Missed Call: iPhone's hazardous chemicals

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Creating a toxic-free future

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Contents

Greenpeace is an independent global campaigning organisation that acts to change attitudes and behaviour, to protect and conserve the environment and to promote peace.

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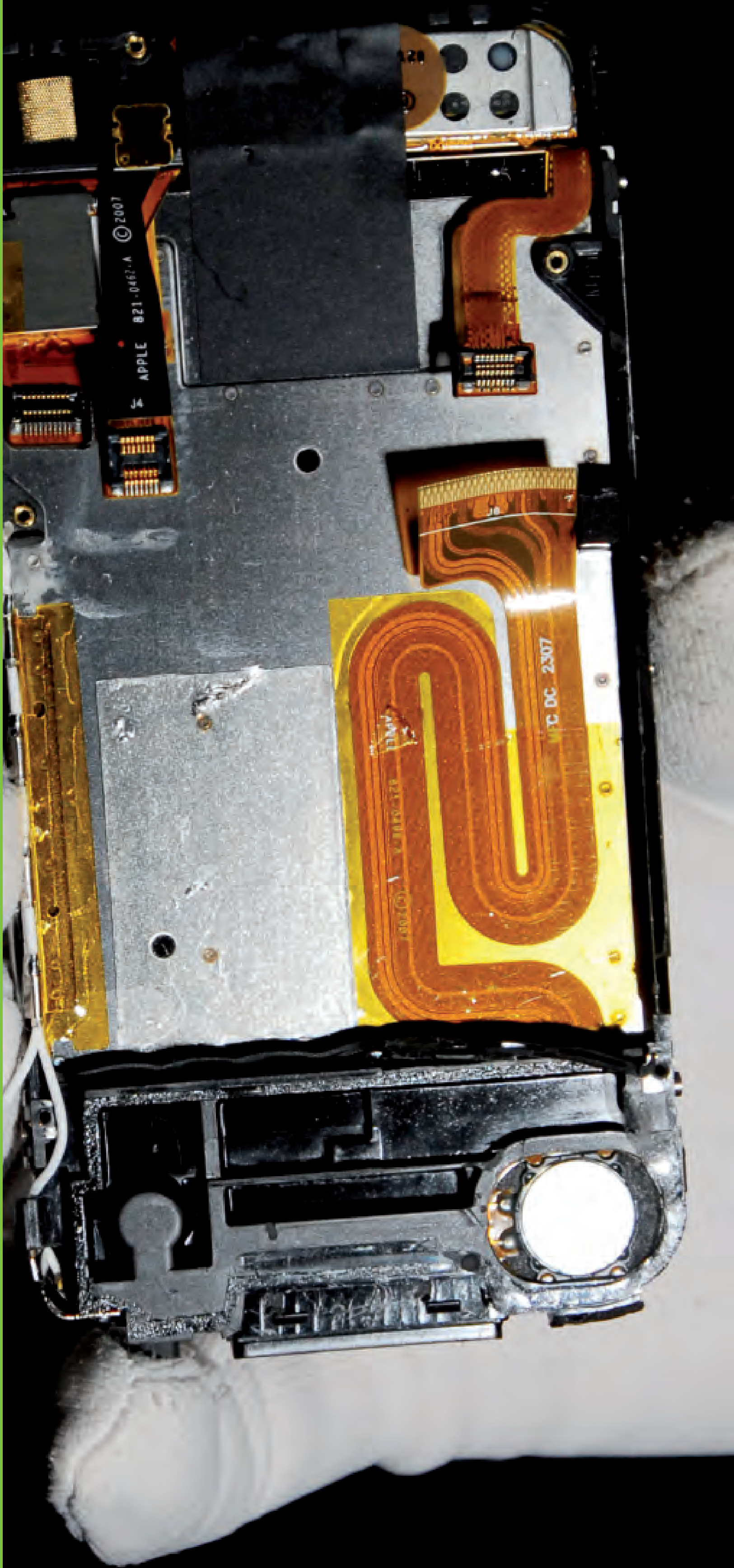

iPhone exposed. As disassembly progresses the iPhone's inner circuitry and components are revealed.

Executive Summary

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In May 2007, Apple announced that all of its new products would be free from brominated flame retardants (BFRs) and the chlorinated plastic polyvinyl chloride (PVC) by the end of 2008. The following month, Apple launched its latest product, the iPhone, to an eager US market and is now gearing up for its release in Europe in November this year. In order to see what progress Apple has already made towards meeting its pledge on hazardous chemicals and materials, Greenpeace purchased an iPhone in Washington, DC in June and forwarded it to laboratories in the UK for deconstruction and analysis.

