Cutting-edge Environmental Technology for Manufacturing Processes

● Fumiyo Takeuchi ● Michiko Noguchi ● Mitsuo Ozaki ● Koichi Kimura

Manufacturing (*monozukuri*) today cannot be considered without environmental awareness. Fujitsu Laboratories Ltd. engages in developing innovative environmental technologies used for manufacturing processes. To conserve the global environment, the use of volatile organic compounds (VOCs), usually contained in paints, is expected to be reduced. Application of water-based paint with no VOC content on information and communications technology (ICT) equipment has been technically challenging so far. This is because it requires a high drying temperature which plastics cannot stand, while the paint must achieve a high coating performance. Addressing this challenge, we have developed a coating emulsion in a core-shell structure to satisfy both low drying temperature and coating performance. As a result, we succeeded in reducing the VOC content by approximately 80%. We have also developed a vapor collection method, a simple pretreatment method for Fourier transform infrared spectroscopy (FT-IR), to improve the detection limit of phthalate esters to less than one percent, a tenfold improvement in sensitivity. Bis(2-ethylhexyl) phthalate (DEHP), a phthalate ester, is a potentially hazardous substance, the same as VOC, and is regulated in some industries in Japan, the U.S. and Europe. Furthermore, it is now being considered as a candidate for next-round regulation under the EU Restriction of Hazardous Substances (RoHS) Directive that regulates electrical and electronic equipment. Identification of DEHP in our products has been a big issue when conducting a acceptance inspection in manufacturing. For this reason, we have studied a new way to separate and condense phthalate esters because the sensitivity of FT-IR currently available does not comply with the requirements of the regulation and it is difficult to detect it coexisting with a matrix of products. The new method makes it possible to carry out more sensitive and simpler acceptance inspections.

1. Introduction

Based on the recognition that building a sustainable society essentially requires environmental technologies, Fujitsu Laboratories is working on research and development for a wide variety of environmental technologies. The R&D includes activities relating to the environmental friendliness of the products and various solutions as well. Products here are considered not only themselves, but also from their manufacturing through to their use by customers and their disposal.

Up to now, we have developed technologies to reduce the environmental impact of information and communications technology (ICT) equipment such as notebook PCs, and these technologies include bioplastics[1] as well as magnesium alloy recycling technology.[2] We have also engaged in developing efficient screening methods[3] of controlled chemical substances within the products in order to comply with the RoHS Directive (enforced in 2006), the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment.

This paper presents recent R&D cases of environmentally friendly technologies and acceptance testing technologies. One is water-based paint technology that can help reduce the use of volatile organic compounds (VOCs), and the other is a new simple detection method for phthalate esters such as bis(2-ethylhexyl) phthalate (DEHP), which is a potentially hazardous substance.

2. Water-based paint technology

VOCs, which are among the substances that cause photochemical smog due to a photochemical reaction in the atmosphere, are mainly contained in paints, printing inks, adhesives, cleaning agents and gasoline. The Ministry of the Environment reports[4] that paints account for about 40% of the emissions of VOCs. Accordingly, reduction of the VOCs contained in paints is an important issue in order to conserve the global environment.

Paints consist of components that provide a film and some solvents that volatilize. The components include resins and pigments to impart colors and shiny brightness. The solvents are used to dissolve the resins and also added for diluting to play important role in making it easier to apply them. Because organic solvents are mainly VOCs, switching from such solvent-based paints to water-based paints, where the solvent is mostly water, is effective for reducing VOCs.

2.1 Development and evaluation of water-based paint

1) Comparison between solvent-based paints and water-based paints

Solvent-based paints contain resins dissolved in the solvent and the resins are coated by volatilization of the solvent. This gives them an excellent film-forming property. Thinners can be selected out of various solvents with different levels of solubility and volatilizing speeds and mixed together for optimization according to the purpose of use.

Meanwhile, water-based paints are generally emulsion paints, in which resin is not dissolved in water but exists as fine particles. As illustrated in the image of film formation of a conventional water-based paint shown in **Figure 1**, evaporation of water brings the resin particles closer and they bond together thermally to form a continuous film. It means that the quality of the bonding is directly reflected in the quality of the physical properties of the coating film. The diluting solvent is only water. A small amount of organic solvent is mixed in as an auxiliary agent that remains on the base material to facilitate bonding after volatilization of water. There is only a small choice of solvents, and therefore it is important to optimize resins to improve the film-forming property with this limited selection.

