Bromine- and Chlorine-Free Printed Circuit Boards (PCBs)

COMPANY PROFILE

NAN YA CCL

Manufacturer of copper-clad laminates used in the manufacture of printed circuit boards (PCBs).

Nan Ya CCL is a division of the Nan Ya Plastics Corporation, which is the market-leading supplier of the laminate material used to connect a printed circuit board's insulating layers together. Nan Ya Plastics Corporation was founded in 1958, and it is now part of a vertically integrated manufacturing corporation, Formosa Plastics.

Headquarters: Taipei, Taiwan
Sales: $6.4 billion (US dollars, 2008)
Employees: 12,529 worldwide

www.npc.com.tw

COMPANY PROFILE

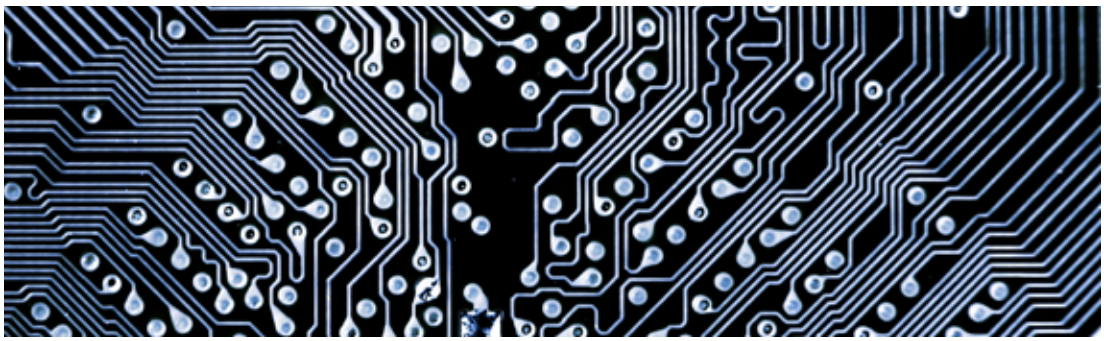
INDIUM CORPORATION

Manufacturer of solder pastes and fluxes for PCB assembly.

Indium Corporation is a premiere materials supplier to the global electronics assembly, semiconductor fabrication and packaging, solar photovoltaic and thermal management markets. Founded in 1934, the company offers a broad range of products, services, and technical support focused on advanced materials science.

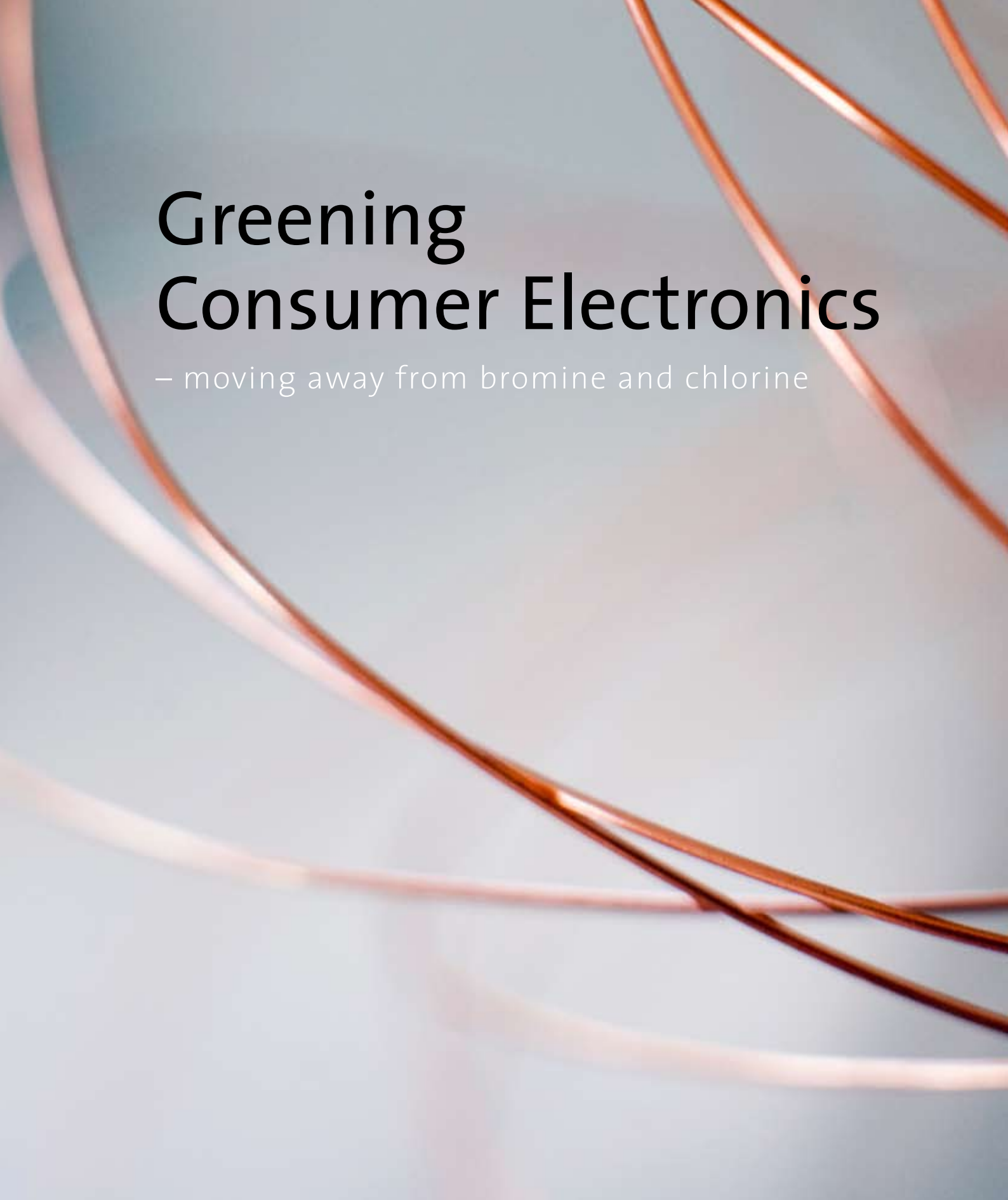
Headquarters: Utica, NY, USA
Sales: Privately held, not publicly disclosed
Employees: Privately held, not publicly disclosed