The iPhone was carefully deconstructed at the Greenpeace Research Laboratories, based at the University of Exeter (UK), and a selection of 18 internal and external materials and components were subsequently forwarded to an independent laboratory elsewhere in the UK for analysis of chemical composition. This analysis focused primarily on those substances regulated under the European Union's RoHS Directive (2005/84/EC), which prevents the use of lead, cadmium, mercury, chromium (VI) and certain brominated flame retardants in electrical and electronic goods. Additional tests were also run for certain other hazardous substances and materials, including PVC and the toxic phthalate plasticisers they commonly contain.

- All components tested appear to be compliant with the requirements of the EU RoHS Directive, to the extent that 1) no cadmium or mercury were detected, 2) lead and chromium were detected in a small proportion of samples and at relatively low concentrations and 3) there was no evidence for the presence of the most toxic and regulated form of chromium (chromium (VI)) in a range of other metal-plated components tested.

- However, half of the components analysed did test positive for bromine, in three cases at over 1% of the total surface chemical composition of the material, suggesting continued widespread use of either additive or reactive brominated flame retardants. Although none of the BFRs covered by RoHS could be detected in the sample with the highest bromine content (10% by weight, in the flexible circuit board of the phone's antenna), all forms of BFR (even if chemically-bound into polymers) can act as a significant source of toxic and persistent brominated pollutants once the iPhone handset enters the waste stream.

- The presence of antimony in four of the components raises additional concerns. Despite its well recognised toxicity, antimony (often used to enhance brominated flame retardant formulations) is not currently regulated under RoHS.

- A high level of chlorine was detected in the plastic coating of the headphone cables, along with phthalates plasticisers at a total of over 1.5% by weight, both characteristic of PVC. Although the use of PVC and phthalate esters is not currently prohibited or even regulated under RoHS, it is worth noting that none of the four phthalates found in this study are permitted for use in components of toys or childcare articles sold in Europe.

- As we were able to analyse only a small selection of the different components and materials, it is not possible (without a lot of additional testing) to conclude that all materials used in the iPhone currently on sale in the USA would comply with EU law.

The fact that a product brought newly to the US market in June 2007 still utilises PVC and brominated flame retardants (even if not those BFRs regulated under the RoHS Directive) suggests that Apple is not making early progress towards its 2008 commitment to phase-out all uses of these materials, even in entirely new product lines. Whether the iPhone model due for release in Europe in November 2007 will also rely on brominated internal components and PVC headphones remains to be seen.

If Apple really wants to reinvent the phone, it needs to design out all hazardous substances and materials from its handsets and peripherals.

Introduction

Analysis of internal and external components from an Apple iPod purchased in the UK during 2007 indicated that brominated materials and PVC were still common to many components[1]. This current study focuses on a more recent Apple product, the iPhone, released in the USA in June 2007[2] and due for release on the European market in early November.

Under European law, all electrical and electronic goods placed on the market in the EU from July 2006 onwards must comply with strict limits relating to a number of specific hazardous chemicals. Under the so-called RoHS Directive[3], homogenous materials and components must not contain more than 0.1% by weight of the heavy metals lead, chromium (VI) and mercury or of the organic brominated flame retardants (BFRs) PBDEs and PBBs, and no more than 0.01% by weight of cadmium. These requirements under RoHS do not, however, address all hazardous chemicals and materials commonly use in electronics. For this reason, the current study of the iPhone focuses not just on issues of RoHS compliance, but also investigates the presence of other hazardous chemical additives and materials commonly associated with electronics, including PVC and additional BFRs additional to those regulated under the RoHS Directive.

Materials and methods

An iPhone was purchased in Washington, DC on 29 June 2007 and forwarded to the Greenpeace Research Laboratories at the University of Exeter (UK) for dismantling and analysis. The handset was dismantled in our laboratory, taking care to avoid contamination with dust and grease and cross-contamination between different components. Individual components were placed in antistatic bags for storage prior to analysis.

