ADHESIVE JOINING OR LEAD-FREE SOLDERING?

Pavel Mach, Aleš Duraj

Czech Technical University in Prague, Faculty of Electrical Engineering, Department of Electrotechnology, Prague, Czech Republic

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Abstract: Low-cost tin-lead solders have been used as interconnecting and surface coating materials in electronics for many decades. These alloys have good electrical and mechanical properties, reasonably low melting point, and good reliability, but they are not nature-friendly. As a result of an effort to eliminate the use of lead-containing solders there have been started different regulation and legislation activities in many countries. Some of them are presented in this paper. There are two basic ways of no-lead replacement: lead-free solders and electrically conductive adhesives. Basic types of lead-free solders and electrically conductive adhesives are presented. Selected methods for testing of quality of soldered and adhesive joints are mentioned, and results of measurements of selected types of lead free solders and conductive adhesives are mentioned, too. It has been found that quality of soldered joints is higher than quality of adhesive ones.

Lepljenje ali spajkanje brez svinca?

Kjučne besede: električno prevodna lepila, spajka brez svinca, lepljen stik, spajkan stik

Izvleček: Cenene spajke na osnovi svinca uporabljamo v elektroniki za povezave in spajkanje že nekaj desetletij. Te zlitine imajo dobre električne in mehanske lastnosti, dokaj nizko temperaturo tališča, so zanesljive, vendar niso okolju prijazne. V mnogih državah so zaradi tega z uvedbo zakonskih uredb zaceli z odpravo uporabe spajk s svincem. Nekatere uredbe predstavimo v tem prispevku. V osnovi obstajata dva načina odprave spajk s svincem: uporaba spajk brez svinca in uporaba električno prevodnih lepil. V prispevku predstavimo obe alternativi skupaj z izbranimi metodami in rezultati preizkušanja kvalitete spajkanih in lepljenih stikov. Ugotovili smo, da je kvaliteta spajkanih stikov boljša od kvalitete lepljenih stikov.

1. Introduction

Driving forces affecting development of new joining materials in electronics are as follows:

- Performance of joints realized using these materials.
- Minimization of impact of joining materials and processes on environment.

Soldering technology based on the use of tin-lead solders has become the most frequent method of conductive joining in electronics. Soldered joints have good electrical and mechanical properties, high reliability, and the price of tin-lead solders is not too high.

On the other hand, lead has been involved among 17 chemicals, which impose the greatest threat to human health. Although the consumption of lead for production of solders for electrical and electronic applications is very low in comparison with consumption of this metal in some other applications (accumulators, paints), producers selling electronic products to the European Union and China, but also in many other countries, pay great effort to be compliant with WEEE/RoHS directives in order to stay on the Single Market. To be compliant means that they will have to convert their soldering technologies from tin-lead soldering to lead-free soldering or adhesive joining starting from July 1, 2006.

A step from tin-lead to lead-free soldering is not easy for manufacturers. It means that they have to convert from the very good known technology toward to the technology, which is connected with many question marks still yet, and which is under continuous development. Replacement of tin-lead soldering by adhesive joining is also connected with many problems: adhesive joining needs different surface finishes of the pads and leads than soldering, temperature profiles requested for soldering and for curing of adhesives are different, the price of adhesives is higher in comparison with the price of tin-lead solders.

There are many other questions connected with the no-lead replacement of tin-lead solders. Which of many lead-free solders will dominate, how the higher temperature of lead-free soldering will influence reliability of electronic components, which types of fluxes will be optimal, if properties of joints soldered by lead-free alloys will be equivalent to that of existing tin-lead solders, others.

Many questions must also be answered for adhesive technology, which has some advantages and some disadvantages in comparison with soldering. The main advantage is the low curing temperature of adhesives, which is substantially lower in comparison with the soldering one. The curing temperature is usually in the range of 110 °C to 140 °C, the time of curing is usually 30 to 120 min. However, there are also adhesives, which are cured at the room temperature for a longer time, e.g. for 48 hours. Significant advantage of adhesives is a possibility to prepare them with isotropic or anisotropic electrical conductivity. Electrical conductivity of isotropically conductive adhesives is uniform in all directions just like electrical conductivity of solders. Anisotropically conductive adhesives have high conductivity in z direction and very low electrical conductivity in other directions. The main disadvantages of electrically conductive adhesives are their low endurance against moisture, lower thermomechanical endurance in comparison with solders, and high price, which mostly depends on the price of silver on the world market (conductive fillers in adhesive formulations provide silver usually, although gold, nickel, copper, carbon and palladium have also been tested in some formulations).

