Abstracts of Papers Presented at the Annual Meeting of the Society held on 25th and 26th May, 1988 in Tokyo

A-1 Conditions to Form the Tabular Silver Chloride Grains in Emulsion
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The purpose of this study is to indicate conditions to form the tabular silver chloride grains, in double-jet precipitations, which belong to the growth form in morphology of crystals.

The conditions are formation constants, bond-nature (electronegativity), molecular size (ion or molecular radii) and number of points of attachment of silver ligands added as impurities of silver chloride to produce the tabular grains. The conditions were found out by adding various silver ligands (CN\(^{-1}\), SCN\(^{-1}\), I\(^{-1}\), S\(_2\)O\(_7\)\(^{2-}\), SO\(_3\)\(^{2-}\), thiourea and its derivatives) into excess Cl\(^{-1}\) aqueous solution. Thus, the silver chloride tabular grains were found to be produces in the case of adding SCN\(^{-1}\), thiourea and its derivatives (methyl-thiourea, ethyl-thiourea, 1, 3-dimethyl thiourea and 1, 3-diethyl thiourea).

A-2 Measurements of the Mobility of Electrons and Holes in AgBr Grains by a Time-of-Flight Technique
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An apparatus for measurements of the drift mobility of electrons and holes in solid state specimens (Time-of-Flight technique) was made and applied to AgBr emulsion grains. Light pulse were exposed to emulsion layers which were contained of cubic AgBr grains (edge length; 1.7 \(\mu\)m), under application of electric pulses. The drift mobilities of electrons and holes in the grains were estimated to be more than 15 cm\(^2\) V\(^{-1}\) sec\(^{-1}\) and 1.1 cm\(^2\) V\(^{-1}\) sec\(^{-1}\), respectively. These values are close to those in large AgBr crystals.

A-3 Relation between the Dispersion and the Delayed Formation of Latent Image Specks at Sulfur Sensitized Emulsion
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In using sulfur sensitized emulsions of octahedral grains and techniques of development rate measurement and gold intensification we studied the relation between the dispersion and delayed formation of latent image specks. High level of sensitization caused large variations in induction periods at development and large dispersion of latent image specks was suggested. Delayed formation of latent image specks at high level of sensitization becomes small. We could not find direct relation between both.

A-4 Spectral Sensitization of Silver Halide by Silver Sulfide and Gold-Silver Sulfide
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Possibility of spectral sensitization to silver halide photography by inorganic sulfide compounds was studied. Treatment in gold-thiourea complex solution eliminated almost all fog caused by heavy sulfur sensitization. We could take clear spectrograms of heavily sensitized emulsion coatings by the treatment after or before exposure. Both showed longer wavelength sensitivity. Silver sulfide specks deposited on sulfur sensitized emulsion grains may be converted to gold-silver sulfide specks by treatment in gold-thiourea complex solution. Both silver sulfide and silver-gold sulfide specks can act as spectral sensitizer to silver halide.

A-5 Effects of Impurities in Pure Silver Behenate upon Photographic Characteristics of Thermally Processed Silver Film
The relationship between impurities of silver behenate and their synthetic conditions is investigated to produce the thermally processed silver (TPS) film on an industrial scale under the well controlled manufacturing conditions.

Fogging (ODmin) increases as pH of sodium behenate solution shifts to a high alkaline side, in spite of no detective difference of the final products (silver behenate) by chemical analysis. This suggests the possibility that Ag2O in the salt and/or reducing catalytic substances from the TPS film.

On the other hand, although chemical composition of the salt is widely changed in an acidic region by more excess HNO3, it hardly affects any initial photographic characteristics.

A-6 Properties of Gelatin Films Treated with Formaldehyde and Mucochloric Acid

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Several properties of gelatin films treated with formaldehyde and mucochloric acid were investigated with varying the reaction conditions such as pH, amount of hardeners and gelatin species. Swelling ratio, sol fraction and its molecular weight distribution were measured. Swelling ratio and sol fraction were affected by reaction pH and gelatin species. The higher component of molecular weight of sol fraction were diminished with storage period though their reactivities varied from limed processed gelatin to acid processed one.