www.indium.com



NAN YA

INDIUM CORPORATION



Greening Consumer Electronics

– moving away from bromine and chlorine

CHEMSEC – FOR A TOXIC FREE WORLD

ChemSec (the International Chemical Secretariat) is a non-profit organisation working for a toxic-free environment. Our focus is to highlight the risks of hazardous substances and to influence and speed up legislative processes. We act as a catalyst for open dialogue between authorities, business, and NGOs and collaborate with companies committed to taking the lead. All of our work is geared to stimulating public debate and action on the necessary steps towards a toxic-free world.

CPA – STRATEGIC SOLUTIONS FOR GREEN CHEMICALS

Clean Production Action, CPA, designs and delivers strategic solutions for green chemicals, sustainable materials, and environmentally preferable products for a closed-loop material economy.

CPA engages with businesses and NGO leaders to hasten the transition to an economy without harm. We coordinate the US-based Business NGO Working Group for Safer Chemicals and Sustainable Materials and we research and promote companies' efforts to transform the toxic chemical economy.

Published in September 2009

Authors: Nardono Nimpuno, Alexandra McPherson, and Tanvir Sadique

Companies highlighted in this report have kindly contributed to the information provided in the substitution case studies. ChemSec and Clean Production Action are solely responsible for all other texts in this report.

Photo: Niklas Maupoix

INDEX

ABSTRACT

Nan Ya and Indium both surmounted numerous obstacles to achieve their ultimate successes in producing bromine- and chlorine-free materials for use in printed circuit boards (PCBs). Nan Ya is the world's largest supplier of the rigid laminates used to connect PCBs' insulating layers, and it was one of the first to produce halogen-free laminates that performed as well as the halogen-containing FR-4 industry standard. Indium developed a new halogen-free solder paste that negates the need for intentionally added bromine and chlorine.

For several decades, brominated and chlorinated compounds have been used extensively in the manufacture of printed circuit boards (PCBs). However, there has been increased demand for PCBs produced without these halogenated chemicals from OEMs and electronics suppliers who have become increasingly aware of the environmental health issues associated with the improper disposal of halogen-containing electronic products.

The main source of halogens in finished PCBs is brominated flame retardant (BFR). Although chlorinated compounds are used to manufacture epoxy resins of the laminate boards, only trace concentrations of chlorine (around 100 parts per million (ppm)) remain in the final product. For this reason, chlorine poses less of a concern.

TBBPA is the brominated flame retardant primarily used to meet fire-safety standards for PCB assemblies. However, PCB assemblies contain hundreds of components, so simply removing TBBPA is not enough to ensure that the entire PCB assembly would consistently comply with the OEM manufacturers requiring that all homogeneous materials (defined within the industry as materials of uniform composition which cannot be mechanically disjointed into separate materials) contain less than 900 ppm elemental chlorine or bromine. As the world's largest supplier of the rigid laminates used to connect PCBs' insulating layers, Nan Ya was one of the first to overcome the technical challenges of taking bromine out of PCB laminates. In the past few years, Nan Ya has increased its sales of bromine- and chlorine-free laminates, and the company now boasts a 24 % share of the global market. The company has offered a bromine- and chlorine-free laminate since 2001, and laminates meeting this definition now account for 8.8 % of Nan Ya's total sales volume.

