mouth feeling. The frequency sweep was obtained the material characterization of gel, paste and liquid material structure. Usually the behaviors were obtained the viscous at low frequency and elastic at high frequency.

Moreover, the time temperature sweeps were observed of change of material properties due to different initiators for material aging, gelation, fusion, curing, crosslinking and degradation. The multiple creep tests were see the slope value deviating from zero and applied for leveling, sagging and stability. Modeling test was described the material functions as mathematical equation. Relaxation test was known the non linear equations incorporate coefficients, which are known as relaxation times.

Reference

- 1.** S. Molesa, D. R. Redinger, D. C. Huang, and V. Subramanian., *Mat. Res. Soc. Symp. Proc.*, 769, (2003).
- 2.** J. Kabachinski., *Biomedical Instrumentation and Technology.*, March/April, (2005).
- 3.** D. Lochun, E. Zeira and R. Menize., *Electronic Components and Technology Conference.*, (2002).
- 4.** V. Subramanian, J. M. J. Frechet, P. C. Chang, D. C. Huang, J. B. Lee, S. E. Molesa, A. R. Murohy, D. R. Redinger and S. K. Volkman., *Proceeding of The IEEE.*, 93, 7, (2005).
- 5.** DuPont's registered trademark.
- 6.** P. H. Kydd: PCT pattern WO 98/37133 (1998).
- 7.** P. H. Kydd: U. S. Patent 6036889 (2000).
- 8.** Alex Brooks Asia-Pacific Technical Sale Exec., Coates Circuit Products, Product Summary.
- 9.** S. Glasstone, K. Leidler, and G. Ecring., *The Theory of Rate Processes.*, IL, Moscow., 1948.
- 10.** V. P. Skripov, E. N. Sinitsyn., *Termophysical properties of liquids in a metastable state.*, Moscow, Atomizdat, 1980, 208p.
- 11.** M. R. Parikh, W. F. Quilty and K. M. Gardiner., *IEEE. Trans. Component. Hybrids, and Manuf. Tech.*, 14(3) (1991).
- 12.** T. X. Liang, W. Z. Sun, L. D. Wang and H. D. Li., *IEEE. Trans. Component. Package. Manuf. Tech. B.*, 19(2) (1996).
- 13.** H. P. Le., *J. Image. Sci. Tech.*, 42(1) (1998).
- 14.** M. Pudas, N. Halonen, P. Granat and J. Vahakangas., *Prog. Organ. Coat.*, 54 (2005).

15.B. J. Lee, S. H. Kim and C. G. Kang., SICE-ICASE Inter. Joint. Conf., Korea, (2006).

16.O. F. Shlensky, L. N. Aksenov and A. G. Shashkov., Thermal Decomposition of Materials – Effect of Highly Intensive Heating., Elsevier Science Publishers B. V., New York, 1991.



Table 1-1. Metal electrical conductivity and thermal conductivity properties

	Electrical conductivity ($\mu\Omega \cdot \text{cm}$)	Thermal conductivity (W/mK)		Electrical conductivity ($\mu\Omega \cdot \text{cm}$)	Thermal conductivity (W/mK)
Ag	1.59	427.0	Fe	9.71	25.1
Cu	1.67	398.0	Pt	10.6	71.4
Au	2.35	315.0	Pd	10.8	75.5
Al	2.66	237.0	Sn	11.0	66.6
Zn	5.92	121.0	Cr	12.9	90.3
Ni	6.84	90.5	Pb	20.6	35.2

Table 1-2. Water-based Ink-Jet Ink Composition.

Component	Function	Concentration, %
Deionized water	Aqueous carrier medium	60-90
Water soluble solvent	Humectant, viscosity control	5-30
Dye or pigment	Provides color	1-10
Surfactant	Wetting, penetrating	0.1-10
Biocide	Prevents biological growth	0.05-1
Buffer	Controls the pH of ink	0.1-0.5
Other additives	Chelating agent, defoamer, solublizer etc.	>1