A-7 Effect of Nonionic Hydrophilic Agents on the Electrophoretic Mobility of Gelatin

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Polyethyleneglycol (PEG) and Tween 80 markedly reduced the mobility of gelatin in SDS-polyacrylamide gel system even at 0.1% level. Tween 80 is more effective than PGE. The effect of these wetting agents is gradually cancelled by the increase of SDS concentration. The wetting agents should therefore compete with gelatin for SDS.

"Forbidden separation" of a1 and a2 bands in the SDS system is enhanced by the addition of the wetting agents. This may caused by delicate change in selectivity of SDS binding to these chains.

A-8 Electrophoretic Analysis of The Gelatin Fraction Recovered from The Silver Halide Surface

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As a possible factor of selection which operates on the adsorption of peptide components of gelatin on the silver halide surface, effect of molecular-weight was examined by SDS-electrophoresis.

The gelatin fraction adsorbed was recovered by two procedure: (1) by dissolution of silver halide crystals with Hypo, (2) by solubilization of the gelatin with SDS treatment. No difference was found between the molecular-weight distributions of recovered and original gelatins when examined by SDS-electrophoresis. In this respect the adsorption seems to be nonselective. Effect of isoelectric point will also be discussed.

A-9 Analysis of Gelatin by High Performance Chromatography with a Photodiode Array Detector

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The purpose of this study is to check the availability of a photodiode array detector (PAD) as a detector of high performance liquid chromatography (HPLC) for the analysis of gelatin. The PAD was applied to the determination of molecular weight distribution (MWD) of gelatin, and that of anions such as nitrate and nitrite in it. The PAD gave
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far more information than a conventional ultraviolet detector. For the determination of MWD of gelatin, the spectral absorption curve of each peak, such as $\alpha$, $\beta$, $\gamma$ peaks, was similar one another. These curves were almost independent of the difference of molecular weight. The PAD also gave much information for the determination of nitrate and nitrite ions, such as three dimensional chromatogram, spectral absorption curves and so on. These results show that the PAD is available for the investigation of gelatin as a detector of HPLC.

A-10 Electrochemical Determination of Iodide Included in the First Developer of Color Reversal Processing

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Iodide concentration of the first developer in color reversal processing has a great influence on the final color image. At present, iodide was determined by potentiometric titration with silver nitrate using a silver electrode. This method requires troublesome pretreatments like filtration. In the present paper, determination of iodide by the voltammetry was attempted, where current-potential curves for the oxidation of silver to silver iodide were measured in the first developer itself using a rotating silver electrode. The pretreatment required for this method was only to lower pH of the developer to about 3. The results obtained by this method agreed very closely with those obtained by the titration.

A-11 Endogenous Formation of Cyanide Compounds during Determination of Total Cyanide in Photographic Waste Solution

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Although, cyanide compounds are not used in photographic processing solutions, cyanide ion is often detected during determination of total cyanide. Various kinds of organic compounds and nitrogen compounds are contained in photographic solutions. Hydrogen cyanide is formed by the reaction among these compounds during distillation for the determination of total cyanide. The formation schemes for hydrogen cyanide from photographic waste solution are as follows:
1. Hydroxylammonium reacts with organic compounds to form HCN.
2. Formaldoxime decomposes to form HCN.
3. Nitrite ion reacts with organic compounds to form HCN.
4. Potassium permanganate oxidizes aromatic amines (color developing agent) to form HCN.

A-12 Investigation of the JIS Method for the Determination of the Cyanide in Photographic Waste Solutions

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No cyanide or complex cyanide are included in any current photographic processing solutions. Cyanide ion, however, was detected during testing by the JIS method. Hydroxylammonium showed a great influence on the formation of cyanide ion. The reproducibility of the colorimetric determination adopted in the JIS method was poor, and cyanide ion detected by it was always smaller than that determined by the potentiometric titration with silver nitrate using a silver electrode.

A-13 Color Correction and Interpolation of Television Pictures for Compact Printing Systems

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The compact color printing systems for newspaper printing from television pictures has been developed, composed of color television, minicomputer and halftone dot generator by Ar laser. In this printing system, color corrective equation was determined to minimize the color difference $\Delta E$ in
the \( L^*u^*v^* \) space between CRT image and printing image. On the bases of this corrective equation, television picture was printed with three basic interpolation methods. Image quality of those obtained image are evaluated and analyzed.

