Bleach-Fixer Using a New Biodegradable Chelating Agent

— Ultra-Rapid Processing Chemical ECOJET HQA-P-03 for Konica Color QA Paper —

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Employed, for a long time, as photographic bleach-fixing agents, have been ethylenediamine-N,N,N',N'-tetraacetic acid iron(III) complex (EDTA-Fe) and the like. Ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) has been employed in many industrial fields such as soap and detergent industry. However, a major problem has been pointed out in that EDTA remains in the environment over an extended period of time due to its low decomposition properties by microorganisms and results in adverse effects to the life in water-based environment. On the market, the German Photographic Chemistry Union (PIV : Photochemischen Industrie Eingetragener Verein) has initiated voluntary reduction of non-biodegradable chelating agents such as EDTA and the like. EU is now considering a similar regulation. Under such circumstances, Chemical Technology Center*, in which products are developed from the important viewpoint of environmental protection, has studied replacement of biodegradable chelating agents. "Ultra-Rapid Processing Chemical ECOJET HQA-P-03 for Konica Color QA Paper" is characterized in that s,s-ethylenediamine-N,N'-disuccinic acid iron(III) complex (s,s-EDDS-Fe), which is a newly developed biodegradable chelating agent, has been placed into practice and exhibited excellent photographic bleaching capability even in rapid processing.

1 Introduction

On the market, PIV has initiated voluntary reduction of non-biodegradable chelating agents such as EDTA and the like. EU is now considering a similar regulation.

Under such circumstances, Chemical Technology Center, in which from the important viewpoint of environment protection, products are developed, has conducted several technical developments earlier than competitors and has succeeded in development of biodegradable bleaching agents [1), 2)]. Currently, the Chemical Technology Center has studied commercial viability of s,s-EDDS-Fe which is one of biodegradable bleaching agents owned by said Chemical Technology Center and has succeeded in the market introduction of ECOJET HQA-P-03. Excellent photographic bleaching performance has been realized even in ultra-rapid processing. Herein, the study results are reported.

2 Development Target

Even though the entire photographic industry is paying close attention to biodegradable bleaching agents, no commercially viable examples of biodegradable bleaching agents have been discovered in the field of rapid processing. The Chemical Technology Center is targeting market introduction of a biodegradable bleaching agent which exhibits excellent bleaching capability even in ultra-rapid processing and is conducting studies of market introduction of photographic chemical which is environmentally excellent.

3 Establishment of Biodegradable Bleaching Agent Technology: Establishment of Core Technologies for an Environmental Consciousness Chemical

It is known that chemicals, which have a structure susceptible to enzyme reaction, are more readily biode-

Table1 Development of Biodegradable Bleaching Agents by Photographic Industries

Konica(KC)	Market introduction of ECOJET HQA-P-03(September 2001)
Eastman Kodak(EK)	Planned market introduction of a biodegradable product (end of 2000)
Fuji-Hunt	Announcement of EnviroNeg Bio-Bleach (C-41) (1997)
Agfa(AG)	Market introduction of Light-BL (September 1997) Announcement of 94 Light BX-NR (Half-Impact) (September 2000)

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gradable, since the biodegradation is a reaction in which chemicals are included in microorganisms in an activated sludge and undergo metabolic reaction through enzyme reaction. Subsequently, we have discovered the relationship between biodegradability and molecular structure while referring to data and references [3), 4)] presented in accordance with the Law Concerning the Examination and Regulation of Manufacture, etc. of Chemical Substances. Subsequently, we have surveyed chelating agents based on our discovery and succeeded in discovery of biodegradable chelating agents which are suitable for photographic processing. Further, we have discovered that, of aminopolycarboxylic acid type chelating agents, structures having Ⅰ)secondary amine, Ⅱ) monoamine based, and Ⅲ) amide bond are specifically advantageous for biodegradability. **Table 2** shows the relationship between the biodegradability and the molecular structure, while **Fig. 1** shows a list of chelating agents which have been surveyed, and **Fig. 2** shows the biodegradability test results, employing the MITI test method, which has been accepted by OECD (the Organization for Economic Cooperation and Development) and

Table2 Relationship between Molecuar Structure and Biodegradability

Amine	・Biodegradability decreases in the order of primary, secondary, and tertiary.
Alkane	・Biodegradability decreases in the order of straight chain, branched chain, and quaternary carbon.
Halogen	・Biodegradability decreases with substitution of halogen.
Molecular weight	・Biodegradability decreases with an increase in molecular weight.

