The Compliance Risk Assessment of EU REACH SVHC in Articles of IC Package by Studies of Analysis Methodology

Renata Hsiao, Fenny Liu, Wein Chen, Han Gung Chen, Liang-Yih Hung and Yu Po Wang
R&D Division, Siliconware Precision Industries Co. Ltd.
No. 153, Sec. 3, Chung Shan Rd., Tantzu, Taichung, Taiwan
Email: renata@spil.com.tw
Tel: 886-4-25341525 ext 6794, Fax: 886-4-25342025

Abstract

Companies may have legal obligations resulting from the inclusion of the Candidate List of substances of very high concern (SVHC) in a concentration above 0.1% w/w in an Article, as defined under EU REACH Regulation and Waste Framework Directive (SCIP Database) if they place articles on the EU market.

Only a few studies have so far been made on how to determine the contents of the Chemical in Product (CiP). The approach to identifying the risk associated with the SVHC in the IC package is mainly to collect and review large information from the supplier chain or by chemical analysis.

This article tries to discuss the current challenges for data collection and identifying risks with chemical substances in the IC package.

Based on the chemical test results of 2-benzyl-2-dimethylamino-4'-morpholinobutyrophenone and bisphenol A, it was found that the test results of SVHC could be affected by numerous factors such as tested sample form (e.g., powder or flaky shaped), tested sample curing conditions, and chemical analytical methods.

Although chemical analysis provides more accurate information for SVHC, when utilizing chemical analysis for checking legal compliance, we still need to compare and analyze the result of chemical substances analysis with the materials self-declaration provided by suppliers to judge whether the data are reasonable.

Key words

REACH, Articles, SCIP, SVHC

I. Introduction

When companies place EEE in the EU market, they must ensure products comply with both EU Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation, and RoHS Directive. Therefore, companies must identify and perform risk assessments of regulated substances contained in products. EU RoHS Directive currently restricts the use of 10 hazardous substances. To demonstrate the compliance of RoHS, material makers of the supply chain are required to provide chemical analysis reports of RoHS restricted substances yearly at the homogeneous material level.

The REACH Candidate List of Substances of Very High Concern (SVHC) is updated twice a year. On 14 June 2023, the European Chemicals Agency (ECHA) published the 28th update of the Candidate List of Substances of Very High Concern, and now it includes 235 substances. Any supplier of an article containing a substance above 0.1% (w/w) in a concentration has to provide the recipient with relevant safety information.

Compared with RoHS, the SVHC management of the ECHA regulation involves the supervision and risk identification of more chemical substances. With the increasing number of SVHCs, it becomes more and more complicated to determine the final content of chemical substances in IC products.

Many experts and international manufacturers suggest or require that the supply chain must provide a Full Material Declaration (FMD) [1]. Establishing an FMD database comparison could solve the cost problem of continuous material information collection from the supply chain under the fast pace of regulations change. However, implementing FMD requirements can also be very challenging mainly due to the inability to compel material vendors to disclose 100% ingredient information against the restrictions of trade secrets and confidential information law.

There are different ways for companies to judge whether substances on the Candidate List are present in their articles. The majority of methodology for identification and assessment for SVHC of REACH is using REACH

declaration surveys, material-related information collection, and representative sample chemical analysis.
The purpose of this study is to judge the rationality of REACH SVHC content deduction and provide information on chemical substances contained in products (articles).

II. Experiment

A. Sample preparation and design

(a) Preparation for bisphenol A test samples
Tested samples of IC product and substrate were prepared by SPIL and substrate vendors. The substrate used is the one specified in the manufacturing IC product design drawing. The tested sample was pretreated and cut into different sizes as 5mm x5mm, 2mm x2mm, and powder size <0.5mm by a third-party laboratory. Sample extraction is performed by sonication extraction, followed by concentration, or dilution of extraction solution, then analyzed and performed by LC/MS/MS.

(b) Preparation of IRGACURE test samples
Commercially available solder mask which contains IRGACURE 369 is coated on a metal substrate as a thin film, then conducted by conditions as Table I below to furnish sample A and B. The solder mask is dried or cured as in final IC product. The test method is referred to US EPA 3550C (2007) and is performed by GC/MS.