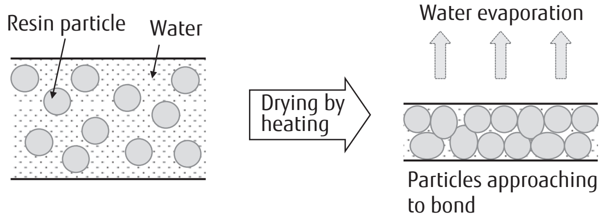

Figure 1
Image of film formation of water-based paint (conventional emulsion).

2) Development goal

Switching the paints used for ICT equipment, such as servers and PCs, to water-based paints has posed problems up to now in terms of the drying process and the required coating performance. One problem with conventional water-based paints is that plastic housings used in ICT equipment cannot endure high drying temperatures that are needed to facilitate bonding and they become deformed. In addition, paint that is applied to housings of ICT equipment requires a high coating performance including a high hardness, good adhesion, chemical resistance, light resistance and designability.

For the new water-based paint, we have set a development goal of achieving both a high coating performance and low-temperature drying of 80°C or below, which allows plastic housings to be coated. In view of manufacturing facilities, we have also aimed to realize workability and facilities that are comparable to those of the current ones.

3) Evaluation methods

The performance required of paint films may vary depending on the application. For application to ICT equipment, especially mobile devices, higher performance is needed. As a primary evaluation, appearance inspection, adhesion evaluation by cross cutting and pencil hardness testing are conducted. Equipment that may be frequently touched with the hands is checked for resistance to cosmetics including hand creams, and OA cleaners, in addition to generally used solvents such as alcohols. In this check, chemicals are applied on the test sample, and it is left to stand for a certain period to confirm that there is no change in the appearance and that hardness and adhesion are maintained. This process is carried out for artificial sweat as well. On the assumption that the equipment will be used in various environments, temperature and humidity cycling tests are also conducted.

4) Selection of resins

For dilution, water is used for water-based paints and no functionality can be expected for water. Accordingly, the degree of optimizing resins is the most important factor that affects both film-forming property and the physical properties of the coating film. As resins to use, we focused our attention on acrylic- and urethane-based resins and their glass-transition temperatures (Tg), selected some resin types to make paints and evaluated the physical properties of the coating film. The drying condition used was 70°C for 30 minutes, and this condition does not cause the plastic to deform.

We confirmed that both the acrylic- and urethane-based resins with high Tg were capable of ensuring pencil hardness. Urethane dispersion showed a coating film with a good appearance but had a problem with resistance to chemicals and artificial sweat. Acrylic emulsion, on the other hand, did not have sufficient film-forming property and cracks appeared in the surface. It is difficult to ensure both a good film-forming property and a high coating performance with one kind of resin and we mixed two kinds of resin to make paints. However, increasing the amount of urethane-based resin reduced the resistance to artificial sweat and increasing the amount of acrylic-based resin reduced the chemical resistance and it was not possible to find out a composition that satisfied all requirements.

To address this problem, we considered an emulsion with a core-shell structure as shown in **Figure 2**. We used different kinds of acrylic-based resins to improve the film-forming property and ensure hardness: a hard resin with a high Tg for the core and a soft resin with a low Tg for the shell. For the base materials, PC-ABS (polycarbonate-acrylonitrile-butadiene-stylene) and PC containing glass fiber were used and an evaluation was conducted on the respective materials. The results showed that the requirements were satisfied for both film-forming property and coating performance including hardness.

2.2 Environmental friendliness evaluation

This new water-based paint developed has the organic solvent content reduced by approximately 80% as compared with the same amount of a solvent-based paint, as shown in **Figure 3**. The amount of volatilized organic solvent, or the amount of VOCs, is reduced in the same way.

A trial calculation of the amount of crude oil consumed for producing paints has given a result that is approximately 54% smaller for water-based paint than for solvent-based paints. Water-based paint is a one-pack type, and so there is no need to consider the pot life. Neither hardeners nor diluting organic solvents are needed. This not only leads to a saving in limited crude oil resources but also contributes to reducing various types of environmental impact as secondary effects including the energy required for mining, processing and transporting resources.