2. Regulation and legislation activities in different countries

There are many activities directed to ban lead from electronic production in different countries /1/.

- **EU**: Activities inside the EU are under the umbrella of the European Parliament and the Council of the European Union.
  - In 1998 the EU introduced a draft directive called the Waste from Electrical and Electronic Equipment Directive (WEEE).
  - In 2000 EU Commission has officially adopted the proposal as two separate but associated draft directives for submission to the European Parliament - WEEE and RoHS (Restriction on Hazardous Substances) /6, 7/.
  - In April 2001 the Environmental Committee of the European Parliament adopted a number of amendments and advanced their progress through the EU legislative process /14/.
  - In May 2001the European Parliament and the Council of the European Union have voted to adopt proposals to amend the date for the hazardous material ban in the WEEE/RoHS draft to 2006.
  - In 2002 the Council of Ministers of European countries has discussed and approved the WEEE/RoHS drafts including the target date 2006. The list of hazardous materials has been reviewed in 2003 and is opened. The Directive, prohibits the use of lead (and five other substances - mercury, cadmium, hexavalent chromium, polybrominated biphenyls, and certain polybrominated diphenyl ethers) in electronics starting from July 1, 2006 /5/.
  - Some European countries are paying great effort to apply these documents into practice as fast as possible, e.g. United Kingdom and Ireland /8, 9/.
- **USA**: There is no existing or pending federal restriction or prohibition on the use of lead in electronics components and productions. On the other hand there are many activities in this field on lower levels:
  - The U.S. Environmental Protection Agency (EPA), under the Resource Conservation and Recovery Act (RCRA) regulates the disposal of lead containing wastes /2/.
  - Manufacturers that process 100 or more pounds of lead are required to file annual Toxic Release Inventory (TRI) reports /3/.
  - The Occupational Safety and Health Administration (OSHA) regulate workers exposure to lead /4/.
  - Legislation focused on waste electronics is under development in many states.
- **Japan**: There are no known laws, pending or otherwise, in Japan, calling for reduction or elimination of lead in electronics. However, it has been proposed a recycling legislation in 1998. This legislation has called for reduction of the use of lead by 1/2 to the year 2000 and by 2/3 to the year 2005. There have also been approved Home Electronics Recycling Law (2001) and a law that requires the recycling of personal computers in (2003) /10/.
- **China**: There are no known laws in China, calling for reduction or elimination of lead in electronics, but such laws are under preparation /11/.
- **South Korea**: With respect the effort to be successful on the EU market, 340 companies representing 95 % of electronic industry have voluntary started to accept EU RoHS Directive. South Korea also enacted law making electronics manufacturers and importers responsible for recycling their products. /12/.

This short outline presents some selected activities only in the field of regulation and legislation related to restriction or elimination of lead in electrical and electronic products and production processes.

It is significant that many big producers use "green" production processes (e.g. Samsung Group has announced a "green" semiconductor product already in 2001, Nortel Networks is very active in this field in the Europe, Motorola and Lucent Technologies in USA, Matsushita (Panasonic) and Sony in Japan). There are also many initiatives coming from independent corporations and electronic industry organizations, such as Department of Trade and Industry (DTI) in the Europe, Japanese Institute of Electronic Packaging (JIEP), National Centre for Manufacturing Science (NCMS) and National Institute of Standards and Technology (NIST) in USA.

3. Criteria for selection of lead-free alloys and electrically conductive adhesives

The replacement of lead soldering by no-lead soldering of adhesive joining is not simple. At first, it has been necessary to appoint criteria for selection of proper materials. These criteria have been appointed with respect to material parameters and to technological parameters as well. The criteria make decision, if it is possible to use a lead-free alloy or electrically conductive adhesive as a substitution of tin-lead solder, possible.