Table I. Curing condition of solder mask

Sample	SVHC	Thermal Cure	UV Exposure
A	IRGACURE 369	Yes	No
B	IRGACURE 369	Yes	Yes

B. Chemical sample properties

(a) Bisphenol A
Bisphenol A as shown in Fig. 1 is a colorless solid organic chemical at room temperature. It is often used as the raw material of resin, especially polycarbonate resin as shown in Fig. 2. In the assembly materials, bisphenol A is often used as a precursor as the raw material of resin in substrates. Studies have found that bisphenol A can affect the endocrine system of the human body. In 2017, bisphenol A was listed as an EU REACH SVHC controlled substance.

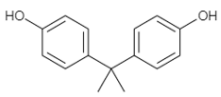


Fig. 1. Bisphenol A structure.

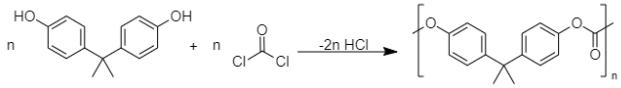


Fig. 2. The synthetic scheme of polycarbonate resin.

(b) IRGACURE 369
IRGACURE 369 as shown in Fig. 3 is widely used in resin synthesis, especially in acrylate and methacrylate resins because of their great absorbance to UV light and the high efficiency of irradiation. To make acrylate monomers assemble to acrylate resin, a radical species is required to be a starter to kick off this chain reaction and open the α-β unsaturated double bonds, this starter is named "photoinitiator".

IRGACURE 369 is an α-aminoacetophenone type photoinitiator, which undergoes α-cleavage upon UV light exposure and furnishes benzoyl radicals and aminoalkyl radicals as shown in Fig. 4. Additionally, with the absence of α-β unsaturated double bonds, this aminoalkyl radical species would be converted to tertiary amines, which could be treated as basic catalyst in reactions such as thermal crosslinking reactions of epoxy resins [2]. Though this high efficiency photoinitiator is well-utilized in resin synthesis field, after the health and environmental evaluation of ECHA, IRGACURE 369 is regarded to be toxic for reproduction and thus was listed in SVHC in early 2020.

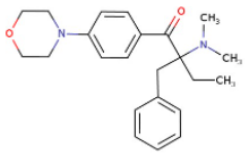


Fig. 3. IRGACURE 369

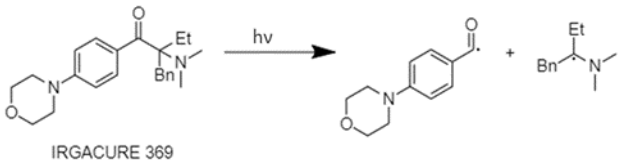


Fig. 4. Radical generation reaction of IRGACURE 369

Table II shows the substances' names and basic hazard information. The boiling points of the listed SVHCs are all higher than 250°C at 101325 Pa., which means that the substances are not easy to volatilize during the manufacturing process.

Table II. Substances information

Substance	Other Names	CAS No.	Hazard
4,4'-isopropylidenediphenol	Bisphenol A, BPA	80-05-7	Toxic for reproduction and endocrine disrupting properties
2-benzyl-2-dimethylamino-4'-morpholinobutyrophenone	IRGACURE 369	119313-12-1	Toxic for reproduction

III. Result and Discussion

A. *Definition of an "article"*

An article is defined in REACH as an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition. The judgment of the European Court of Justice on 10 September 2015 in case C-106/14 [3] clarified the scope of the notification and communication obligations under Articles 7(2) and 33 of REACH, which also applies to articles that are present in complex products. Any article containing a Candidate List substance above a concentration of 0.1 % (weight by weight) has to meet REACH and WFD regulations.

Calculation of the concentration of a Candidate List substance in articles can use the following equation [4]:

$$Conc_{CL\ subst.\ in\ article} = \frac{m_{CL\ subst.\ in\ article}[kg/article]}{m_{article}[kg/article]}$$

Where,

$Conc_{CL\ subst.\ in\ article}$ is the concentration (w/w) of the Candidate List substance in the article or complex object;

$m_{CL\ subst.\ in\ article}$ is the weight (in kilogram) of the Candidate List substance in the article or complex object;

$m_{article}$ is the weight (in kilogram) of the article or complex object.