2.3 Application to products

We have developed a water-based paint that can be used for plastic housings and applied it to parts such as the main unit front panel of two models of the UNIX server SPARC M10 released in 2013 (**Figure 4**). As compared with conventional solvent-based paints,

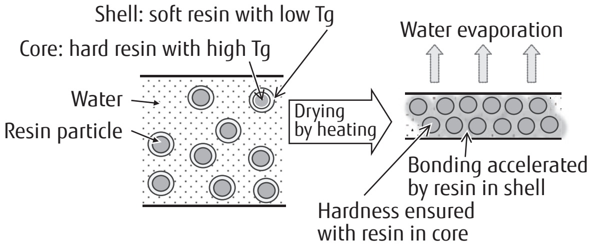

Figure 2
Image of film formation of newly developed water-based paint.

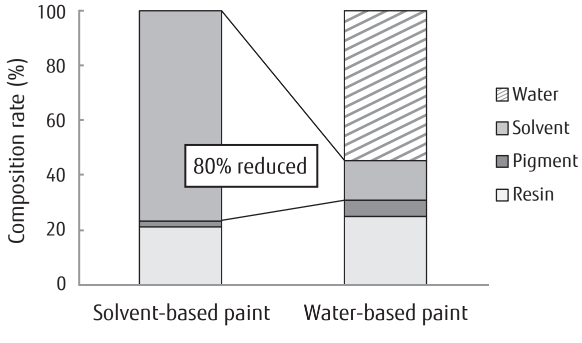

Figure 3
Comparison of composition between solvent- and water-based paints.

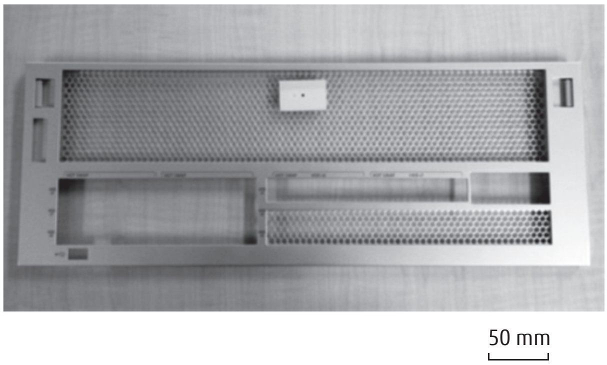

Figure 4
Front cover coated with water-based paint.

this paint can reduce the amount of crude oil used for one panel by 54% and the amount of VOCs by 80%. Housings of ICT equipment are often made of plastics and switching these paints to a water-based paint can significantly reduce environmental impact such as the generation of VOCs. We intend to expand the application of this paint while considering the materials of housings, the design, quality and production volume.

3. Technology to identify presence of phthalate esters

Lately, commercialized products have been required to meet various global regulations for hazardous chemical substances such as the EU RoHS Directive and the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulations (enforced in 2009) that especially have a significant impact on the Fujitsu Group's products. The Fujitsu Group has established basic policies and rules in relation to design and manufacturing of products to deal with regulated chemical substances contained, and built a framework for their operation and management.[5] Within this framework, Fujitsu Laboratories is responsible for the development of some technologies to identify the presence of regulated hazardous substances as selecting materials at the design stage and accepting materials in manufacturing. In particular, screening analysis methods for the acceptance inspections are required to be simpler and more efficient. Up to now, proprietary technologies, for example a pretreatment method that can polish and sample an electrode plating material on a sheet of lapping film[6] to detect lead (Pb) within the plating on chip part with X-ray fluorescence analysis, have been developed ahead of regulations, and applied across the Fujitsu Group.

3.1 Trends of regulations on phthalate esters

Phthalate esters are in widespread use as plasticizers to primarily soften polyvinyl chloride (PVC). At the same time, DEHP, which is produced in the largest quantities of all phthalate esters, poses a problem of a potential health impact and its use for toys and nursery items is regulated in Japan, the U.S. and EU. In the EU, it has also been classified into the "carcinogenic, mutagenic and reprotoxic substances" group as a substance of concern and was included in the Authorization List of the REACH regulations on February 17, 2011. In addition, it is considered as a candidate for next-round regulation under the EU RoHS Directive. However, it has been difficult to detect by a simple acceptance inspection with an attenuated total reflectance (ATR)—Fourier transform infrared spectroscopy (FT-IR) because of the lower detection sensitivity limit with reference to the regulation value and the influence of other additives in test samples. Accordingly, we have attempted to develop a vapor collection pretreatment method for a simple acceptance inspection.