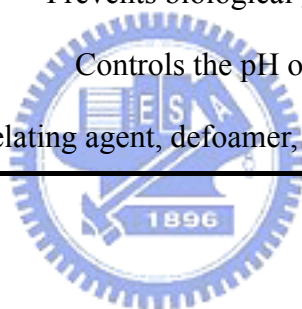


Table 1-3. Kinetic equations of heterogenous decomposition of solids

Basic Factors	Function
Two-dimensional motion of an interface	$(1 - \alpha)^{1/2}$
Three-dimensional motion of an interface	$(1 - \alpha)^{2/3}$
Linear diffusion	$1/2\alpha$
Three-dimensional diffusion	$3(1 - \alpha)^{2/3} / 2[1 - (1 - \alpha)^{1/3}]$
Prout-Tompkins' mechanism	$\alpha(1 - \alpha)$
Avrami-Erofeev's mechanism	$(1 - \alpha)[- \ln(1 - \alpha)^{1-1/n}]$
Ultimate decomposition temperature T_{ul}	$(1 - \alpha) \exp[A/(1/T - 1/T_{ul} + \Delta)]$

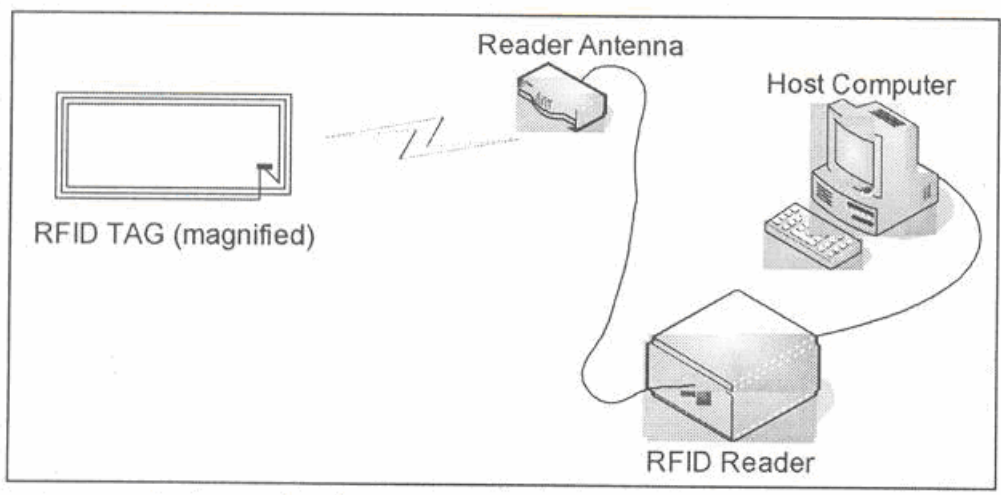


Figure 1-1. A typical RFID System.

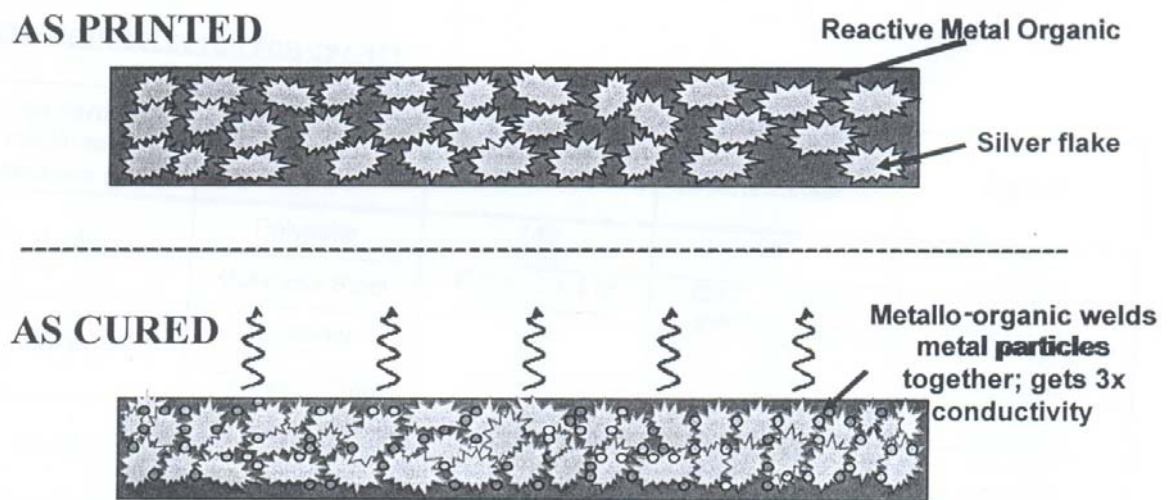


Figure 1-2. The diagram of Parelec Inc innovative 2-step low curing and roll-to-roll printing metal ink process [6].,