**A-14 Color Image Quality and its Spatial Frequency Characteristics (1)**

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It is well known that the image quality is dependent on the spatial frequency characteristics of image, especially the low frequency components of portraiture give considerable effect for its sharpness. However, relatively little study has been done on the effects for sharpness of color image. In this study, color images processed by various spatial frequency filters were evaluated and analyzed. This experimental result shows that the spatial frequency characteristics of red and green components of image gives more considerable effects than blue one for color image quality.

**A-15 A Fast Algorithm of Computing Color Gamut for Subtractive Color Mixture**

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In subtractive color mixture, it was found that the boundaries of a color gamut in a chromaticity diagram correspond to the intersections of the gamut’s equilightness curvature plane and the planes limiting dye amount space. On the basis of this relationship, a fast algorithm for computing color gamuts was developed. After computing color gamuts and comparing the results with those obtained from another algorithm, the new algorithm was found just as accurate, but much faster. Computing and plotting together take only 3.5 to 5.5 minutes when using personal computer.

**A-16 High Image-Quality Laset Color Printer**

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A laser color printer has been developed to depict continuous tone color images with high resolution and high fidelity. Three lasers, He-Cd laser (\( \lambda = 441.6 \) nm), Ar+ laser (\( \lambda = 514.5 \) nm), and He-Ne laser (\( \lambda = 632.8 \) nm) are employed for the blue, green, and red exposures. Maximum resolution is 40 c/mm (80 lines/mm) and variation of density reproduction is below 1.5 when measured by color difference. Image quality of the output images is well comparable to that of actual color photographs.

**A-17 Evaluation of Image Quality for Noisy Images (1)**

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Image quality of images corrupted by computer-generated uniform and gaussian random variables was evaluated and analyzed. Signal-to-noise ratio (S/N) and MTF of noisy images were measured and compared with the observer rating values (ORV). From these experiments, it becomes clear that S/N was well correlated with ORV. However, MTF was not correlated with ORV and hence it is necessary to define the measurement method of MTF for noisy images.

**A-18 Noise Analysis of HDTV-Electrocinematographic System**

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Recently, electrocinematography based on HDTV technique is attracting social interests. Noises of color negative film images prepared electrocinematographically may be different from those of conventional motion picture film images, because the former may include additional noises from HDTV camera, laser beam recorder or due to signal processings such as aperture corrections. The Wiener spectra were measured on negative film images of N1.5 to N7 gray patches prepared by the two systems. The results show that the electrocinematographic images are far more noisy at lower luminance gray patches than the conventional ones.
A-19  Edge Preservation at the Image Restoration of Noise Degraded Images Using Kalman Filter

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The purpose of this work is to materialize real time restoration of the image degraded by signal-independent Gaussian noise. A new method proposed here is based on one dimensional recursive estimator known as a Kalman filter to reduce processing time. This method is a kind of smoothing filter which preserves the sharpness of image. Because the noise at edges is not conspicuous, the estimated value at a pixel is regarded as the observed value at the pixel if the difference between the estimated and the observed values is larger than the standard deviation of noise. This method preserves sharpness of image better than ordinary smoothing method.

A-20  Studies on Color Image Telecommunication with Highly Detailed Level. (Part 3)
—Color image and type face transmission—

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On Oct. 24, 1986, the authors successfully transmitted detailed color images between Tokyo and Osaka using total scanners, communication units, modems etc., via NTTs telephone network.

With our successful experiment as a starter, there have been increasing cases of color image transmission across the country.

In this study, we transmitted color image and type face, and then evaluated the output images and type face.

The Hell 399 ER color scanner was used to input image and type. Color image signals were coded at score value of 5 (the highest image compression ratio), and then type faces were scanned in Res 24, 36 and 48 (line/mm).

With the use of NTTs telephone network, it was easy to trasmit highly detailed color image and type face.