3.1 Criteria resulted from basic material parameters

Materials used for conductive joining in electronics must have primarily high electrical conductivity, bond strength and high thermomechanical endurance. However, they must satisfy also other criteria.

These criteria /2/ comprises the liquidus temperature, pasty range, wettability, area of covering (the test is based on the measurement of coverage of copper test piece by solder), drossing (the test is based on the measurement of amount of oxide formed in air on a surface of molten solder after a fix duration at soldering temperature), TMF (lifetime at a given failure rate compared to that of (eutectic) Sn/37Pb, for a specific configuration of a board and solder joint), coefficient of thermal expansion, creep, yield strength and elongation. According to these criteria 79 alloys as candidates for substitution of tin-lead solders have been chosen /13/.

Criteria for selection of electrically conductive adhesives as a substitution of tin-lead solders are TMF, coefficient of thermal expansion, creep, yield strength and elongation.

3.2 Criteria resulted from basic technological parameters

Criteria resulted from basic technological parameters are related to possibility of transformation of contemporary soldering technology for tin-lead soldering to lead-free technology. These criteria are not related to adhesive joining.

The most significant criteria are as follows /13/:

- The melting temperature has to be similar to that of eutectic tin-lead solder. The reason of this request is evident. If the temperatures of tin-lead and lead-free soldering will not be too different, contemporary soldering equipment would be usable without significant changes. It would also not be necessary to increase temperature resistance of some electronic components.
- Narrow plastic range.
- Capability of being fabricated into contemporary physical forms of solder, such as wire, preforms, ribbon, spheres, powder, and paste. This condition is again related to the possibility of the use of contemporary soldering equipment without bigger changes.
- Adequate wetting properties and viscosity.
- Good wettability of leads and pads.
- Acceptably low dross formation when used in wave soldering. This is one of basic conditions for trouble-free wave soldering.
- For paste, adequate shelf life and performance.

4. Viable lead free alloys and electrically condutctive adhesives

4.1 Lead-Free Alloys

Many lead-free alloys, which satisfy criteria for selection mentioned above, have been investigated /15, 16/. However, with respect to the electrical, mechanical and other properties and especially with respect to the price of alloys, only few of them have been recommended for the practical use in common applications. Properties of the alloys are usually compared with the properties of eutectic 63Sn-37Pb solder or with 62Sn 36Pb 2Ag solder. Favorites differ from region to region.

In the Europe the consortium BRITE-EURAM has recommended the use of alloy 95.5Sn 3.8Ag 0.7Cu as the all-purpose solder. Other potential alloys are 96.5Sn 3.5Ag, 9.3Sn 0.7Cu, Sn Pb Bi and Sn Ag Sb.

In the U.S. the National Manufacturing Initiative (NEMI) has recommended alloy 99.3Sn 0.7Cu for wave soldering and alloys 96.5Sn 3.5Ag and 95.5Sn 3.9Ag 0.6Cu for reflow soldering. Other favorite alloys are 96.5Sn 3.5Ag 4.8Bi and 58Bi 42Sn.

In Japan the Japanese Electronic Industry Development Association (JEIDA) has recommended alloys 96.5Sn 3Ag 0.5Cu and 89Sn 8Zn 3Bi for wave soldering, medium and high temperature reflow and 42Sn 57Bi 1Ag for low temperature reflow /16, 17/.

4.2 Electrically conductive adhesives

Electrically conductive adhesives (ECA) are composites consisting of polymer insulating matrix (binder) and electrically conductive filler /18/. There are two basic types of ECAs: adhesives with isotropic electrical conductivity (ICAs) and adhesives with anisotropic electrical conductivity (ACAs, z-axis adhesives). ACAs are usually, in film or paste form, interposed between opposite surfaces which would be joined and application of heat and pressure causes conductive particles to be trapped between these surfaces. This way an adhesive joint is realized. ACAs are of two basic types: preprocessing anisotropic and postprocessing anisotropic /19/.