A total of 18 individual components and/or materials (listed in Table 1 below) were forwarded to an independent analytical laboratory for analysis of surface elemental composition using XRF (X-Ray Fluorescence spectrometry). This analytical technique yields data on the composition of a number of chemical elements (with a detection limit in the range of 20 parts per million, ppm, or 0.002% of the total composition), with a focus on those of regulatory concern under the EU RoHS Directive (i.e. cadmium, chromium, mercury, lead and bromine. Identification of bromine indicates the presence of brominated additives or polymeric materials used for fire retardancy purposes). In addition, XRF gives an indication of the presence of certain other elements of environmental and toxicological concern, including antimony (frequently used as a synergist in brominated flame retardant formulations[4] and commonly found in electronic wastes[5]) and chlorine (for which high concentrations in plastic materials commonly indicate the presence of PVC).

Removal of the rear panel revealing the iPhone's circuitry and battery.

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Table 1: description of the 18 different components and materials from the iPhone which were subjected to surface chemical composition analysis using XRF.

Sample code	Sample description
XRF-2	Black plastic outer casing over antenna
XRF-4 *	Flexible antenna circuit board
XRF-5	Flexible printed circuit board
XRF-6	Plastic surrounding headphone socket
XRF-8	Foam attached to camera to circuit board connector
XRF-9	Flexible camera housing
XRF-10	Silver-coloured battery casing
XRF-12	Flexible printed circuit board
XRF-14	White internal cables connecting to antenna
XRF-16	Foam rubber material surrounding microphone
XRF-17	Internal casing material beneath antenna
XRF-21	Surface material of Samsung NAND flash memory chip
XRF-27	Main rigid circuit board
XRF-28	Solder pad on circuit board
XRF-30	Solder connection to battery
XRF-31	Surface material of chip with blue sticker
XRF-33 *	Headphone cable
XRF-36	Rubberised base material of USB cradle

* subsequently selected for more specific and detailed chemical analysis.

Results

Detailed results from the XRF analyses are provided at Annex 1. In summary:-

1) no evidence was found for the presence of the heavy metals cadmium or mercury in any of the 18 samples analysed (above the detection limit of 20 ppm);

2) low concentrations of total **chromium** (100-280 ppm) were found in some of these materials, but there is no reason to believe that any significant quantities of the chromium present was in the most toxic form chromium (VI). Although it was not possible to confirm the absence of chromium (VI) in those components testing positive for chromium, separate chemical analysis in our laboratories of a range of other plated components in the phone (especially screw heads) found no evidence of chromium (VI);

3) **lead** was found in four of the components/materials, at concentrations ranging from 10 to 80 ppm, well below the compliance limits under RoHS (1000 ppm). These included the black outer casing of the phone beneath which the antenna was located (XRF-2), one of the internal flexible circuit boards (XRF-5), an internal rubber component in the region of the microphone (XRF-16) and the Apple-branded rubberised base of the USB cradle/docking station (XRF-36);

4) **bromine** was detected in half of the samples tested (9), at levels ranging from 10 ppm to a high of 100 000 ppm (or 10% of the total surface composition of the material). The highest concentrations were found in the flexible circuit board which makes up the antenna (XRF-4). Next highest were in the headphone socket (XRF-6, 41 000 ppm) and a circuit board inside the phone (XRF-27, 14 000 ppm). Both the flexible antenna and the headphone socket also yielded positive readings for **antimony** (though levels of antimony could not be quantified), probably arising from the use of antimony trioxide as a synergist in the flame retardant mix. Antimony was also detected in surface samples of two of the chips tested (XRF-21 and XRF-31), again along with significant bromine concentrations (2 400 and 3 200 ppm respectively). Although not currently regulated under the RoHS Directive, there are substantial concerns regarding the toxicity and carcinogenicity of the form of antimony used in such applications[6]. There is evidence that the presence of antimony in some brominated polymers can also enhance the formation of brominated dioxins and furans during combustion[7], though without disclosure of the types of brominated materials used in the iPhone, it is not possible to determine the relevance of this mechanism in this case;

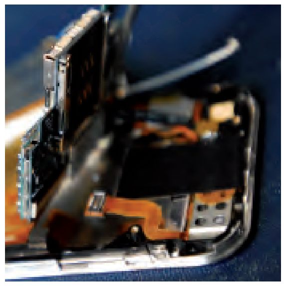
5) one sample, namely the white headphone cable (XRF-33), showed a high level of chlorine, indicating that the cable casing is made from PVC.