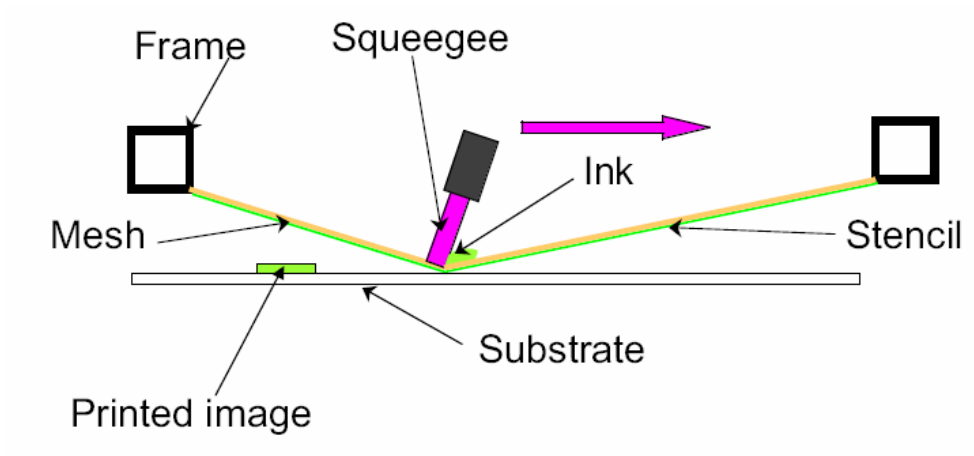


Figure 1-3. Illustrates the manufacturing of the screen printing.



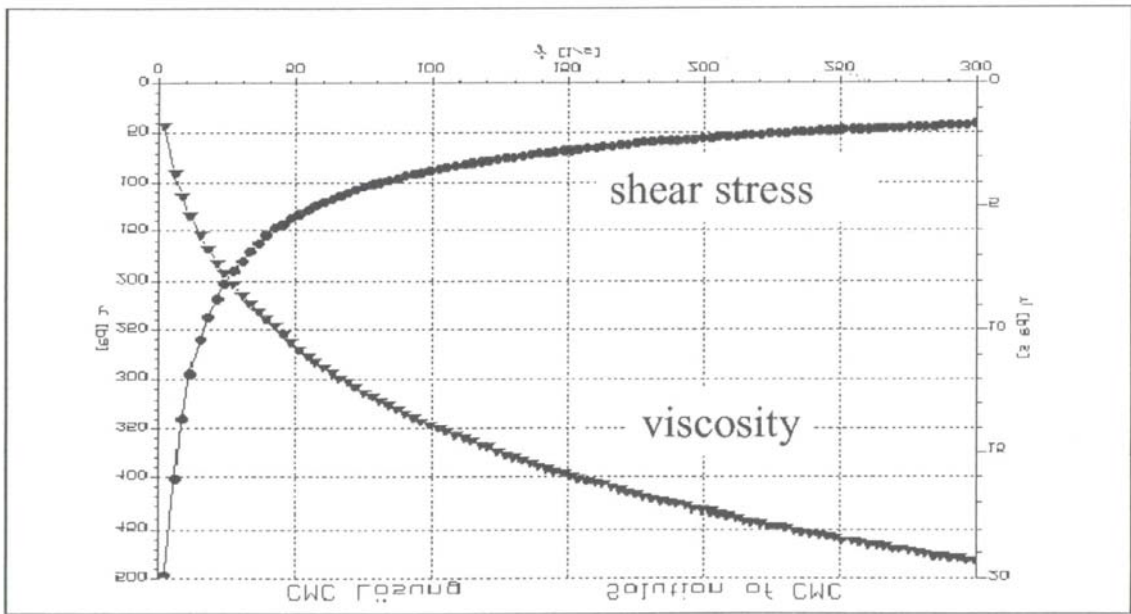


Figure 1-4. The Shear Thinning Flow Behavior.

