



GSCN was established in 2000 to promote research and development for the Environment and Human Health and Safety, through the innovation of Chemistry .

Only One Mother Earth

Tisato KAJIYAMA
President, Kyushu University



According to the creation story found in the *Kojiki* (Record of Ancient Matters, dated from AD 712), Amatsu-hidaka-hiko-hono-ninigi-no-mikoto descended from heaven with the divine mandate from his grandmother, the sun goddess Amaterasu Omikami, to plant rice and pacify the idyllic land of Japan. But recently Japan has not looked so idyllic. One used to look out at the mountains off in the distance in sharp relief, but over the last couple of years those days have become few and far between, even here in Kyushu. This is mainly due to the yellow dust and smoke aerosols from coal combustion that drift over from China. Even on Tsushima Island which has almost no industry they've had to start issuing photochemical smog alerts, and the air pollution has gotten so bad here in Kyushu that many are starting to experience health problems. Many days the smog is so thick that one cannot see 100 meters distance, and I imagine that Amatsu-hidaka-hiko-hono-ninigi-no-mikoto would have a difficult time finding Japan if he descended from heaven today! Certainly Japan and East Asia have benefited enormously from the economic development of China, Korea, and other countries of the region, but this same development has led to rapid deterioration of the environment. Concern over these issues led us to organize a campus-wide initiative to explore "East Asian Environmental Issues" as part of Kyushu University's centennial celebration in 2011, and to launch an international industry-university collaborative project bringing together some of the best minds from Kyushu University, across the country, and around the world.

As the pace of science and technology-driven industrial productive activity accelerated in the 20th century, the balance between environment sustaining biological production and environment damaging pollution has gotten seriously out of kilter, and especially in the latter half of the 20th century, the load on the global environment has become unsustainable. Now assailed from every side by harmful UV rays through the depleted ozone layer, global warming due to greenhouse gas concentrations, the blighting effects of acid rain on plants and buildings, and a host of other environmental ills, we can no longer afford to wait. These are issues that must be addressed now if we are to forestall disaster and protect our one and only mother earth. Effective harnessing of science and chemical technology is absolutely indispensable to achieve sustainable societies and bountiful and healthful lives on our one and only planet earth.

Construction of a green chemistry recycling system for fluorine

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In the realm of chemistry, research from the standpoint of green sustainable chemistry has flourished since the 1990s. In the field of fluorine chemistry, technology and resources have emerged as major themes and the development of environmentally friendly resource recycling processes is crucially important, but the unique properties of fluorine compounds have presented enormous challenges and little headway has been made so far. Our group is primarily concerned with the unique challenges presented by fluorine chemistry, and here we provide a summary overview of our success in developing bonding and cleaving methods utilizing the biodynamics of fluorine compounds.

Quest for fluorine-systems material degrading bacteria

Before we can build a green chemistry recycling system for fluorine resources, we must first develop technologies harnessing bacteria and enzymes. This involves first recovering fluorine materials in the form of fluorine ions using bacteria to dissolve fluorine-system material, then attempting to incorporate fluorine atoms into molecules by fluorinating enzymes. A number of monofluoroacetic acid degrading bacteria have been reported including

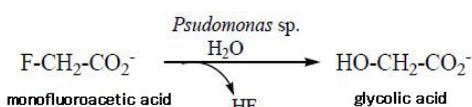


Figure 1 Defluorination by microorganisms
Pseudomonas sp. are hydrolytically defluorinated

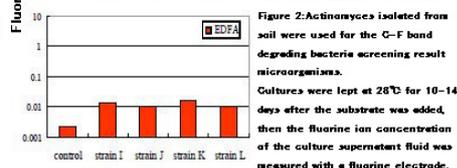
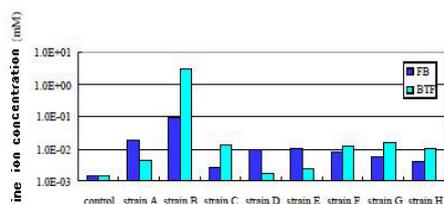


Figure 2: Actinomyces isolated from soil were used for the G-F bond degrading bacteria screening result microorganisms. Cultures were kept at 28°C for 10-14 days after the substrate was added, then the fluorine ion concentration of the culture supernatant fluid was measured with a fluorine electrode.