A-21  An Approach to 3-D Photomicrograph by A Light-sheet Scanning Technique

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A photomicrograph has two fatal features of shallow depth of field and lack of perspective. A device is built up for eliminating the disadvantages. Thin beams are used to illuminate an object selectively and magnification of each part of the object varies by a zoom lens. As magnification increases, the device is fallen into hard conditions of focusing in addition to provide thin beams required. We take a step to stop down the aperture of objective adequately, and the effects of the operation on image quality are checked to 40x magnification. The results show that the device appears to useful for 3-D photomicrography.

A-22  Identification of Localization of Drugs in Human Cells with Fluorescence Photomicrography

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Drug-induced photosensitivity in human skin includes both phototoxic and photoallergic reactions. Some phototoxic drugs such as psoralens have been used to skin-photochemotherapy as photosensitizer. To examine the mechanisms of phototoxic reaction of drugs, we tried to identify the localization sites of drugs in human skin cells. Most of phototoxic drugs show the fluorescence with exciting UV-A (320-400 nm) light. Firstly, a commercial reflected light fluorescence microscope was improved with inducing UV-A light. Secondary, properties of fluorescence probe on drugs were determined with various kinds of solvents before the fluorescence microscope observation. In case of psoralens, 8- and 5-methoxypsoralen, we determined that both drugs are incorporated in nuclei of human skin cells. The identification method can widely apply
to the examination of affinity sites of fluorescent drugs in cells.

**A-23 Study on Photography from “Potokarahii”, Manuscript of Kohsai Udagawa in Middle 19th Century—I**

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Kohsai Udagawa (1821-1887) was a famous chemist in Japan. He lived from the last days of the Tokugawa shogunate to the early days of the Meiji era. Present paper concerns to interpretation of his manuscript about albumen wet plate photography, named “Potokarahii”. It is supposed that the old document is probably a translation from a Dutch technical book. It contains preparation and image formation on a silver iodide-albumen photosensitive layer. It consists of following items; introduction, cleaning of glass plate, preparation and coating of iodide-albumen solution, sensitization, light exposure development, fixing, washing and drying. Interpretation was a little difficult, because the manuscript was composed of classical Chinese characters, “hentai-kana”, classical Japanese character, and old Dutch technical terms and units.

**A-24 Study on Photography from “Potokarahii”, Manuscript of Kohsai Udagawa in Middle 19th Century—II**

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Photographic process of albumen wet plate from “Potokarahii”, Manuscript of Kohsai Udagawa was experimented. Sensitometry of the plate was carried in a time scale exposure method, because of extremely low sensitivity. Photographic speed calculated from the result was equivalent to ISO $4 \times 10^{-4}$. Development time was shortened by treatment with saturated gallic acid solution before light exposure. Solarization of image appeared in the higher exposure region without the treatment. In addition to them, it was desired to add silver nitrate into a gallic acid developer, to obtain a negative image on the wet plate. Spectral response to a Xenon arc lamp was observed in the range of 332 nm–484 nm with maximum speed at 442 nm.

**A-25 Poster Printer Using Direct Thermal Recording**

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A new 8-times enlarging copier (Poster Printer 100) has been developed by using Direct Thermal Recording method which enables most simplest maintenance for users. Compact and low cost copying machine was realized by employing contact imaging sensor and serial thermal heads. As copying paper, seven different pieces were developed, colored base paper, single color copying paper as well as black color with white base for standard type. This Poster Printer 100 with following specifications is now available and widely used at various occasions among corporations, educational authorities, public transportation and labor unions for poster presentation.

- Original document size: A4, B4 letter size
- Copy print size: A1 or A2
- Image reading: Contact imaging sensor with 8 dots/mm
- Recording: Serial thermal heads with 2.8 dots/mm
- Reading/recording speed: 70 sec. (A4 to A1 enlargement)
- Machine size: 1084 (W) × 270 (D) × 142 (H) mm
- Weight: ca. 13 kg

**A-26 The Conversion of Photo-Image into Printing-Image**

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We invented the new technology of nonlinear-image conversion system from continuous-tone to half-tone, so called Gold Imaging Soft (G.I.S.), that is able to adapt, under any conditions of color-originals and printing-image wanted.

From this G.I.S., we can expect surely to have adequate and predictable color separation curves through the normal separation method from both standard quality color-originals and non-standard ones.

And, by this technology, we can avoid the powerful electric computer and memory unit need to calculate to get the equations of separation curves that are drawn by scanner operator's experiences.