Both thermoplastic and thermosetting materials are used for adhesive matrix of ECA. The main advantage of ECAs with thermoplastic matrix is easy rework or repair of adhesive joints, main disadvantage is low thermal resistance, the joints must not be heated near to the temperature of the glass transition of adhesive.

Thermosetting resins are cross-linked by curing. Shrink of adhesive caused by the cure reaction, causes compressive force inside the adhesive, which increases of electrical conductivity of a joint. Different materials are used as thermosetting adhesives: acrylic resins for applications under 100 °C, epoxy resins for temperatures to 200 °C, and polyimide and silicone resins for applications up to 300 °C. Rework or repair of adhesive joints fabricated of thermosetting adhesives is difficult /20/.

Fillers of ECAs are of different materials. Particles have different shapes. Typical material of filler is silver, but other materials such as gold, nickel, copper or palladium can also be used. Some ACAs have the particles with nonconductive core of glass or plastic material coated with a conductive layer.

The particles have different forms. They are usually spherical with diameter of 3 to 15 μm, sometimes flakes or grains are used. Particles of different forms can be combined, e.g. filler can consist of 40 % balls and 60 % flakes.

5. Measurements of basic electrical and mechanical properties of soldered and adhesive joints

Basic parameters, which are usually measured on soldered and adhesive joints, are: the electrical resistance, the tensile strength, the shear strength, and the thermomechanical resistance. The changes of these parameters after different types of climatic load are also investigated. As for the adhesive joints, their resistance against DC current or current pulses is also examined.

It has been found /21/ that the electrical resistance of the joints has substantially lower sensitivity to changes in joining material than nonlinearity of the current vs. voltage characteristics of the joint. The measurement of nonlinearity is significant for adhesive joints especially, where it makes a deeper analysis of changes in adhesive, caused by its aging, possible.

The theory of nonlinearity, based on an assumption that nonlinearity of the current vs. voltage characteristic is dominantly influenced by thermal movement of vacancies inside the material, has been derived by Zhigalsky /22/. It has been found that this theory, which has been derived for description of nonlinearity of thin metallic films, is also usable for description of nonlinearity of electrically conductive adhesives /23/. The relationship between the voltage U_3 of third harmonics and the temperature T can be described by the equation:

$$U_3 = \Psi \exp\left(-\frac{\Phi}{T}\right) \quad (1)$$

Here Ψ and Φ depend on the joining material, on the thermal resistance of the joint, on the thickness of the layer between a lead of a component and a pad, on the thermal dilatation of the layer and on other parameters.

Other theory of nonlinearity is based on an assumption that nonlinearity of the current vs. voltage characteristic is dominantly caused by potential barriers inside the material /24/. According to this theory, the current I_T flowing through the material can be described by the equation:

$$I_T = 2N_T A \exp\left(-\frac{e\phi_I}{kT}\right)\left[\frac{eU}{kT} + \frac{e^3U^3}{3!(kT)^3} + \frac{e^5U^5}{5!(kT)^5} + \dots\right] \quad (2)$$

Here N_T ... total number of barriers, A ... material constant, e ... charge of an electron, ϕ_I ... high of the potential barrier, k ... Boltzman constant, T ... temperature, U ... voltage across the joint.

The measurement of the resistance of the joint is mostly carried out in four-point arrangement by the use of an ohmmeter for the measurement of low resistances.

Different types of equipment are used for the measurement of nonlinearity. One possible arrangement of such equipment, based on evaluation of inter-modulation distortion generated by nonlinearity of a measured component, is shown in Fig. 1.

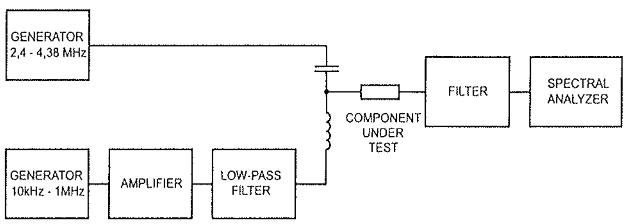

Fig. 1 Schematic diagram of equipment for measurement of nonlinearity of current vs. voltage characteristic

Mechanical properties of soldered and adhesive joints, usually their tensile strength and shear strength, are examined by a pull off test of a component mounted on a testboard using soldering or adhesive joining. Different types of breakers are used for these measurements.