Other PCB materials that have historically included bromine are solder paste and flux. Solder paste is a viscous compound, and it typically consists of 90 % powdered metal and 10 % flux by weight. The paste is used to affix integrated circuits and connectors to the PCB. The halogenated compounds in the flux serve as activators, which help facilitate the soldering process.

Although industry organizations had been classifying fluxes based on their halide content since the 1970s, Indium's engineers determined that these older "halide-free" designations did not ensure compliance with IEC's current halogen-free speci-

fication. Halogenated compounds can be either ionic or covalently bonded. Tests specified by the IPC (originally the Institute for Printed Circuits), the association representing companies in the electronic interconnection industry, only detect one of two kinds of chemical bonds that halogenated compounds can form, and it isn't the covalent bonds typically found in fluxes. Therefore, the IPC test method may suggest that there are no halogens present when it could be loaded with covalently bonded halogens. The IPC method also tests the flux prior to heating and soldering. The soldering process actually evaporates about 50 % of the flux but virtually none of the halogens, so the concentration of halogen in the residue is about twice as much as in the raw flux.

To successfully produce PCB solder pastes and fluxes that meet the IEC's current halogen-free designation, which was defined as 900 ppm of bromine or chlorine, Indium successfully overcame a complex set of technical challenges. Indium and Nan Ya are now part of the group of suppliers that have the technical expertise to produce PCB materials that meet the reliability standards required for their halogenated counterparts. This group of PCB material suppliers is now well-prepared to meet the supply demands when new OEMs ramp up their production of Br-Cl-free electronic devices. That's important, because the International Electronics Manufacturing Initiative (iNEMI), an industry-led consortium of approximately 70 electronics manufacturers, suppliers, and related organizations, predicts that the global market for bromine- and chlorine-free PCBs is set to more than double from approximately 6 % of the overall electronics marketplace to over 12 %. Bromine- and chlorine-free PCBs are already in mobile phones and laptops sold in high volumes. Currently 50 % of mobile phones use bromine-free laminates.

OVERCOMING TECHNICAL CHALLENGES

Some of the big hurdles that had to be overcome to produce bromine- and chlorine-free PCB assemblies first came to light when PCB component manufacturers were grappling with how to remove lead from their products to comply with the EU's RoHS directive. Because removing lead and halogens required some of the materials used to produce PCBs to be redesigned, companies were able to capitalize on the opportunity to find solutions that simultaneously met RoHS and bromine- and chlorine-free requirements.

Halogen-free laminates

One of the first steps Nan Ya and other laminate manufacturers were required to take to develop new methods and processes to reliably produce bromine- and chlorine-free PCB laminates was finding a new flame retardant to replace TBBPA. The use of reactive TBBPA (the form primarily used in PCBs) complicated compliance with new material standards since it is bound into the polymer and no longer detectable as a compound in the final product. Most laminate manufacturers moved to reactive phosphorus-based flame retardants, which changed some of the laminates' physical, thermal, and electrical characteristics. Some electronic devices had to be redesigned to ensure that they could operate reliably with the newly formulated PCBs.

Nan Ya worked to successfully overcome the following technical challenges of bromine- and chlorine-free laminates:

- Increased brittleness of the material could cause cracks, which compromised the reliability of the device.
- Poor adhesion strength to the copper conductive layer could cause a phenomenon known as delamination in which the copper layer peels away from the epoxy.
- The hardness of the material caused issues during the etching phase of PCB assembly, resulting in instability in the manufacturing process.
- The hardness of the material also incurred additional costs because of the additional wear on equipment such as drill bits.

In the past few years, Nan Ya has increased its sales of bromine- and chlorine-free laminates, and the company now boasts a 24% share of the global market.

iNEMI's assessment showed that bromine- and chlorine-free laminates met or exceeded the performance in eight of the nine tested categories.