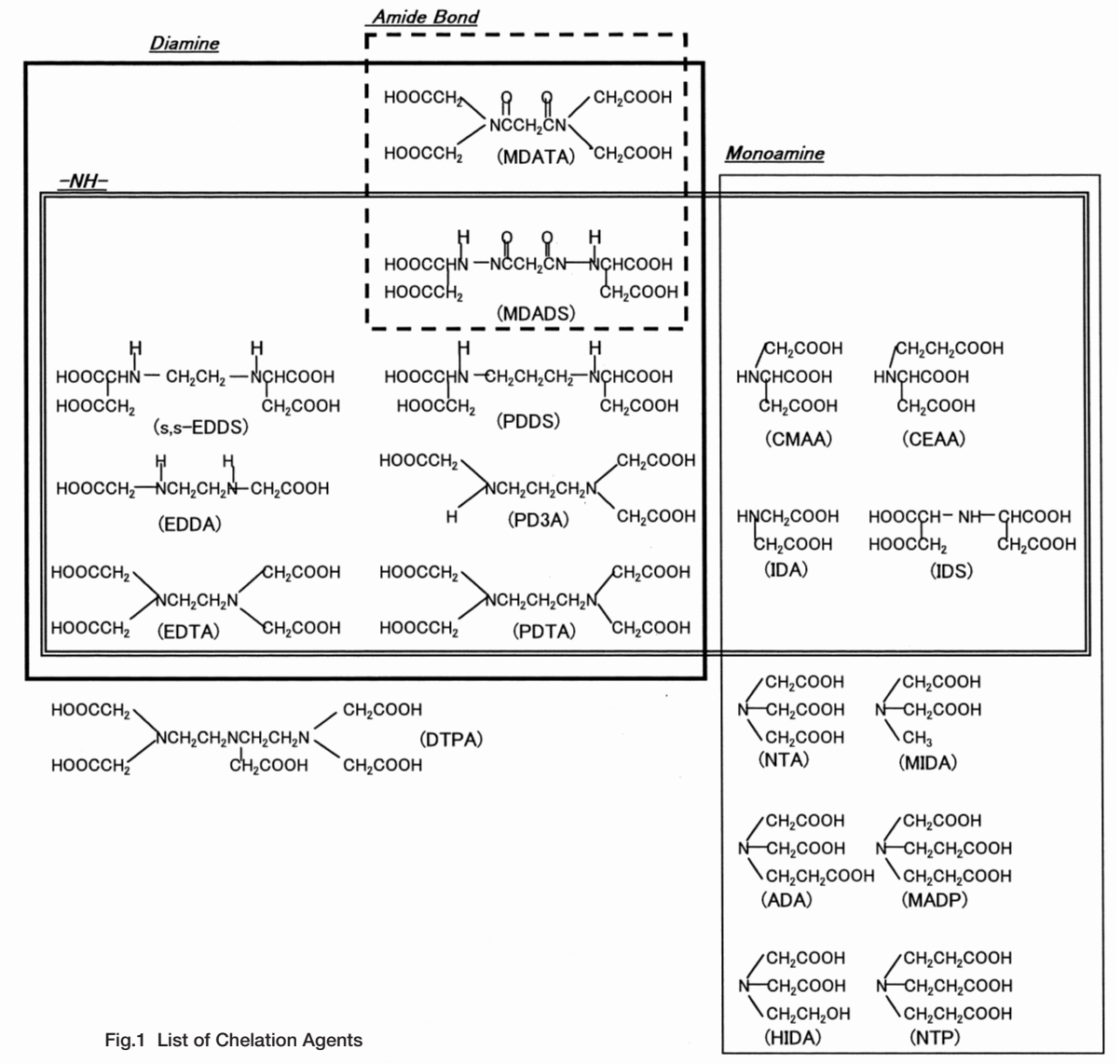

Fig.1 List of Chelation Agents

also accepted by the Law Concerning the Examination and Regulation of Manufacture, etc. of Chemical Substances. Subsequently, chelating agents, which exhibit at least 60 percent biodegradability, have tridentate or higher ligands, and form stable chelates with an Fe ion, were evaluated for bleaching performance in photographic processing. As a result, it was possible to discover a biodegradable bleaching agent, s,s-EDDS-Fe, which exhibited excellent photographic bleaching performance. Further, as used herein, the term "s,s" is used to refer to an optical isomer.

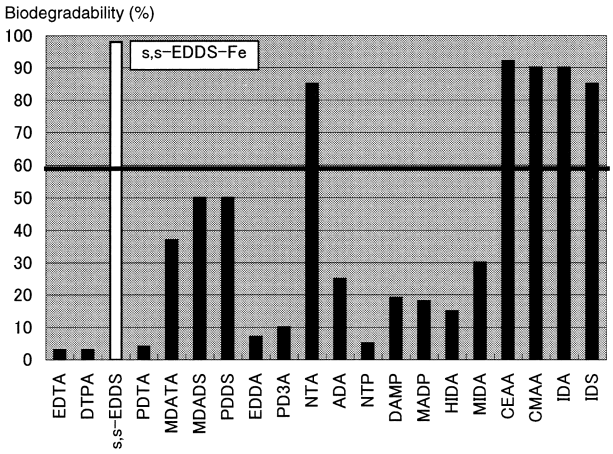

Fig. 2 Biodegradability Test Results(MITI Test)

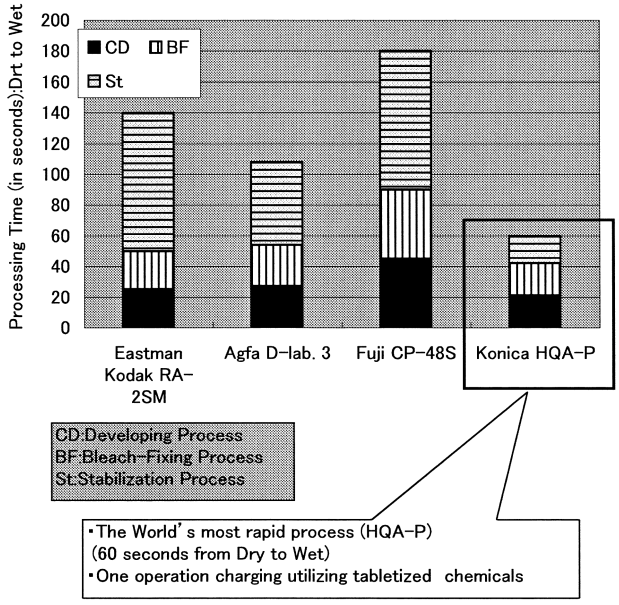

Fig.3 Features of ECOJET HQA-P Chemical

4 Investigation for Commercial Application of s,s-EDDS-Fe

Adaptability of s,s-EDDS-Fe for ultra-rapid processing was evaluated. **Fig. 3** shows the features of ECOJET HQA-P chemical.

4．1 Photographic Bleaching Performance during Ultra-Rapid Processing (Silver Bleaching Capability, Minimization of Leuco Dye Formation, and Storage Stability)

The bleaching agent, s,s-EDDS-Fe, exhibited silver bleaching capability which was quite similar to a diethylenetriamine-N,N,N',N",N"'-pentaacetic acid iron(III) complex (DTPA-Fe), while exhibiting minimized pH dependence, and was superior to EDTA-Fe. The minimization of leuco dye formation was slightly inferior to EDTA-Fe at a pH of less than 6.3, while the same was excellent at a pH of more than or equal to 6.3. The storage stability was excellent, being the same as for DTPA-Fe.