Based on the outcome of these XRF screening analyses, two of the 18 materials were selected for more specific and detailed chemical analysis (using gas chromatography/mass spectrometry) at the same analytical laboratory:-

a) the flexible circuit board which made up the antenna of the phone (XRF-4) was analysed for the presence of the extractable (additive) brominated flame retardants PBDEs (excluding the 'decaBDE' form, which is currently exempted under RoHS) and PBBs;

b) the white casing of the headphone cable (XRF-33) was analysed for the presence of a range of phthalate esters commonly used as plasticisers in flexible PVC, including those phthalate esters prohibited from use in toys and childcare articles in the EU.

Disassembly progresses with removal of one of the phone's main circuit boards.



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Further details of the methods employed can be provided on request.

Despite the very high bromine content, the flexible antenna circuit board contained no detectable residues of PBDEs (<30 ppm), including octa- and nona-BDE, nor of PBBs, (though the absence of PBBs is not unexpected given that these are historically used chemicals that are now are largely obsolete). Two limitations to the analysis performed are worth noting:-

i) the limits of detection are relatively high (as the method is designed primarily to test compliance with the RoHS Directive), such that any small traces of PBDEs (below regulatory significance) would not have been detected;

ii) the exclusion of decaBDE from the analysis (also for regulatory reasons) means that even high concentrations of this flame retardant would not have been detected in this study. However, were decaBDE present at high levels, it is likely that the analyses would have detected the presence of nonaBDE and octaBDEs which are commonly present at significant levels as contaminants in decaBDE formulations.

While these are significant limitations, it is possible to conclude that the flexible antenna circuit board, at least, would be in compliance with existing EU laws on the presence of brominated flame retardants. Although the possibility cannot be ruled out that the high levels of bromine detected in this component resulted from the presence of decaBDE or another additive brominated flame retardant not addressed by RoHS, it seems more likely (on the basis of experience with similar components in various brands of laptop computers[8]) that the bromine is present in a reactive polymeric form (such as cross-linked TBBPA-based formulations) or, at least, in poorly extractable oligomeric forms which cannot be quantified using gas chromatographic techniques. Whether in additive or reactive form, the presence of such high proportions by weight of bromine in such materials is of concern with respect to the disposal or recycling of end-of-life iPhone handsets, as even cross-linked organic-bound bromine can contribute to the formation of toxic chemicals, including persistent and bioaccumulative brominated dioxins and related compounds during thermal destruction or processing[9].

The flexible plastic of the headphone cable did yield high concentrations of extractable additives, namely phthalate esters (more commonly known as phthalates), comprising a total of over 1.5% of the overall weight of the material.
In total, four phthalates were detected, dominated by DEHP (at 11,400 ppm, or 1.1% by weight), followed by DnBP (5,070 ppm, or 0.5%), DiNP (725 ppm, or 0.07%) and DiDP (75 ppm, or 0.007%). These figures, together with the presence of high levels of chlorine, strongly indicate that the headphone cable is made of PVC, plasticised with phthalates including those banned for use in toys and childcare articles in the EU[10]. Furthermore, these results are similar (though higher overall) than those found in previous analyses of headphone cables sold with an Apple iPod, for which we have confirmed the presence of PVC (DEHP 6,000-6,900 ppm; DnBP 2 200-2,700 ppm; DiNP 2 100-2,700 ppm).

The two most abundant phthalates in the headphone cables of both the iPhone and iPod are those classified in Europe as 'toxic to reproduction: category 2'[11], as a result of their ability to interfere with sexual development in mammals, especially in males. These phthalates are prohibited from use in all toys or childcare articles put on the market in Europe (with a limit of 0.1% by weight), according to Directive 2005/84/EC. The two other phthalates found in the headphones sold with the iPhone (DiNP and DiDP) are prohibited under the same Directive from use in toys and childcare articles if they can be placed in the mouth by children. Although it is unclear whether headphones from an iPod or iPhone could ever be classified as components of toys or childcare articles, it is clear that the presence of high levels of phthalates in such materials could contribute to overall levels of exposure to such chemicals for the user, including children.

Conclusions

Of the 18 different internal and external components and materials tested from an Apple iPhone purchased in the USA in June 2007, all would appear to be compliant with the requirements of the EU's Directive on use of certain hazardous substances in electronics and electrical goods (the RoHS Directive). In particular:-

- no cadmium or mercury were detected;
- lead and chromium were detected in a small proportion of samples and at relatively low concentrations;
- there was no evidence for the presence of the toxic and regulated form of chromium, chromium (VI), in a range of other metal-plated components tested (primarily screw heads).