Engineers eventually developed new technologies that relied on different curing agents and alternative proprietary formulations. These solutions allowed PCB material manufacturers to offer bromine- and chlorine-free components that are as reliable as the halogen-containing FR-4 material that is considered an industry standard. A testament to how effectively laminate manufacturers, and the industry as a whole, have dealt with these issues comes from an extensive 2007/08 iNEMI evaluation that investigated the technical performance of bromine- and chlorine-free laminates. The organization evaluated nine key physical, thermal, and electrical properties of the new laminates by comparing them with the FR-4 material. iNEMI's assessment showed that the bromine- and chlorine-free laminates met or exceeded the performance in eight of the nine tested categories (see table [add position info]). In the ninth category, peel strength, some but not all bromine- and chlorine-free laminates boards met the performance of FR-4 laminates. In its evaluation, iNEMI stressed that not all bromine- and chlorine-free laminates were equivalent and all performed differently than the FR-4 material. iNEMI is currently conducting a project to further evaluate bromine- and chlorine-free laminates PCB materials, with an eye toward developing industry standards for producing such materials.

PERFORMANCE OF HALOGEN-FREE VS. BROMINATED LAMINATES

(+ means better, - = worse and o = indifferent)

Thermal properties	Thermal expansion	Lower	+
	Thermal conductivity	Higher	+
Physical properties	Flammability	Equal	o
	Moisture absorbtion	Comparable	+ / o
	Peel strength	Lower	- / o
	Modulus	Equal	o
Electrical properties	CAF resistance	Higher	+
	Dielectric constant	Slightly higher	+
	Dissipation factor	Lower	+
Workability	Drill bit wear	Higher	-

**Reprinted with permission from iNEMI*

It is important to note that the bromine- and chlorine-free PCBs perform with better thermal reliability in the higher temperature manufacturing environment required to produce RoHS-compliant lead-free electronic devices. They also have a lower dielectric constant, which results in a more stable electric circuit. This renders the signal strength from one point of a circuit to another more predictable.

BROMINE- AND CHLORINE-FREE SOLDERS AND FLUX

To reliably produce bromine- and chlorine-free solder and flux, Indium had to overcome two major challenges: "graping" and "head-in-pillow defects."

GRAPING is a phenomenon in which the flux-to-powder ratios are reduced due to a variety of reasons. The exposed solder powder then combines into a mass instead of being dispersed evenly, which creates unreliable solder joints. To solve the problem, PCB manufacturers redesigned their products to reduce exposed metal traces and increase the use of solder mask defined pads. This creates a "well" around the pad and helps to keep the flux around the solder paste deposit, which assists with the effectiveness of the flux. Indium also had to change its process by using a higher volume of solder paste and optimizing the airflows in its reflow ovens.

HEAD-IN-PILLOW DEFECT (HIP) is a common failure in the industry that occurs when the solder paste does not mix with the metal on certain types of semiconductor packages. This failure causes the circuit in the electronic device to fail. There are several reasons for these types of failures to occur, including:

- oxidation being present where the semiconductor package meets the solder during certain phases of the production process;
- PCBs not designed for optimal performance with bromine- and chlorine-free flux; and
- using insufficient quantities of solder paste during the process.