Thermomechanical fatigue is investigated, too.

6. Experiments

Adhesive and soldered joints have been realized by assembly of SMT resistors of the type 1206 with "zero" resistance (jumpers) on a testing PCB (FR4, Cu). The pads have been cleaned by a standard way; no additional surface finish has been used. Seven resistors have been mounted on one board. The testing board (see Fig. 2) makes two point or four-point measurements of the resistances of the joints possible.

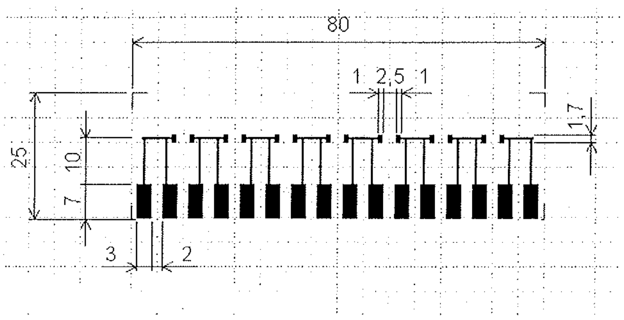

Fig. 2 Testing board (dimensions are in mm)

Adhesive joints have been realized using three one component and three two-component types of adhesives (epoxy resin, Ag filler). The difference among the adhesives has also been in types of particles of the filler (balls, flakes, combination balls/flakes 80/20).

Lead-free solders have been of the types 96.5Sn 3.5Ag and 95Sn 5Ag.

Properties of adhesive joints and the joints soldered with no-lead solder have been compared with the properties of the joints soldered with the solder 62Sn-36Pb-2Ag.

Climatic load has been realized at a climatic chamber. Three types of climatic load have been used: aging at the temperature of 120 °C, aging at the temperature of 80 °C and the humidity of 80 % RH, aging at the humidity of 100 % RH. The time of aging has been 300, 500, 700 and 1000 hours.

Influence of a static mechanical load has also been investigated: the test boards assembled with the "zero" resistors using soldering or adhesive joining have been mounted in a fixture, where they have been compassed. The compassed testing board with the mounted resistors is schematically shown in Fig. 3. Dimensions of the resistor are marked in Fig 4.

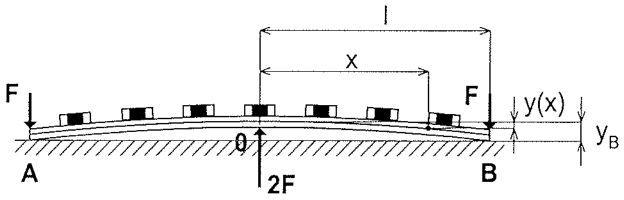

Fig. 3 Compassed testing board with the assembled resistors

The joints have been loaded with different load according to their location with regard to the midpoint of the board. It has been derived that the shear force F_S and the shear stress d_S in the soldered or adhesive joints of the resistor

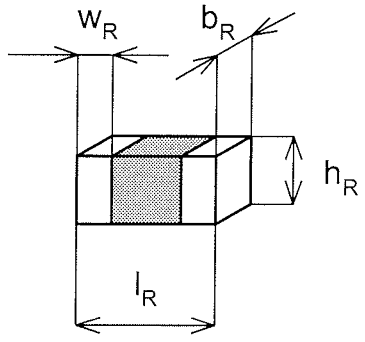

Fig. 4 Dimensions of the resistor

located in the middle of the testing board can be calculated according to the equations:

$$F_S = \frac{E_R S_J \Delta l_R}{l_R} \quad (3)$$

$$\delta_S = \frac{F_S}{S_J} \quad (4)$$

Here E_R ... Young's modulus of elasticity of the body of the resistor, S_J ... contact area of the resistor on the pad, Δl_R ... elongation of the resistor after compassing of the board, l_R ... length of the resistor. The calculated value of the shear force in joints of the resistor located in the middle of the test board is 52.5 N.

