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Letter of Opinion on Proposed PFAS Regulations

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Toyo Ink Group has responded to various chemical substance regulations in order to deliver safe and secure products to consumers. The Japanese Printing Ink Makers Association's self-regulatory selection criteria refer to REACH SVHC and CLP regulation reproductive toxic substances. In this way, European regulations on chemical substances are considered to have a great influence on the protection of the environment and the health of people around the world. For example, we will explain examples of responses to PFOS and PFOA, which have already been regulated. PTFE (polytetrafluoroethylene) wax is commonly used as a surface protection component for printing inks, and the previous grade contained PFOS and PFOA as impurities in the PTFE wax. At present, we have switched to all grades with less than 25ppb of these ingredients to respect REACH.

However, regarding the proposal to collectively restrict PFAS (Per- and Polyfluoroalkyl substances) exceeding 10,000 substances, we believe that there are no effective substitutes for some uses, and that the impact on industry will be enormous. We consider this to be an excessive measure, and have expressed our opinion at ECHA's public consultation as follows.

□□□UV curable ink

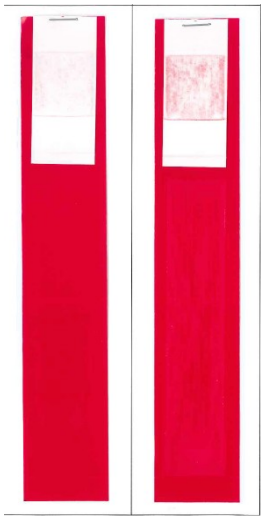
UV curable inks have the advantages of instant curing, non-containment of volatile organic compounds (VOCs), and a wide range of applications from paper to plastic, and are widely used in printed materials around us. Specifically, it is used in food, pharmaceutical, and cosmetic packaging, seals and labels, business forms, cards, cups, tubes, information publication printing, commercial printing, etc. Because of this diversity of end uses, PTFE waxes are used in many products and likely have an impact on consumers.

□□□□□Protection of package surface

PTFE wax, which falls under the definition of PFAS, has been used for printing inks for a long time because it has excellent abrasion resistance, heat resistance, and sliding properties. For example, packages contain information that needs to be reliably conveyed to consumers, such as ingredient labels, and printing inks are formulated with surface protective ingredients so that this information is not damaged by abrasion during transportation. Especially in the case of surface printing on paper containers, etc., the printing surface is the outside, so abrasion resistance is particularly important. Among the surface protection ingredients, PTFE wax is effective from the viewpoint of reliably delivering the information written on the package to many end users. Silicon is sometimes used as a surface protection component other than PTFE, but because of its high releasability, foil stamping and gluing are not possible. Foil stamping and gluing are possible with PTFE wax, which does not impair the current design. Other commonly used printing inks include polyethylene wax, microcrystalline wax, paraffin wax, Fischer-Tropsch wax, rice wax and carnauba wax. Although these waxes are less abrasion resistant than PTFE waxes, they can be foil stamped and glued, so they may be an alternative in some applications, but the risk of abrasion remains.

Figure 1 shows the abrasion resistance results when PTFE wax (0.9%) was removed from UV offset red ink. A printed matter was prepared and cured by UV irradiation. After that, the printed matter and blank paper were placed on top of each other, and a load of 500 g was applied, and rubbed repeatedly 10 times. The test piece on the left contains 0.9% PTFE wax, and the test piece on the right is without PTFE wax.

Figure 1-1. Effect of PTFE on abrasion resistance



One of the advantages of PTFE wax is its good suitability for offset printing. In offset printing, lithographic printing is performed, and images are formed by the repulsion of dampening water. In offset printing, the film thickness per 1 color is around 1μ, and by using a type of PTFE wax with an average particle size of 3 to 5μ, excellent abrasion resistance is achieved. When trying to impart equivalent abrasion resistance to waxes other than PTFE, it is necessary to select waxes with a large particle size. As a result, the dampening water causes wax to agglomerate, causing printing problems such as piling on the blanket of the offset press. If the wax agglomerates accumulate on the blanket, the frequency of cleaning the printing machine will increase, so it is expected to have a negative impact on the environment, such as longer working hours, increased use of cleaning agents, and increased waste paper.

□□□□□Heat-resistant applications

PTFE wax has high heat resistance, and other waxes cannot be expected to have such heat resistance. For example, when printing on thermal paper, heat of 200°C or higher is applied to the printing surface, so if melted wax adheres to the thermal head, printing quality will be impaired. A thermal head is a heat-generating head used in thermal printers, and has a structure in which minute heat-generating elements are arranged. By heating the heating element according to the data, letters and pictures are printed on printed matter that reacts with thermal energy. Thermal paper is used in a variety of situations. For example, it is used in logistics operations such as shipping labels. Elimination of surface protective ingredients with high heat resistance from inks for thermal paper will result in poor printing, which may affect the supply chain.