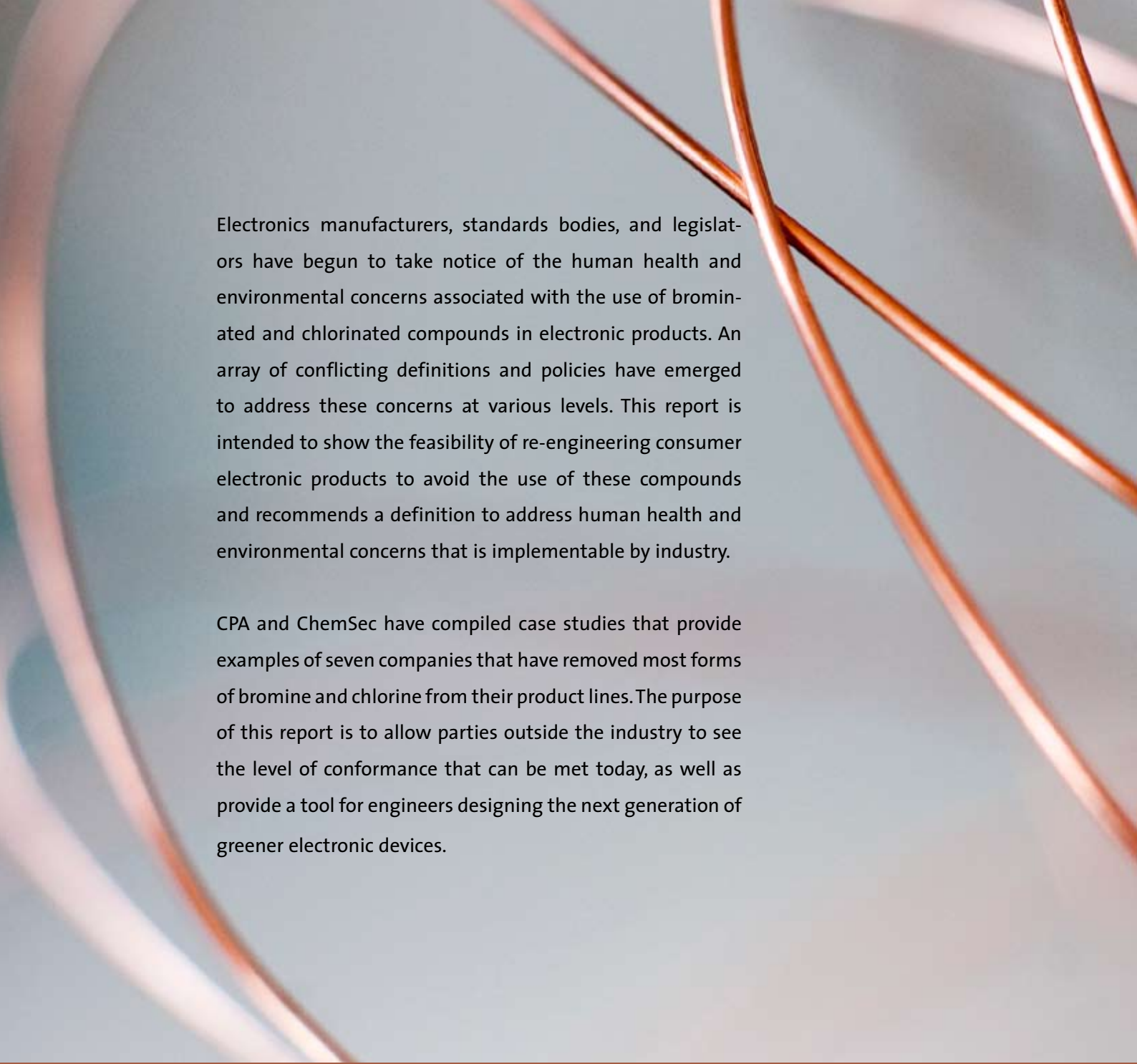
To prevent this type of failure, Indium developed a new solder paste that expanded what is known as the oxidation barrier. The new solder reduced the need for increasing the use of bromine- and chlorine-free activation agents. This innovation is considered a major breakthrough, and it enables the production of PCBs that comply with the 900 ppm threshold for bromine and chlorine without compromising the reliability of the product.

GOING FORWARD

Nan Ya and Indium provide key examples of an industry finding workable solutions to the technical challenges manifested by the transition to bromine- and chlorine-free materials. Some of these solutions required minor tweaks to current processes, while others led to better PCB design and more efficient manufacturing. However, the 5 to 30 % cost premium associated with these new PCB materials is still a major issue. The higher prices are largely attributed to the following factors: a relatively small number of OEMs specifying bromine- and chlorine-free components; the higher costs of new flame retardants; and the residual costs incurred in developing the new design and production processes necessary for bromine- and chlorine-free PCB assembly.

Now that much of the research needed to develop the new materials and techniques has already been conducted, many PCB material suppliers are prepared to meet the supply demands expected when large OEMs ramp up their production of new bromine- and chlorine-free consumer electronic devices. The predictability of a more guaranteed market demand for these products, such as a government mandate and/or a higher number of OEMs specifying them, will allow suppliers to more efficiently scale-up their production and lower product costs.

The bromine- and chlorine-free PCBs perform with better thermal reliability in the higher temperature manufacturing environment required to produce RoHS-compliant lead-free electronic devices.



Electronics manufacturers, standards bodies, and legislators have begun to take notice of the human health and environmental concerns associated with the use of brominated and chlorinated compounds in electronic products. An array of conflicting definitions and policies have emerged to address these concerns at various levels. This report is intended to show the feasibility of re-engineering consumer electronic products to avoid the use of these compounds and recommends a definition to address human health and environmental concerns that is implementable by industry.

CPA and ChemSec have compiled case studies that provide examples of seven companies that have removed most forms of bromine and chlorine from their product lines. The purpose of this report is to allow parties outside the industry to see the level of conformance that can be met today, as well as provide a tool for engineers designing the next generation of greener electronic devices.

International Chemical Secretariat

Box 7005, SE-402 31 Göteborg, Sweden
Tel: +46(0)31-711 04 95
E-mail: info@chemsec.org

www.chemsec.org

CPA (North America)

P.O. Box 153, Spring Brook, NY 14140, USA
Tel: +1 716-805-1056
E-mail: alexandra@cleanproduction.org

www.cleanproduction.org