Pseudomonas indoloxidans, *P. cepacia*, *Moraxella* sp., *Burkholderia* sp. and other gram-negative bacteria, as well as the fungal species *Fusarium solani*, and the dissolving mechanisms (see Figure 1) have been described in detail. Our work on degrading bacteria focused on Benzotrifluoride (BTF), Difluoroacetic acid derivative, Difluoroethanol, and other materials whose molecules contain multiple fluoride atoms. Considering that in fast screening of drugs and other bioactive compounds you normally count yourself lucky to get a single candidate after screening tens of thousands of samples, we were amazed at the extremely high probability of candidate species in our trials. Specifically, we found that 4 out of 350 species of FB exhibited degradation ability, 5 out of 350 species of BTF showed degradation ability, and 4 out of 250 species of EDFA showed degradation ability. The FB and BTF in particular exhibited the highest degradation ability for the same bacteria species, at a concentration of several percent of the added substrate.

Fluorinating Enzyme (Fluorinase)

The enzyme (fluorinase) that produces fluorine-system material from inorganic fluoride ions was discovered from actinomyces streptomyces cattleya, is capable of synthesizing C-F bonds from inorganic fluoride. Surprisingly, we found that, in organisms, fluorine could be introduced into S-adenosyl-L-methionine (SAME) that was supplied as methylated substrate. Virtually all organisms use SAME as methylation substrate because the DNA methylation reaction is so critically important for organism self-recognition, but I suspect that this fluorination reaction may be the first example of a very different way in which SAME is used

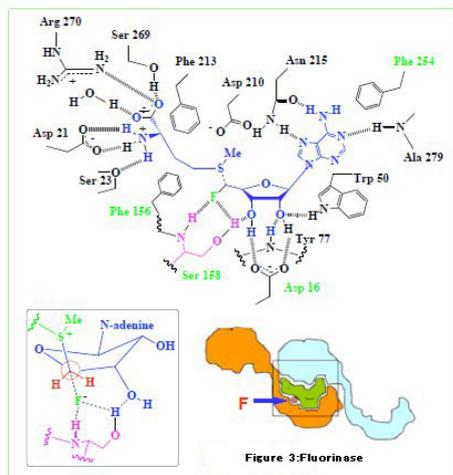


Figure 3-Fluorinase

Fluorinase produces an adenosine fluorine derivative by fluorinating the 5'-position carbon. The reaction structure is thought to be an S_N2 type reaction in which the 5'-position carbon is nucleophilically attacked by fluoride ions from the back of the sulfur atom in the center.

Seeking to increase the activation of the enzyme fluorinase, the authors tried various systems by incorporating proteins that were denatured and deactivated by heat and various other kinds of stress into chaperone proteins with the ability to replicate and into GroE proteins, and succeeded in improving the activation by close to four times. As one can see in Figure 2, the fluorinase reaction site is sandwiched between the mutually different fluorinase N-terminal domain and C-terminal domain, and the fluoride ions settle into a fluoride ion pocket formed by

amino-acid residue on the N-terminal domain side. The first contact is made with the 158th serine, but we infer that the 156th phenylalanine is crucial in the formation of the desolvation environment. Moreover, it is thought that the 16th aspartic acid determines the orientation of the 158th serine residue hydroxyl group via the SAME ribose ring and hydrogen bonds, and one can easily infer that this transformation of the amino acid could cause the pronounced change in affinity toward the fluoride ions. Currently, the authors are designing fluorinase variants while anticipating a more complete fluoride ion pocket structure, and trying to construct a more evolved type of fluorinase in their laboratory.