A-27 A Study of Adsorption of Dye to the Cubic AgBr Grains in Dried Emulsion Layers
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We have measured the amount of dye adsorbed on AgX grains in dried thick emulsion layer (120~150 μm), using the Kubelka-Munk function. As a result, we found that saturated amount of Dye I (3, 3'-Bis (4-sulfobutyl)-9-methylthiacarbocyanine) adsorbed on the cubic AgBr grains in dried thick emulsion layer is less than that in liquid emulsion. Correlation of the amount of Dye I adsorbed in dried thick emulsion layer with physical and photographic properties of AgBr grains was examined.

A-28 Spectral Sensitization of Multi Structure Crystals
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Using octahedral grains of various structures with an edge length of 2.0 μ and a cyanine dye, we performed experiments to examine the adsorption characteristics of MSCs (Multi Structure Crystals).

The dye used in this study barely adsorbed to the homogeneous AgBr emulsion grains, but adsorbed well to MSCs whose shell halide composition was AgBr.

This phenomenon can not be explained by the crystal habit or halide composition. It shows that the adsorption behavior of the MSCs is related to the nature of their cores.

A-29 Study on Detection of Transferred Electron from Exitied Dyes in Spectral Sensitization
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Direct detection of transferred electron from exitied cyanine dye to AgX in spectral sensitization was tried to measure by the donor-acceptor system.

Multi layer cell (Au/TEOA HCl/Cyanine dye/AgCl/Au) were constructed by the evaporation method. Electrons from exitied dyes were detected by photoinduced current. The induced spectral current was correspond to absorption spectra of cyanine dye.

The experimental results suggest that the direct detection of transferred electrons thus developed by us is useful in, investigating sensitization mechanism of dyes in AgX photography.

A-30 UPS Measurement of Electronic Structures of Thin Layers of Cyanine and Merocyanine Dyes and Discussion on Various Factors in Condensed Phases
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The ionization energy and Fermi Level of cyanine dyes as well as those of merocyanine dyes were measured by use of UPS, and compared with their polarographic reduction half-wave potential and excitation energy. Discussions were made on various factors influencing the electronic energy levels of the dyes in condensed phases.

A-31 J-aggregation of Anionic 2, 2'-Cyanine Dye
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Salted-out J-aggregation of anionic 1, 1'-disulfo-butyl-2, 2'-cyanine (potassium salt, Dye 2) has been studied. Moderately dilute aqueous Dye 2 solutions were mixed with concentrated sodium sulfate solu-
tions, and the mixtures were examined spectro-
photometrically with a multichannel photodetector.
J-aggregation was observed at dye concentrations
higher than $2 \times 10^{-4}$ mol/l in the presence of 0.5
mol/l sodium sulfate. In spite of the negative
charge, Dye 2 J-aggregated under almost the same
conditions as positively charged 1,1'-diethyl-2,2'-
cyanine (chloride, Dye 1). Presence of sodium sul-
fate also favored the dimerization of Dye 2 at
concentrations slightly lower than necessary for J-
aggregation.

A-32 Observation of the Development Process of
Silver Halide Microcrystals by High-resolution SEM

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To investigate the development process, we di-
rectly observed the developed grains and silver
filaments of silver halide microcrystals using an
in-lens FESEM (Field Emission Scanning Electron
Microscope).

This high-resolution FESEM made it possible to
observe these small, developed grains (edge length:
$0.27 \mu$) and filaments (diameter: $\sim 200 \AA$) with the
low accelerating voltage of $2 \text{kV}$.

Moreover, in order to prevent damage from light
and heat, the specimens were not evaporated and
were cooled to $-120^\circ \text{C}$ during observation.

A-33 Control of Hydrazine-Nucleated Infectious
Development

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In hydrazine-nucleated infectious development,
one of the practical problems is black spot (BS).
In this paper, we described BS morphologically,
and two restraining means of BS, different each
other in mechanism. One of them is the anion
charge barrier, formed by the adsorption of some
kind of dyes on AgX. The other is timing con-
trol between fogging development and following
infectious development by organic acid polymer.
It was also suggested that the active species in the
infectious development has anion charge, and that
some side reactions of oxidized hydroquinone have
significant role.