Figs. 4 - 1 through **4 - 3** show the evaluation results, and **Table 3** shows the list of performance comparison results.

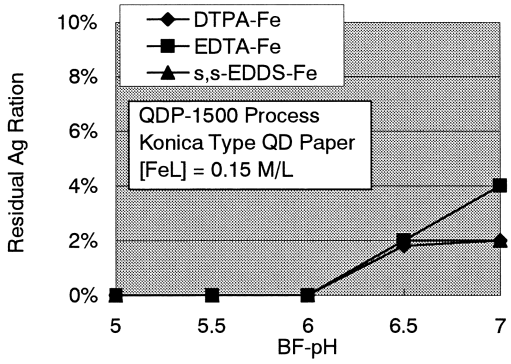

Fig.4-1 Silver Bleaching Capability

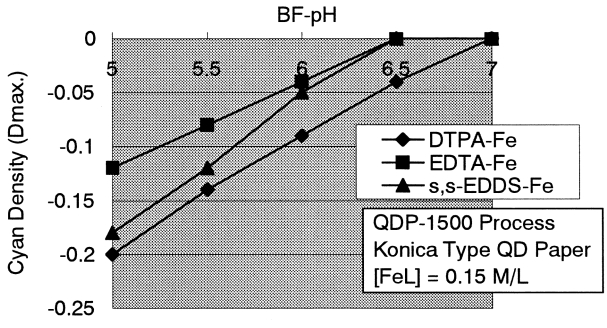

Fig.4-2 Minimization of Leuco Dye Formation

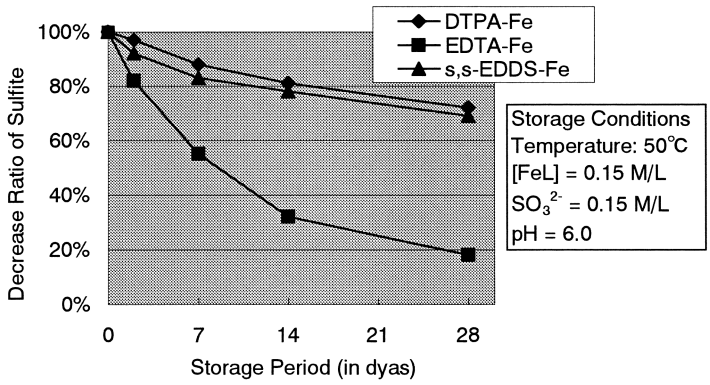

Fig.4-3 Storage Stability

Table3 List of Performance Comparison Results

Bleaching Agent	Biodegradability	Silver Bleaching Capability	Minimization of Leuco Dye Formation	Storage Stability
DTPA-Fe	poor	Good	Fair (>pH6.5)	Good
EDTA-Fe	Poor	Good	Good	Poor
s,s-EDDS-Fe	Good	Good	Good (>pH6.3)	Good

4．2 Commercial Application of a New Biodegradable Bleaching Agent

It was found that s,s-EDDS-Fe exhibited excellent photographic bleaching performance even in ultra-rapid processing by adjusting the pH to at least 6.3. However, at a pH of less than 6.3, the minimization of leuco dye formation was slightly insufficient. In order to realize more consistent processing performance, further investigation was performed. As a result, a technique was discovered in which s,s-EDDS-Fe was employed in combination with EDTA-Fe which resulted in excellent minimization of leuco dye formation, whereby the commercial application of the biodegradable chelating agent, s,s-EDDS-Fe, was achieved.