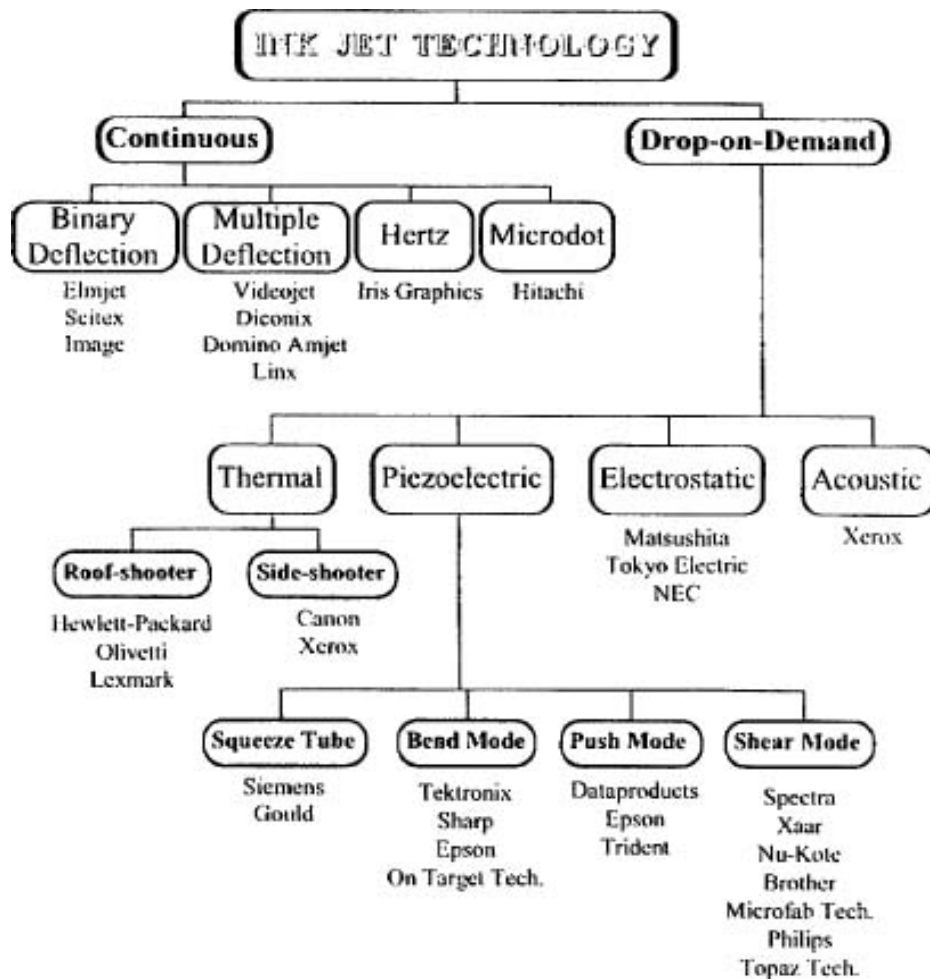


Figure 1-5. Ink-Jet technologies map[13].

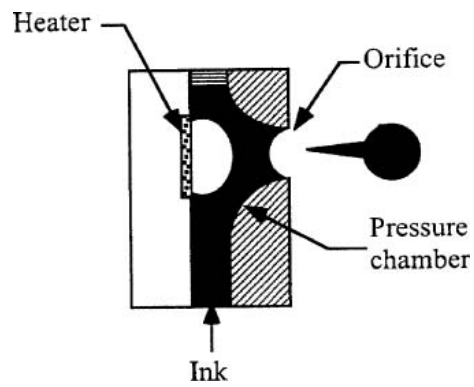


Figure 1-6(a). A roof-shooter thermal ink-jet [13].

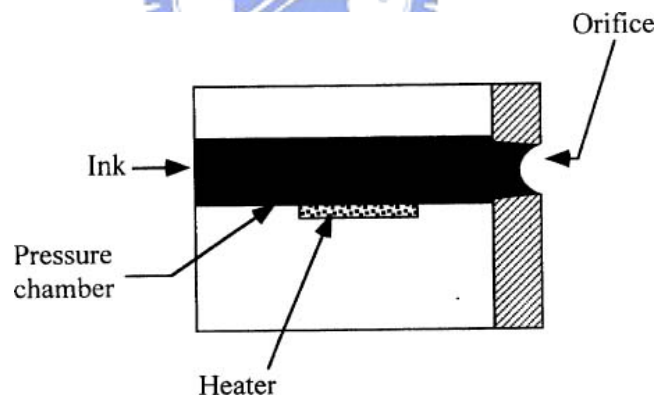


Figure 1-6(b). A side-shooter thermal ink-jet [13].