3.2 Issues with present analysis methods

Typical analysis methods for phthalate esters include gas chromatography-mass spectrometry (GC-MS), which allows a high-accuracy measurement of the type and concentration of a phthalate ester, and FT-IR, which cannot identify the type but is capable of verifying whether or not phthalate esters are included in a product if they are contained at a concentration of about 10 wt%. The former requires expertise such as test sample pretreatment with organic solvents and data analysis, many person-hours and expensive analysis equipment, which makes it difficult to apply to an acceptance inspection. The latter does not require complicated sample pretreatment and provides a method suited for screening that can detect a phthalate ester by determining absorption peaks of 1, 2-substituted benzene, which are characteristic structures of phthalate esters. The FT-IR equipment is less expensive than GC-MS as well. However, it has issues to address such as the insufficient detection sensitivity of 10 wt% as compared with 0.1 wt% specified by the regulation of the RoHS, etc. and the difficulty in detection due to the influence of other components including color materials and additives contained in test samples made of products.

3.3 Development of vapor collection method

To solve these issues as described above, we have developed a vapor collection method (**Figure 5**), a simple test sample pretreatment method. In this method, the plasticizing components such as phthalate esters in test samples are evaporated by heating the test samples and the vapor is collected on a thin film consisted of pure PVC, thereby concentrating the plasticizer components so as to reduce the influence of other components including color materials. By using FT-IR to analyze the samples made by this method, phthalate esters that exist in testing samples by about 1 wt% can be detected. The requirements for this collection method are as follows.

1) Vaporize the target substances such as DEHP efficiently from within additives such as other plasticizers;
2) Collect the generated vapor as much as possible on a collection film;
3) Absorb the vaporized material homogeneously into the collection film.

To fulfill these requirements, a number of temperature conditions must be set appropriately, including the duration and temperature of the sample's heating, the temperature of the collection film and the spacing of the heating and collection surfaces in consideration of radiant heat. It is also necessary to ensure that the test environment is managed in ways such as the setting the collection film thickness and providing partitions to prevent the vapor from diffusing. In addition, in order to make this method suitable for use in an acceptance inspection, it is necessary to improve the operation efficiency and reduce the operation steps.

To address these issues, we have cooperated with related departments to develop vapor collection equipment (**Figure 6**).[7] Operating efficiency has been improved by making it easier to set and manage the temperature conditions of the sample and collection film and by using a cartridge to set the sample to allow anybody to stably collect vapor within a short period of time of about 5 minutes. Various collection conditions can also be fine-tuned to make it possible to further improve the lower limit of detection by carrying out a

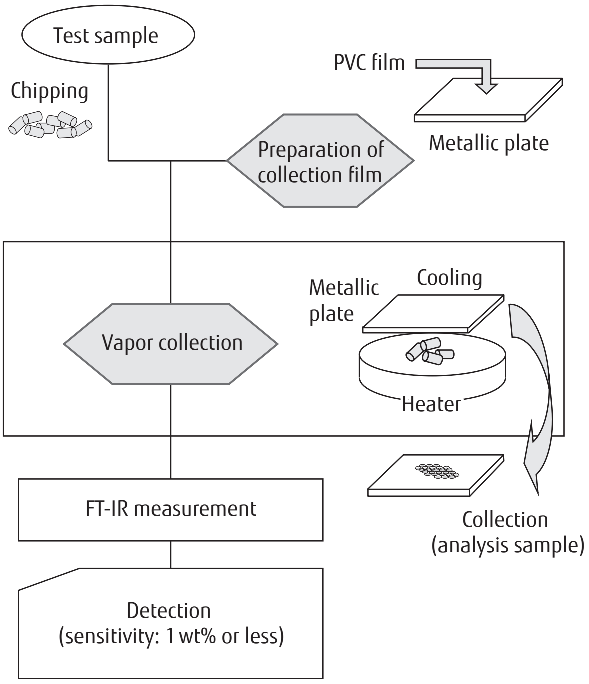

Figure 5
Procedure for analysis of phthalate esters by vapor collection method and FT-IR.