Tensile force F_T and tensile stress τ in the joints of the middle resistor can be described by the equations:

$$F_T = \frac{3 E_R J_{ZR}}{l_R^3} y_R \quad (5)$$

$$\tau = \frac{F_T}{S_J} \quad (6)$$

Where J_{ZR} ... cross section module of a body of the resistor, y_R ... deflection of the end points of the resistor against its middle point.

The calculated value of F_T is 2.42 N. The comparison of the calculated shear and tensile forces influencing the soldered or adhesive joints of the middle resistor shows that the shear force dominates. Derivation of equations (3) ... (6) has been presented elsewhere /25/. Similar equations like (3) ... (6) can be derived for every resistor on the board.

7. Results of experiments

Changes of properties of soldered and adhesive joints caused by climatic ageing have been published elsewhere /26/. An example of results of climatic aging of one type of soldered joints is shown in Fig. 5.

Properties of mechanically loaded joints have been published in /21/. An example of changes of the resistance and nonlinearity of adhesive joints loaded with the static mechanical load and aged at the temperature of 120 °C, is

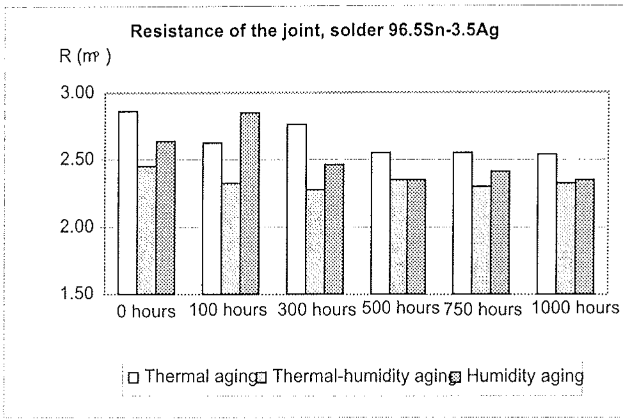

Fig. 5 Climatic aging of soldered joints

shown in Fig. 6 and Fig. 7. Pay attention to changes of the resistance and nonlinearity of the joints. Whereas the changes of the resistance are in the range of 4 to 35 mΩ, the changes of nonlinearity are in the range of 10^{-7} to 2.10^{-4}. Nonlinearity is substantially more sensitive to the changes in material than the resistance of the joint.

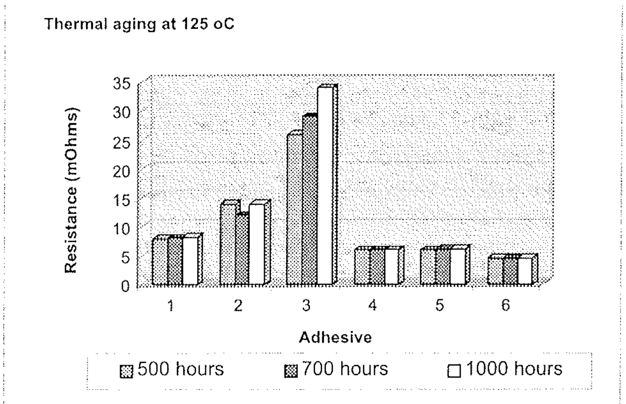

Fig. 6 Resistance of adhesive joints fabricated of 6 different types of adhesives with epoxy resin matrix and Ag filler (1 ... 3: two-component adhesives, 4 ... 6: one-component adhesives). The joints have been loaded with the static mechanical load (F_S = 52.5 N, F_T = 2.42 N) and aged at the temperature of 125 °C.