Constructing recycling processes for fluorine resources

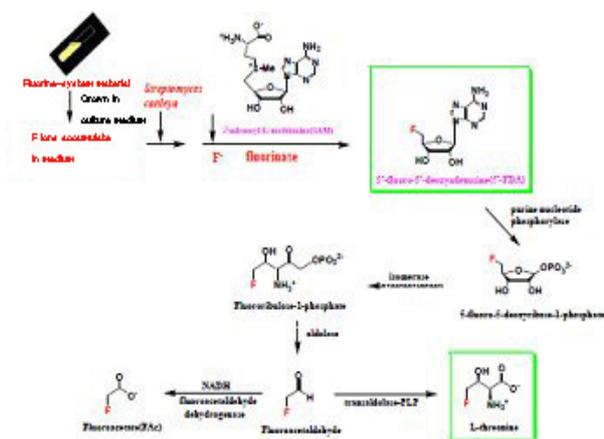


Figure 4: Development of cycling processes for fluorine resources

Now that we know it is indeed possible to dissolve and synthesize fluorine-system materials through biodynamics, we are investigating to see if it is possible to incorporate fluoride ions created by cleaving into molecules using the enzyme fluorinase. As a result, the prospect of "constructing recycling processes for fluorine resources" using some type of fluorine-system material is looking increasingly likely. Headway in fluorine chemistry toward "sustainable development" is moving us closer to the "construction of recycling processes in fluorine science." Such a system involves the convergence of different fields and transcends time and space by incorporating fluoride ions produced by dissolution using natural bacteria into molecules by different bacteria using artificially created fluorine-system materials.

Development and Further Progress of Environmentally Friendly “CTP Waterless plate” and its Printing System

Kazuki Goto Toray Industries, Inc.

While arguing internationally about the environmental problem of earth levels, the offset printing industry is also forced to respond to environmental problems, such as VOC (Volatile Organic Compound) reduction and cut-off of developing solution waste, as urgent issues. On the other hand, in the printing industry, the CTP (Computer To Plate) system, writing the digitized data on a computer in the offset plate directly by laser, is replacing quickly the conventional exposure system, using silver halide film and UV light, with the background of digital technology progress. Recently, in response to such trends, Toray has succeeded in development and commercializing “CTP Waterless plate” and its printing system, through invention of novel image forming mechanism, which enables using infrared laser light for image forming, is suitable for any printing application widely, and is environmentally friendly because it does not by-produce any waste from developing solution nor dampening water and is additionally effective for VOC reduction.

This “CTP Waterless Plate”, Toray has developed, is used as offset printing plate after procedures of reaction of heat sensitive layer by laser exposure, and removal of silicone rubber layer by subsequent development (Figure 1). There are three key points of technology.

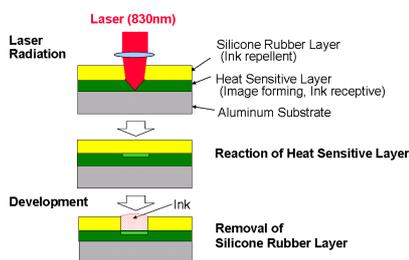


Figure 1 Structure and Plate Making Process of Waterless CTP Plate

First point is the invention of novel image forming mechanism called “Photo (thermal) exfoliation mechanism” through original design of photo functional polymeric materials and control of absorption property of laser light. In this mechanism, big temperature distribution in the heat sensitive is generated by infrared laser exposure, and top surface of the heat sensitive layer reacts. As a result, adhesion strength between heat sensitive layer and silicone rubber layer of laser exposed area decreases, and the silicone rubber

layer is removed by subsequent development. Higher sensitivity has been achieved by effective use of temperature distribution generated by laser exposure.

Second point is selection and further improvement of water development system. Automatic developing machine is used for development of CTP waterless plate, and in the procedure silicone rubber layer is removed by rotating brush after absorption by pretreatment liquid. This system does not by-produce any harmful developing waste.