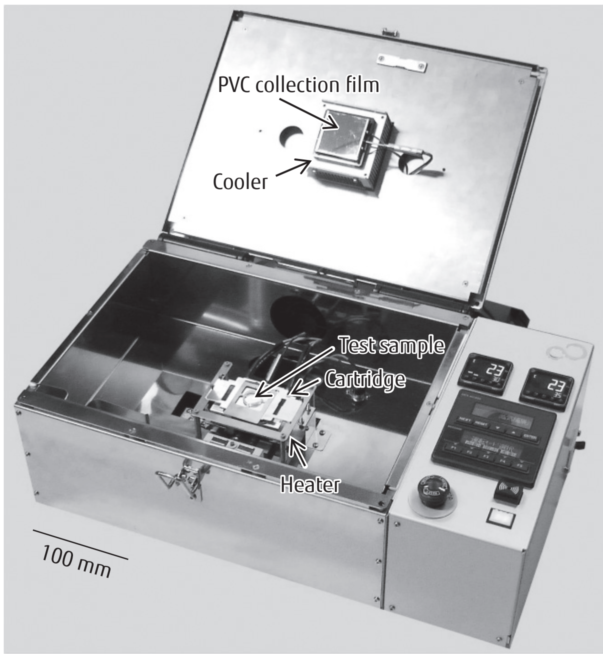

Figure 6
Vapor collection equipment.

detailed examination of the collection conditions and to make optimized samples for various measuring conditions of FT-IR.

3.4 Future developments

The vapor collection pretreatment method allows a detection limit improvement of phthalate ester screening analysis with FT-IR by one order of magnitude to about 1 wt%.

The acceptance inspections by applying the method can reduce the certain substances including risk and offer safer and securer products. In the future, we intend to put in place a delivery system of the vapor collection equipment and collection films and proceed with preparations to apply the method to acceptance inspections in step with the regulations, in view of the trends of regulations in the RoHS.

4. Conclusion

This paper has presented cutting-edge environmental technologies recently developed by Fujitsu Laboratories. One is intended for manufacturing processes: water-based paint technology to reduce the emissions of VOCs. And the other is the vapor collection pretreatment technology to improve the detection limit of acceptance inspections with FT-IR.

In the Environmental Action Plan, Stage VII, the Fujitsu Group aims to conduct business activities that contribute to solving wide-ranging social issues including conservation of the global environment and realization of a sustainable and affluent society. Fujitsu Laboratories is committed to making continued contributions in the future by conducting research and development of innovative environmental technologies used for manufacturing processes.

References

1) K. Kimura et al.: Research and Development of Bioplastics and Application to Products. *FUJITSU*, Vol. 59, No. 2, pp. 127–133 (2008) (in Japanese).
2) K. Kimura et al.: Recycling Technology for Magnesium Alloy Housings. *FUJITSU*, Vol. 54, No. 6, pp. 458–464 (2003) (in Japanese).
3) M. Ozaki et al.: Efficient and Unique System for Verifying Containment of Hazardous Substances. *Fujitsu Sci. Tech. J.*, Vol. 41, No. 2, pp. 209–216 (2005).
4) Ministry of the Environment: Volatile Organic Compound (VOC) Emission Inventory Study Group (2013) (in Japanese).
https://www.env.go.jp/air/osen/voc/inventory.html
5) H. Yagi et al.: Management of Chemical Substances Contained in Products. *FUJITSU*, Vol. 62, No. 6, pp. 688–694 (2011) (in Japanese).
6) Fujitsu Laboratories et al.: Fujitsu Develops Efficient Method of Analysis for Lead Contained in Solder Plating of Chip Components (in Japanese).
http://pr.fujitsu.com/jp/news/2007/09/14-1.html
7) Fujitsu Laboratories et al.: Fujitsu Develops Simplified Method to Identify the Presence of Phthalate Esters.
http://www.fujitsu.com/global/about/resources/news/press-releases/2013/0321-04.html

Fumiyo Takeuchi
Fujitsu Laboratories Ltd.
Ms. Takeuchi is currently engaged in development of environmentally friendly paints.

Mitsuo Ozaki
Fujitsu Laboratories Ltd.
Mr. Ozaki is currently engaged in research on environmental solutions.

Michiko Noguchi
Fujitsu Laboratories Ltd.
Ms. Noguchi is currently engaged in research related to development of analysis methods for regulated chemical substances.

Koichi Kimura
Fujitsu Laboratories Ltd.
Mr. Kimura is currently engaged in development of materials of housings.