In addition, NIP (No Impact Printer) aptitude is required for printing forms. In NIP, heat of 200°C or more is applied to fix the toner, so low-melting wax cannot be used, so PTFE wax is used. Elimination of PTFE wax from the printing ink used for NIP would impair printability due to the adherence of dissolved components to the NIP drum.

The heat resistance test results are shown below. The eraser is placed on the print surface, and the paper is placed on the eraser. Then, it is crimped at 230°C for 10 seconds. Less adhesion to the eraser side is better. Left is UV offset ink with PTFE wax, right is polyethylene wax replaced. This test result

shows that it is difficult to replace PTFE.

Figure 1-2. Effect of PTFE on heat resistance

(2)Heat set ink

Heat set web offset printing provide commercial printings such as advertising catalogs, magazines, comics, etc. This printing system has drying, folding, and cutting process in the same line, feeding rolled paper to the press continuously, which enables high-speed printing. This drying process is unique to heat set printing and uses hot air at 150°C to 200°C to dry.

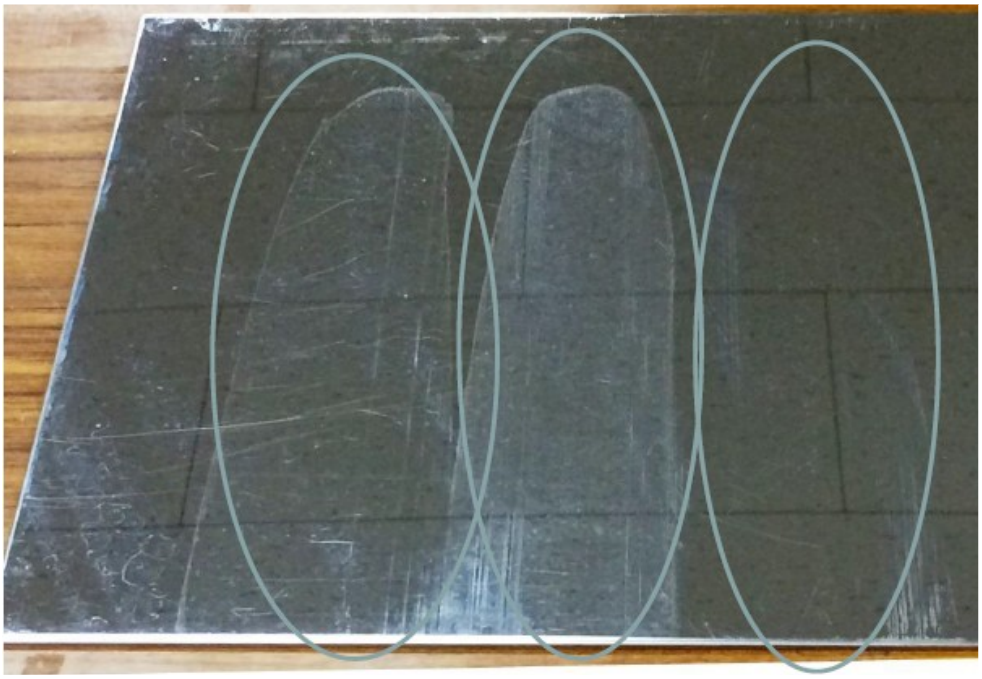
(2-1) Rub resistance and Heat-resistant for High-speed heat set printing

Rub resistance is important since the printing speed is high, about 10m/sec. Without the enough property, scratches occur on the printed surface, and the product value will be lost. PTFE, PE, paraffin waxes are generally used for offset printing ink in order to give rub resistance. For heat set ink, heat resistant is also required for these waxes because of high temperature (200℃ or higher) drying process. PTFE is well known for its heat resistant and low coefficient of friction. PE or paraffin waxes which have low melting point would change their particle size and surface structure in the drying process, and cannot give inks enough property. Therefore, PTFE is essential material in heat set ink composition.

(3) Screen ink

Screen ink is used in various applications such as smartphone casings, motorcycle exteriors, and insulating films for flexible substrates. All of these applications require high durability and reliability. In smartphones, scratch resistance is demanded, but currently, only FTFE has a lower friction coefficient than polyethylene to achieve this. Similarly, for motorcycle exteriors, solid wax that can exhibit scratch resistance at high temperatures of 120°C or higher is demanded, and currently, only FTFE can achieve this. Similarly, for flexible substrate applications, only FTFE can exhibit scratch resistance when exposed to high temperatures of 260°C during the manufacturing process. Therefore, FTFE has become an essential material for industrial applications.