Third point is design and development of new silicone rubber material. In the CTP waterless plate, micro meters of thin layer made from this silicone rubber material plays a role of ink repellent layer. Consequently, the printing system with this CTP waterless plate by-produce no waste from dampening water, which is inevitable with the conventional offset printing and contains IPA (Isopropyl alcohol). In addition, this printing system provides high and stable printing quality without any special technicians because of easy control of printing condition.

Compared with conventional offset printing system using dampening water, the printing system with CTP waterless plate has advantages of lower environmental loads as well as of higher printing property and economical efficiency (Figure 2).

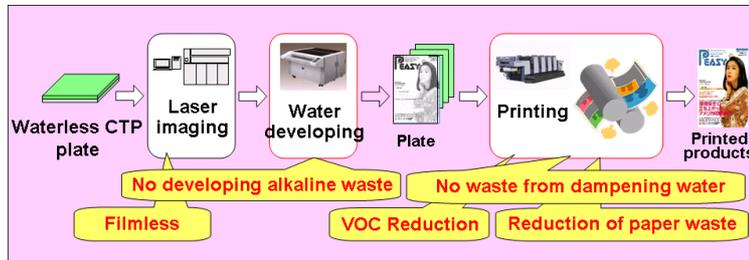


Figure 2 Environmentally Friendly Waterless CTP Printing System

This system does not require any films, does not produce developing alkaline waste in developing process, does not produce any waste from dampening water in printing process, and reduces VOC derived from dampening water. Moreover, it contributes to reduce amount of paper waste at beginning of printing job.

One of the recent topics about R&D of CTP waterless plate is development of chemical less CTP waterless plate called as “INOVA”, which does not require any chemical liquid, even pretreatment liquid during development procedure. Toray is continuing R&D activity to improve environmental properties of CTP waterless plate more.

Symbolized by the attachment of “Butterfly Logo” (Figure 3), waterless printing is spreading



Figure 3 “Butterfly Logo” representing Waterless Printing

worldwide and also accelerated by organizations such as Waterless Printing Association which has head offices at the US, EU, and Japan. There are some movements observed which lead to waterless printing as a big trend near future, such as authorization and recommendation in “Offset Printing Service: Green Standard Guideline”, higher ratio of users at “Green Printing Factories” authorized by Japan Federation of Printing Industries, and

recommendation in Green Purchasing Guideline of government and municipal offices.

The adoption of waterless printing is expanding year by year in the field of general commercial printing, and rapidly expanding in the field of newspaper printing especially in Europe. Another movement spreading to package printing and CD/DVD printing field is also observed. Furthermore, new application for printable electronics field is also expected. Waterless printing is expected to expand and to be developed further in the future.

The 8th Green and Sustainable Chemistry Symposium

March 6-7, 2008

Hitotsubashi Memorial Auditorium, Tokyo Japan

Organized by GSC Network, Japan

Thursday, March 6

Human-useful, Environmentally Benign Organic Synthesis

KOBAYASHI Shu, Tokyo Univesity

Recent Trend of BioPlastics

INOMATA Isao, Japan BioPlastics Association

<Poster Session>

Japan and Africa: the wasted chances for more fruitful and sustainable cooperation

Sanga Ngoie Kazadi, Ritsumeikan Asia Pacific University

GSC from the view point of risk management of chemicals

URANO Kohei, Yokohama National University

Innovation of Soft and Wet Gel: A Key Material for Life Science

GONG Jian Ping, Hokkaido Universtiy

<Awarding Ceremony, Reception>

Friday, March 7

METT's policy in promoting technology-based innovation

TOKUMASU Yuji, Ministry of Economy, Trade and Industry

Press Meets Risk Communication

KOIDE Shigeyuki, Yomiuri Shimbun

<'7th GSC Award Lectures>

A Cross Section of Sustainable Chemistry -Present Status and Prospect of Molecular Imaging Technology for Visualizing Human Health *

NISHIMOTO Sei-ichi, Kyoto University

GSC within the Mitsubishi Chemical Holdings Group, utilizing core technologies

TANAKA Eiji, Mitsubishi Chemical

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