4．3 Edge Staining

It has been known that staining at the edge of paper (edge staining) occurs due to bleaching agents. Effects of practical use of s,s-EDDS-Fe for edge staining were investigated, employing absorption spectra as well as practical processing. The results of the absorption spectra showed that s,s-EDDS-Fe had properties similar to EDTA-Fe. Compared to DTPA-Fe, s,s-EDDS-Fe resulted in relatively small absorbance in the visible region. Further, in practical processing, the combination of s,s-EDDS-Fe with EDTA-Fe resulted in less edge staining than DTPA-Fe. DTPA-Fe, having a relatively large absorbance in the visible region resulted in marked staining, even though its residual amount was minimal in paper. By replacing DTPA-Fe with s,s-EDDS-Fe, it was found that edge staining was minimized. **Fig. 5 , 6** shows the results.

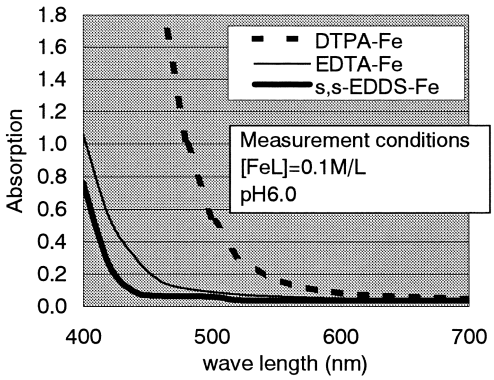

Fig.5 Absorption Spectra

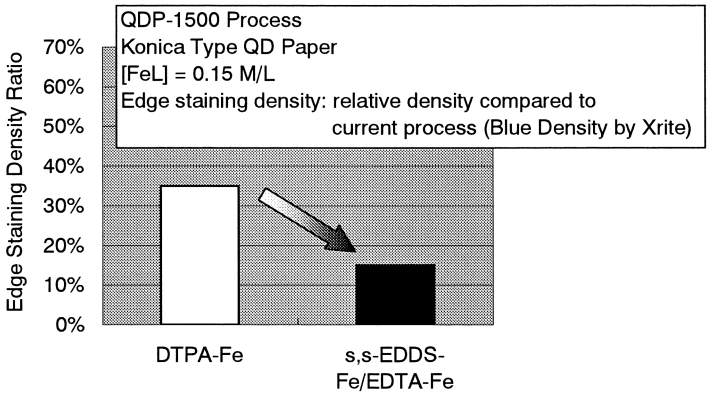

Fig.6 Edge Staining

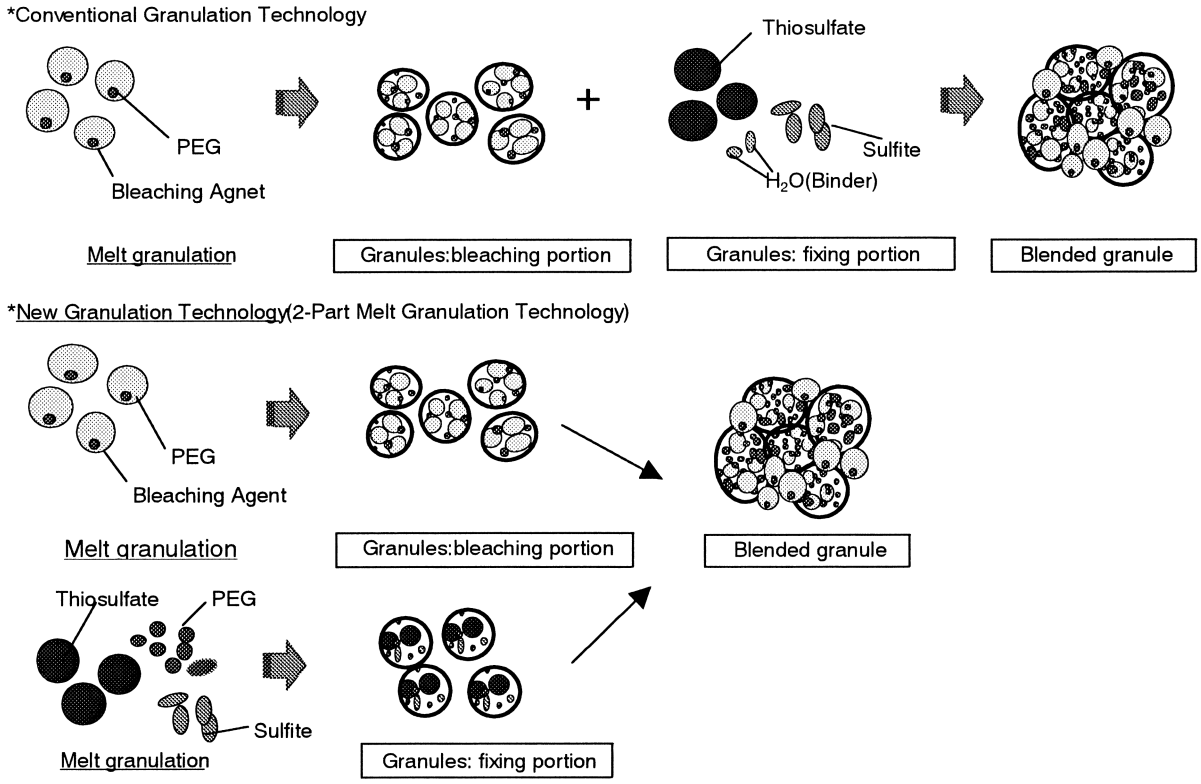

Fig.7 New Granulation Technology

5 Tabletizing Technologies

In order to apply s,s-EDDS-Fe to ECOJET HQA Chemical, its tabletizing was investigated. In conventional technology in which tablets are formed through granule formation, the bleaching portion is subjected to melt-granulation, and then blended with the fixing portion, water is added as a binder so that physical properties of the resulting tablets are enhanced through the effects of melting and the binder water. However, when s,s-EDDS-Fe was used, it was found that the conventional granulation technology resulted in degradation of storage properties of the resulting tablets. As a result, the investigation was conducted to overcome said problems.

5．1 Investigations of Causes of the Degradation of Physical Properties and Establishment of a New Granulation Technology