The photo shows the results of a heat-press test using a metal plate (150°C x 10MPa, 30 minutes) with different types of ink: polyethylene wax-based ink, amide wax-based ink, and FTFE based ink. The white opaque parts indicate where the ink film is attached to the metal plate.



polyethylene wax-based ink amide wax-based ink, FTFE based ink.

(4) Gravure Ink (Ink for Building Materials)

Ink for building materials is used to print designs such as wood patterns and stone patterns on floors, doors, walls, furniture, cabinets, balconies, and other surfaces in detached houses, condominiums, halls, shopping malls, and public facilities. Compared to inks used for food packaging, paper products, and books, which have a required durability of 10 to 20 years, the ink for building materials requires materials with an even longer durability.

Due to the specific usage environment, it is necessary to have weather resistance, particularly against light, water, and temperature. Fluororesin is known to have high durability because of its strong atomic bonding force, making it the best choice compared to urethane-based, PVC-based, acrylic-based resins used in inks for food packaging, as mentioned earlier.

As a specific example, when measuring the color change (ΔE) of printed materials using fluororesin-based ink and urethane/PVC-based ink and conducting an accelerated weathering test for approximately 500 hours, the ΔE of the fluororesin-based ink is 7, while the ΔE of the urethane/PVC-based ink is 56, clearly indicating that the color change of the fluorioresin-based ink is minimal and excellent. There are no other resins that have an

equivalent durability to fluororesin, and finding a substitute is considered difficult.
Furthermore, the evaluation time for weather resistance of alternative products takes at least 2 years using accelerated weathering tests and over 10 years using actual outdoor exposure weathering tests. Therefore, replacing it within a few years is considered impossible.

□□□Metal Decorating Inks

Metal decorating inks are applied to various metal products used anywhere in our lives, such as beverage cans, food cans, aerosol cans, promotional tins, caps, and so on. Especially, metal decorating inks for metal sheet printing have to satisfy simultainiously several requirements: not only printability, but also overprintability, abrasion resistance and hardness of dried ink films, and etc. In this industry, PTFE wax is one of the key materials that can solve some trade-off issues in ink design. Since the most of current inks for metal sheet decoration is enabled to provide good performance by PTFE wax, it is concerned that the substitution of PTFE wax in ink design may lead their performance degradation. Moreover, such substitution will require various hygienic evaluations of altanative ink design to the metal packaging application in food, pharmaceutical and cosmetic fields, resulting that a very long transition term will be required.

For instance, in the metal sheet printing process, each printed metal sheet is continuously piled on the top of previously printed metal surface, so that the printed surface is suffered from rubbing by the edge and/or backside of the metal sheet piled on it. You might think that this situation is similar to the printing on paper and plastic described in other sections, but the specific gravity of the metal sheet used for metal containers is much higher than that of paper or plastic. Therefore, the magnitude of the frictional energy applied to the surface of the printed ink on metal is greater than on the paper or plastic. That means that the abrasion resistance required for metal decorating inks is much higher than that other uses.
This characteristic (specific gravity of metal) also affects all over the transportation process of manufacturing metal packagings. Metal containers that are continuously transported on a processing line have greater kinetic energy than paper or plastic containers. Therefore, contact between the metal container and each part of the processing apparatus may cause defects on the surface of the printed matter, which is higher than in the case of paper or

plastic containers.This is also one of the reasons why metal printing inks are required to have higher abrasion resistance than inks for paper and plastic printing.
In addition, in the metal sheet printing process, different color ink layers are often overlaid on the previously dried ink layers. Therefore, it is necessary to ensure the wettability and adhesion between newly printed ink layer and former printed and dried ink layer. In this industry, that kind of property is called “overprintability”. Generally, waxes and slip control agents (lubricants) improve abrasion resistance of inks, but they maight also lose inks overprintability. Nevertheless, some of PTFE wax which provide good abrasion resistance of inks can overcome the trade-off relationship between abrasion resistance and overprintability.
As the result, for many years metal printing and processing processes have been designed on the premise of the performance of inks using PTFE waxes.

Thus, it is expected that the replacement of PTFE wax suitable for metal decorating inks will require not only adjustment of ink formulation sutisfing the above mentioned properties, but also various verifications in a wide variety of applications. In particular, defects in printed matter used on food and pharmaceutical containers not only impair information that should be reliably conveyed to consumers, such as ingredient labeling on containers, but also cause contamination of food and pharmaceutical products.
Here, we emphasize that the evaluation in the wide varaiety of application which employs metal decoration inks will take a very long time to confirm individual safety issues.