B. *Legal and requirements for substance in articles*

(a) Waste Framework Directive (WFD) (Art. 9)

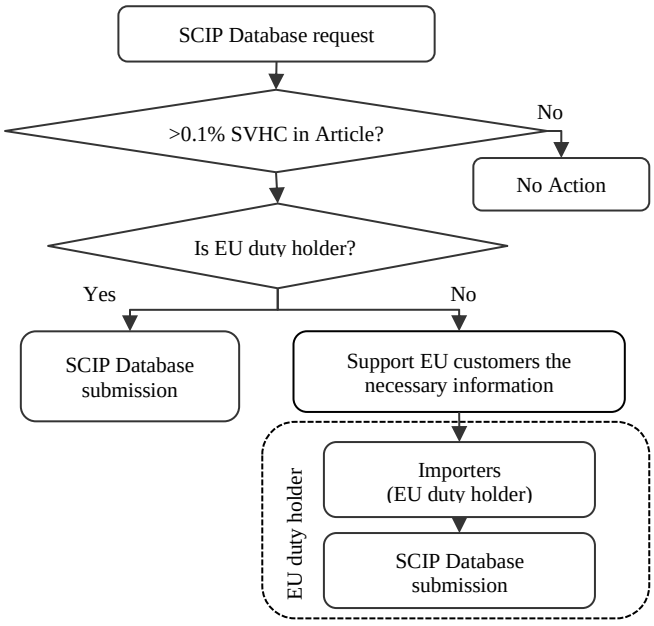


Fig. 5. SCIP obligations

Fig. 5 and Table III illustrate the obligation for suppliers of articles to meet SCIP notification and EU REACH Article 33 requirements [5], [6].

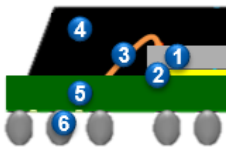
Table III. Obligations of article supplier

Conc. CL subst.	REACH (Art. 33)	WFD (Art. 9)
> 0.1% (w/w) in an article	Safe use of articles information	SCIP notification

C. *Article or Complex Objects*

Table IV shows IC products may consist of mixtures of several items and ingredients. To date, there has been little agreement on the definition of "article" for the industry. Different claims may result in different judgments of legal obligation. To comply with communication and notification obligations, we have to determine which materials of IC products are articles. If several articles were joined or assembled into an IC product, the IC product is a complex object. We have to identify which materials of IC products are articles and judge the concentration of an SVHC in each article. The definition of article is based on the "Once an Article, Always an Article" principle [7].

Table IV. Article or Complex Objects

Complex Object	No.	BOM	Article
IC 	1	Die	Yes
	2	Adhesive	No
	3	Wire	Yes
	4	Mold compound	No
	5	Substrate	Yes
	6	Solder ball	No

D. *Influence of different sample sizes and structure*

Fig. 6 shows BPA-containing materials and bisphenol A extraction results. It can be seen that no significant correlation was uncovered between BPA-containing materials in substrate content and bisphenol A extraction results. One explanation for this is that extraction results may be affected by substrate structure and uniformity of the sample preparation.

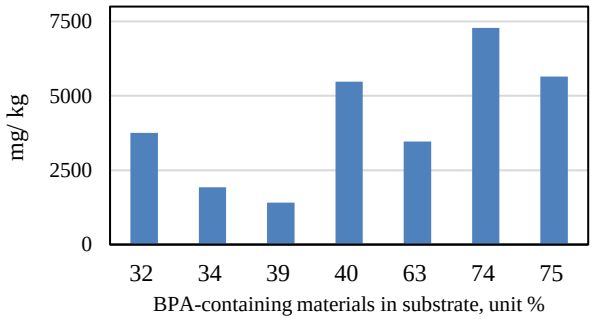


Fig. 6. Various % BPA-containing material in substrates with BPA extraction results.

Table V shows the chemical analysis of bisphenol A on the substrate. Compared to the powder size sample and 2mmx2mm size sample, reduction of the sample size leads to much better extraction efficiency.