Differences in physical properties of bleaching agents were compared, and degradation which causes during storage of tablets were investigated. As a result, s,s-EDDS-Fe was found to be markedly soluble in water. It was also found that during storage, s,s-EDDS-Fe was dissolved in the binder water and the like, even though being in a minute amount, and reacted with reducing agents such as fixing agents. Accordingly, a new granulation technology was investigated aiming at enhancement of the storage stability without resulting in degradation technology was investigated aiming at enhancement of the storage stability without resulting in degradation of physical properties, and without adding of water as a binder.

Fig. 7 shows granulation flow. In conventional granulation technology, only the bleaching agent was granulated. However, in the new granulation technology, the fixing agent was also granulated. As a result, a 2-part granulation method was developed in which the bleaching agent as well as the fixing agent was coated with chemically inactive polyethylene glycol (PEG), so as to form a thin layer, whereby the enhancement of physical properties as well as the storage stability of tablets were achieved.

6 Summary

A commercially viable biodegradable bleaching agent has been realized which exhibits excellent photographic bleaching performance even in ultra-rapid processing. Subsequently, an environmentally friendly chemical (a bleach-fixing agent) has been introduced onto the market in a tablet form as the world's first product for minilabs.

Konica intends to contribute to society while developing leading environmentally friendly technologies.

7 References

1） Japanese Patent No. **3116194**
2） Japanese Patent No. **3208686**
3） "Kashinho no Kizon Kagaku Busshitsu Anzensei Tenken Data Shu (Collection of Safety Inspection Data of Known Chemical Substances in the Law Concerning the Examination and Regulation of Manufacture etc. of Chemical Substances)", edited by (Zai) Kagakuhin Kensa Kyokai
4） Morio Yashiro and Shinsaku Shiraishi, Dai 42 Kai Saku To (The 42nd Complex, etc.) 1E02 (1992)