Abrasion resistance

Performance required to prevent defects such as scratches due to rubbing of the printed material during the printing process and product transportation in general.

Pencil hardness under heating conditions

Performance necessary to prevent defects such as scratches even when printed materials that retain heat immediately after ink drying collide with each other or collide with the transport line.

Overprintability

The performance required to accurately reproduce the images as per the approved master sample.

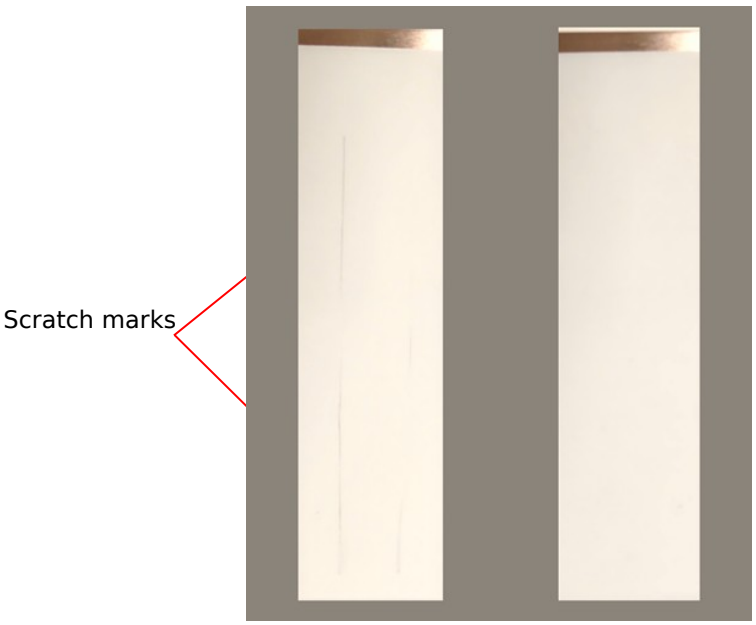
Table 5-1 shows the ink performance with various lubricants.

Table 5-1. Evaluation of various lubricants for a metal decorating ink

	No Lubricant	Silicone lubricant	Paraffin waxes	PTFE wax
Abrasion resistance	Poor	Excellent	Good	Excellent
Hardness above 80℃	Poor	Good	Poor	Excellent
Overprintabillity	Excellent	Poor	Good	Excellent

According with our investigation, almost all silicone lubricants induce great decrease of the surface tension of inks, and impairs the overprintability of inks. Most of paraffin waxes do not provide sufficient abrasion resistance and pencil hardness above 80 degrees Celsius, although the printed matters in the metal decorating application keep its temperature over 80 degrees Celsius for a while of transportation in the process immediately after drying. In addition, some of paraffin waxes cause impairing of overprintablility because of low surface tention domains at the surface of ink layer, which are formed by the migration of melted wax.

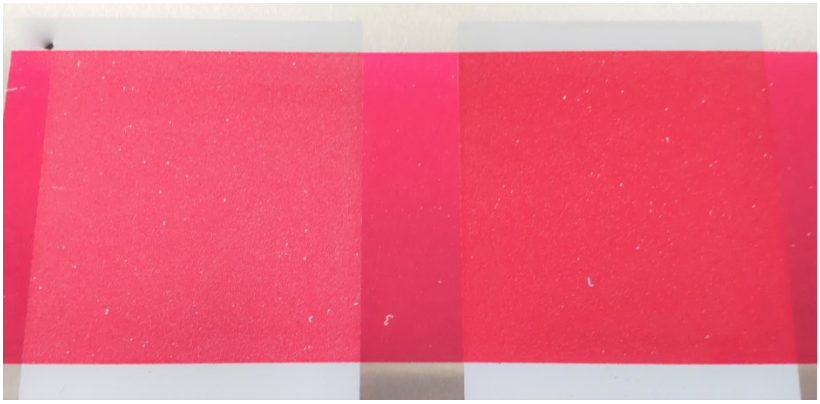
In contrast, PTFE wax has heat resistance and does not melt at the drying temperature of metal printing ink (150-200°C) and retains its particle shape. Therefore, the abrasion resistance of inks which employ PTFE wax is sufficient for metal decorating application not only at room temperature but also at high temperature, and the overprintability is also not impaired (Fig. 5-1, 5-2).



Paraffin wax PTFE wax

(Good) (Excellent)

Figure5-1. Abrasion resistance



Paraffin wax PTFE wax

（Good） （Excellent）

Figure5-2. Overprintabillity