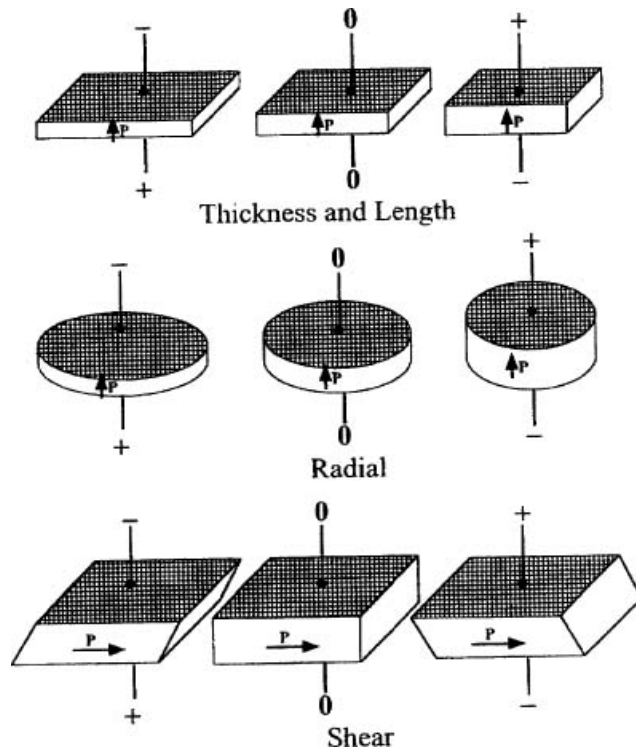


Figure 1-7. Basic deformation modes of a piezoceramic plate [13].

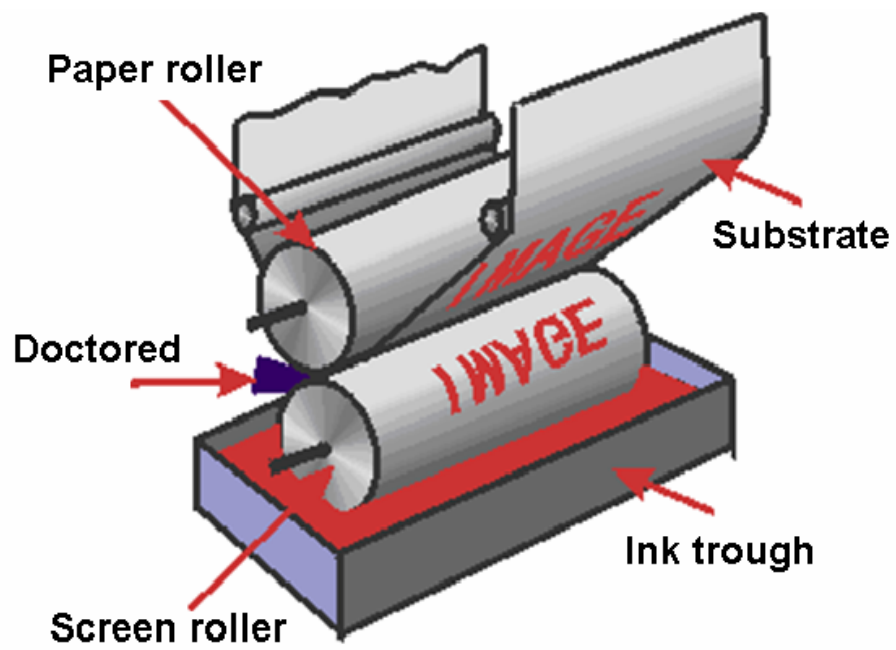


Figure 1-8. The structure charts of gravure printing



Figure 1-9. Actual gravure printing machine [15].

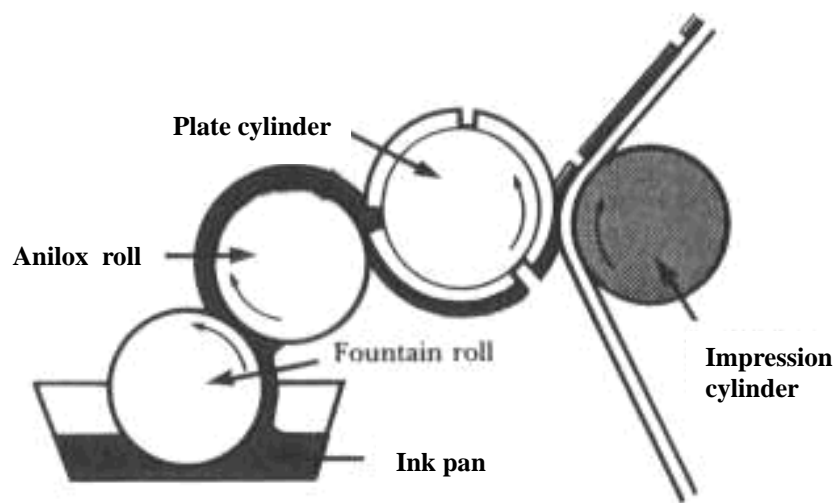


Figure 1-10. The Charts of the Flexo Printing.