Table V. Chemical analysis of BPA with substrates.

Substrate	BPA ratio	BPA in substrate	Sample size
BGA001	1x	>0.1% (w/w)	2mmx2mm
	6x	>0.1% (w/w)	powder
BGA002	1x	<0.1% (w/w)	2mmx2mm
	8x	>0.1% (w/w)	powder

The possible reason is the larger contact surface between the tested sample and the extraction solvent. As shown in Table VI, the smaller the sample size of the material, the shorter the path the solvent has to travel, which indirectly decreases the time for maximum bisphenol A extraction. The smaller sizes also have a much larger surface area and hence provide a greater mass transfer rate. [8], [9].

Table VI. Sample size and solvent contact

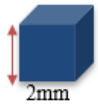
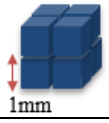
Extraction	Sample A	Sample B
Surface Area S= LxWxSide	Small S=2x2x6 =24	Large S=1x1x6x8 =48
		
Solvent contact		

Table VII shows the results of the bisphenol A test. The test of all samples is pretreatment as powder size < 0.5mm. When fixing the content percentage of BPA-material in substrate, comparing sample A with sample C and sample B with sample D, we can see that the thickness of the substrate increases, and the amount of bisphenol A extracted increases. The substrate is a composite material composed of copper foil, CCL-core resin, solder mask, and metal materials (solder, nickel plating layer, gold plating layer, etc.). The reason may be related to the homogeneity of the test sample and the solvent extraction contact with the larger resin volume.

Table VII. Chemical analysis of BPA in substrates

Sample	Substrate thickness (mm)	BPA-materials /Substrate	BPA ratio
A	0.2	39%	1x
B	0.26	74%	4x
C	0.36	40%	3.8x
D	0.56	74%	5.1x

Fig. 7 shows the result of bisphenol A chemical analysis in IC products and substrates. Substrate* means the bisphenol A concentration in a substrate is calculated based on the IC product test result. IC* means the bisphenol A concentration in the IC product is calculated based on the substrate test result. There are several ways to determine the content of the chemical in the product (CiP). For samples A and B, the content of BPA in the substrate calculated by the IC product test results is lower than the actual test result of the substrate. To avoid the influence caused by the difference between the sample test results and the substance judgment basis, the chemical analysis must consider a representative sample. If the chemical substance is no longer chemically changing at the process stage, a chemical analysis may be considered at the homogeneous material level.

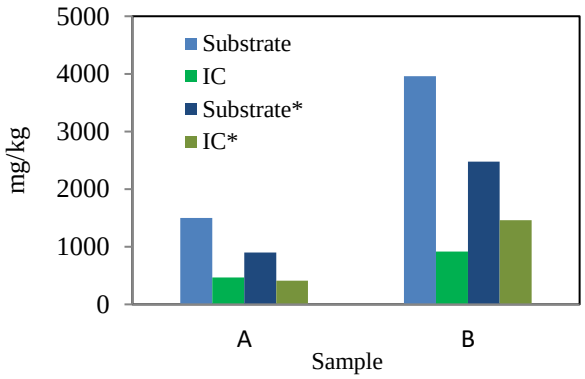


Fig. 7. Bisphenol A content with various structure samples.

Fig. 8 shows the chemical analysis of bisphenol A on the resin material; the result of bisphenol A amount is in the order as follows: powder size >2mmx2mm >5mmx5mm. Reduction of the sample size (from 5mmx5mm to 2mmx2mm) caused approx. 3 times increase in test result for bisphenol A. Reduction of the sample size (from 5mmx5mm to powder size) caused approx. 10 times increase in test results for bisphenol A. We determined the effect of sample size on extraction for bisphenol A.

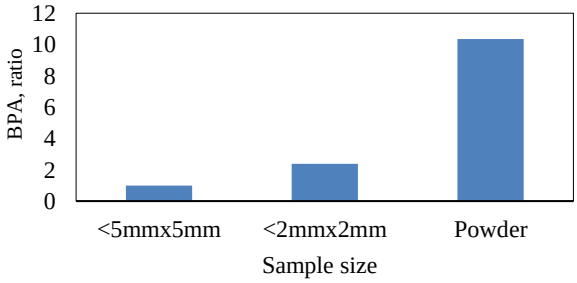


Fig. 8. Chemical analysis of BPA with various sample sizes.