Nevertheless, it should be noted that:-

1) despite efforts to include as wide a range of different components and materials as possible in the analyses, the study was inevitably limited in scope to those 18 samples tested. It is not possible, therefore, to conclude from these results that all components and materials used in the iPhone model currently on sale in the USA would be RoHS compliant if brought to the European market. This would need to be the subject of more detailed investigation;

2) half of the components analysed tested positive for bromine, in three cases at over 1% of the total surface chemical composition of the material, suggesting continued widespread use of either additive or reactive brominated flame retardants. Although none of the PBDEs or PBBs covered by RoHS could be detected in the sample that yielded the highest bromine content (100,000 ppm or 10% by weight in the flexible antenna circuit board), even chemically bound bromine can act as a significant source of toxic and persistent brominated pollutants once the iPhone handset enters the waste stream;

3) the presence of antimony in four of the components raises additional concerns. Despite its well recognised toxicity, antimony (often used to enhance brominated flame retardant formulations) is not currently regulated under RoHS.

4) the presence of high levels of chlorine in the plastic coating of the headphone cables, combined with that of phthalate esters at a total of over 1.5% by weight, strongly indicates that the headphones supplied with the iPhone model on sale in the USA are made from PVC. Once again, although the use of PVC and phthalate esters is not currently prohibited or even regulated under RoHS, it is worth noting that none of the four phthalates found in this study are permitted for use in components of toys or childcare articles sold in Europe.

5) also of concern is the fact that the battery was, unusually, 'hardwired' (glued and soldered) in to the handset, hindering replacement and rendering material separation for recycling or appropriate disposal more difficult, and therefore less likely to occur.

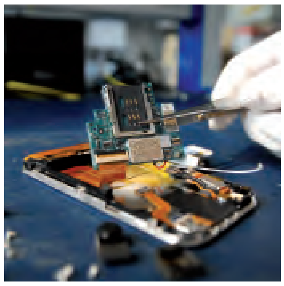
The fact that a product brought newly to the US market in June 2007 still utilises PVC and brominated flame retardants (even if not those BFRs regulated under the RoHS Directive) suggests that Apple is not making early progress towards its 2008 commitment to phase-out all uses of these materials, even in entirely new product lines. Whether the iPhone model due for release in Europe in November 2007 will also rely on brominated internal components and PVC headphones remains to be seen.

The iPhone's battery and a circuit board. Wires from the iPhone's battery are soldered to the circuit board making replacement and separation for recycling more difficult.

Annex 1: detailed results from XRF analysis of 18 iPhone components and materials. All values are parts per million (ppm)

Sample code	Sample description	Bromine (Br)	Cadmium (Cd)
XRF-2	Black plastic outer casing over antenna	<20	<20
XRF-4 *	Flexible antenna circuit board	100 000	<20
XRF-5	Flexible printed circuit board	90	<20
XRF-6	Plastic surrounding headphone socket	41 000	<20
XRF-8	Foam attached to camera to circuit board connector	<20	<20
XRF-9	Flexible camera housing	<20	<20
XRF-10	Silver-coloured battery casing	<20	<20
XRF-12	Flexible printed circuit board	<20	<20
XRF-14	White internal cables connecting to antenna	<20	<20
XRF-16	Foam rubber material surrounding microphone	<20	<20
XRF-17	Internal casing material beneath antenna	10	<20
XRF-21	Surface material of Samsung NAND flash memory chip	2 400	<20
XRF-27	Main rigid circuit board	14 000	<20
XRF-28	Solder pad on circuit board	150	<20
XRF-30	Solder connection to battery	3 100	<20
XRF-31	Surface material of chip with blue sticker	3 200	<20
XRF-33 *	Headphone cable	<20	<20
XRF-36	Rubberised base material of USB cradle	<20	<20

* subsequently selected for more specific and detailed chemical analysis.



One of the two main circuit boards of the iPhone. Analysis detected bromine, suggesting that it contains brominated flame retardants

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Chromium (Cr)	Mercury (Hg)	Lead (Pb)	Other
<20	<20	10	-
<20	<20	<20	Antimony (Sb)
180	<20	80	-
100	<20	<20	Antimony (Sb)
<20	<20	<20	-
160	<20	<20	-
280	<20	<20	-
<20	<20	<20	-
<20	<20	<20	-
<20	<20	60	-
<20	<20	<20	-
<20	<20	<20	Antimony (Sb) Chlorine (Cl)
<20	<20	<20	-
<20	<20	<20	-
<20	<20	<20	-
<20	<20	<20	Antimony (Sb)
<20	<20	<20	Chlorine (Cl)
<20	<20	50	-

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