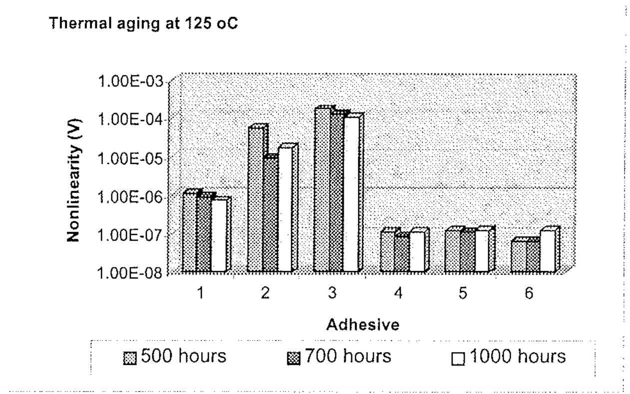

Fig. 7 Nonlinearity of adhesive joints fabricated of 6 different types of adhesives with epoxy resin matrix and Ag filler (1 ... 3: two-component adhesives, 4 ... 6:one-component adhesives). The joints have been loaded with the static mechanical load (F_S = 52.5 N, F_T = 2.42 N) and aged at the temperature of 125 °C.

Results of experiments, focused on investigation of influence of current pulses on properties of adhesive joints, have been presented in /27/.

Comprehensive results of our experiments with 6 types of electrically conductive adhesives and two types of lead-free solders are presented in Tab. 1 to Tab.4. Incomplete results have also been published in /21, 25, 27/.

8. Conclusions

Situation in the field of replacement of tin-lead solders by nature-friendly joining materials such as no-lead solders and

Tab. 1 The resistances of the joints

Joining material	Resistances of the joints
2-component adhesives	4 to 15 mΩ
1-component adhesives	8 to 30 mΩ
Lead-free solder	1 to 3 mΩ
Tin-lead eutectic solder	1 to 2 mΩ

Tab. 2 Changes of the resistances of the joints after the climatic load (1000 hours)

Joining material	Thermal aging (125 °C)	Thermal-humidity aging (80 °C/80 % RH)	Humidity aging (100 % RH)
2-component adhesives	Low (5 to 10 %)	Middle (20 to 40 %)	High (50 to 100 %)
1-component adhesives	Low (5 to 20 %)	High (50 to 100 %)	High (50 to 100 %)
Lead-free solder	Lower than 5 %	Lower than 5 %	Lower than 5 %
Tin-lead eutectic solder	Lower than 5 %	Lower than 5 %	Lower than 5 %

conductive adhesives has been discussed. The most promising lead-free alloys have been mentioned. Methods of investigation of properties of soldered and adhesive joints have been presented together with examples of some results.

Tab. 3 Nonlinearity of the joints

Joining material	Nonlinearity of the joints
2-component adhesives	0.06 to 10 μV
1-component adhesives	0.8 to100 μV
Lead-free solder	~ 0.1 μV
Tin-lead eutectic solder	~ 0.1 μV

The values presented in tables have been found for the soldered and adhesive joints fabricated by assembly of the resistors with "zero" resistance of the type 1206 on the testing PCBs. Other results can be found by the use of other types of components.

It has been found that the investigated electrical, as well as mechanical, properties of the adhesive joints are worse than the properties of the soldered joints. The adhesive joints are also less resistant to the climatic load than the soldered ones.

Such results have been assumed. In general, metal alloys are more resistant to climatic aging than composites based on epoxy resin.

It is possible to claim that quality of the joints soldered by no-lead and tin-lead solders is comparable. Quality of the adhesive joints is lower. On the other hand, electrically conductive adhesives are unsubstitutable in such applications, where it is necessary to create a conductive joint without a heat shock. Especially ACAs have promising prospective in electronics packaging.

9. Acknowledgments

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Tab. 4 Changes of nonlinearity of the joints after the climatic load (1000 hours)

Joining material	Thermal aging (125 °C)	Thermal-humidity aging (80 °C/80 % RH)	Humidity aging (100 % RH)
2-component adhesives	Middle (20 to 50 %)	High (50 to 250 %)	Very high (>250 %)
1-component adhesives	High (50 to 250 %)	Very high (>250 %)	High (50 to 250 %)
Lead-free solder	Low (5 to 20 %)	Very low (<5 %)	Very low (<5 %)
Tin-lead eutectic solder	Very low (<5 %)	Very low (<5 %)	Very low (<5 %)

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Pavel Mach, Aleš Duraj

Czech Technical University in Prague, Faculty of Electrical Engineering, Department of Electrotechnology
Technická 2, 166 27 Prague 6, Czech Republic
mach@fel.cvut.cz

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