E. Function and final content of chemicals in materials

The content of SVHC may somehow become more or less during the article maker's manufacturing process. Any process condition shall be considered to see if it will affect the presence of SVHC when evaluating its content. For some species designed to be consumed or reacted, the SVHC may get lost in the manufacturing process.

IRGACURE 369 is extremely UV sensitive which eventually leads to decomposition owing to its α-cleavage during UV exposure. In practical cases, UV light is always implemented for boosting the synthesis of acrylate resin in solder mask. If lacking the consideration of UV light and judging the conformity of SVHC from uncured raw material directly, the evaluation may present a huge gap between practical cases. Table VIII shows that the remaining ratio of IRGACURE 369 in solder mask without UV exposure is amazingly 91 times higher than that with UV, giving a completely different regulative conclusion.

Table VIII. SVHC Conformity of IRGACURE 369

Sample	SVHC	Thermal Cure	UV Exposure	Remaining Ratio	<0.1% in Article
A	IRGACURE 369	Yes	No	91x	No
B	IRGACURE 369	Yes	Yes	1x	Yes

III. Conclusion

This paper has demonstrated some factors which may influence the regulative conformity by real case. The results of the chemical analysis showed that the extraction amount of bisphenol A increased as the size of the tested samples decreased. When it comes to substrate thickness, a better result for the extraction of bisphenol A could be found with increased thickness. Using detection result to estimate the content of chemical substances in IC products is an available way while the detection in homogeneous materials level is more recommended and accurate than deducing from complex objects. For reactive substance, such as IRGACURE 369, which is easily reduced after manufacturing process, the sample preparation for chemical analysis must be evaluated with the sample of the final state of the product.

By EU REACH Article 33, suppliers of articles are obliged to provide enough safe use information to recipients when SVHC was contained in articles with a concentration above 0.1% (weight by weight). When utilizing chemical analysis data for checking legal conformity, companies should carefully consider whether the analytical method and test sample could highly reflect the practical experience and the definition of EU REACH.

Finally, we still have to understand that for complex objects, it's essential to consider the worst-case scenarios to comply with EU REACH SVHC and WFD requirements.

Acknowledgment

The authors would like to thank the Connectivity and Products - RSTS and Central Chemical Laboratory of SGS for technical assistance. A special thanks also are extended to suppliers. Thank you to all who have contributed to this study.

References

[1] A. Wu," Doing Business in the Age of Transparency: A case study of Full Material Disclosure in the electronics sector*"* IIIEE Theses 2018:36.

[2] H. Kura, H. Oka and J. L. Birbaum, "α-aminoacetophenones as photobase generators", 1999. Available: https://www.osti.gov/etdeweb/servlets/purl/20051970

[3] CJEU, C-106/14, para 49. Available: https://curia.europa.eu/juris/liste.jsf?language=en&td=ALL&num=C-106/14

[4] ECHA, 'Guidance on requirements for substances in articles, 2017, Available: https://echa.europa.eu/legislation

[5] ECHA, SCIP, Available: https://echa.europa.eu/scip

[6] T. Becker." The SCIP Database under Directive (EU) 2018/851*"*, ICRL, 2019, pp. 147-156. Available*:* https://doi.org/10.21552/icrl/2019/4/4

[7] Greensoft, "Solving the EU REACH "Once an Article, Always an Article" Problem ", 2019. Available: https://greensofttech.com/solving-the-eu-reach-once-an-article-always-an-article-problem/

[8] S. A. Makanjuola, "Influence of particle size and extraction solvent on antioxidant properties of extracts of tea, ginger, and tea–ginger blend" 2017 Nov; 5(6): 1179–1185.

[9] A. Yeop, J. Sandanasamy, S. F. Pang, S. Abdullah, M. M. Yusoff, and J. Gimbun1" The effect of particle size and solvent type on the gallic acid yield obtained from Labisia pumila by ultrasonic extraction", FluidsChE 2017.