A-34 On the Mechanism of Bleaching of Developed
Silver

The Effect of Development Inhibitors on
the Rate of Bleaching of a Color Negative
Film

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After bleaching of a color negative film, a part
of developed silver in the film remain, that is,
“tailing” appear on residual silver vs bleaching
time curve. A cause of the tailing was that 1-
phenyl-5-mercapto-tetrazoles (PMT) liberated from
DIR coupler adsorbed on the developed silver and
reiarad bleaching reaction by EDTA-Fe(III) BF
bath. The tailing was reduced by an addition of
2-mercapt-benzimidazole (MBI) in the BF bath.

These effects of the additives can be interpreted
as the effects on the kinetics of the cathodic re-
duction of EDTA-Fe(III) at a silver electrode and
the anodic dissolution of a silver electrode in thio-
sulfate slution.

A-35 Electrochemical Model Experiments upon the
Morphology of Dye Clouds

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The rate of the deamination and the coupling of
quinonedimines (QDI) and the coupler concentra-
tion in the emulsion are important factors deter-
mining efficiency of the dye formation. On the
other hand, these affect the image quality. In the
present paper, the effect of these factors upon the
morphology of dye clouds was studied using an
electrochemical model, where the emulsion includ-
ing solvent dispersion coupler was coated on an
optically transparent electrode and $p$-phenylene-
diamines were oxidized on it to produce QDI quan-
titatively. The dye cloud was observed under a
microscope. The experimental data were compared
with those calculated by the digital simulation
 technique.
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A-36 Photofading Reactions of Aerated Solutions of Magenta Dyes with Carbonyl Compounds

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Excitation of carbonyl compounds (CCPD) by near ultraviolet rays fades magenta dyes (MD) in aerated ethanol solutions with CCPD considerably fast. Effects of acid, alkali and oxygen on the fading reactions are investigated elaborately. Additions of HCl up to 10^{-4} M and NaOH up to 10^{-3} M have almost no effect on the fading reactions in degassed solutions but have strong effect on the reactions in degassed solutions. In the latter the fading rate increases in accordance with acid concentration and decreases with NaOH concentration. Moreover the fading rate decreases in accordance with O_{2} pressure. Form these results it is concluded that the fading reaction in aerated solutions is also initiated by ketyl radical of CCPD.

B-1 Photochromism of WO_{3} and its Application

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Photochromism of WO_{3} films was investigated. It was found that photochromic reaction is promoted by the existence of a reductant, like as methanol, at the surface of the films. The increase of absorbance (ABS) value, which is induced by the irradiation, is equal to or less than 0.1 in pure benzene and in propylene carbonate. In the solution that contains about 0.05 vol. % methanol, the increase of ABS value becomes two times that in the pure solvent. In the nitrogen gas that contains about 0.5 vol. % methanol vapour, the increase of ABS becomes two times that in the dry nitrogen gas. In both cases, the increase of ABS is saturated when the concentration of methanol is several vol. %. The color induced by the irradiation can be erased by electrochemical oxidation.

B-2 Study of Electrochromic Reactions by In Situ Electrogravimetry (IV)

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The mechanism of electrochromic reactions in WO_{3}/H^{+} systems was studied in situ by measuring the small change of WO_{3} electrode with the liquid phase quartz crystal microbalance (LPQCM). A new type LPQCM, in which the electrodes for oscillating circuitry were formed by indium-tin oxide (ITO) under the WO_{3} electrode, was designed to examine the relationship between the change of optical density and the amount of injected cations to the WO_{3} films. The change in optical density to specific weight change was dependent on the amount of injected cations. This implied that the coloring efficiency of the WO_{3} electrode was affected by the degree of cation injection.

B-3 Pattern Formation of Conducting Polypyrrole by Photo-sensitized Polymerization

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Fabrication of conducting polymer pattern is considered to be one of the most important subject in the field of molecular electronic devices. A novel photo-sensitised polymerization of pyrrole is investigated in order to form fine conducting polymer pattern on insulating materials. In this method, both photo-sensitizer which can oxidize pyrrole and sacrificial oxidant which do not directly oxidize pyrrole are required for oxidation of pyrrole. It was proved that the photo-sensitized polymerization proceeded according to the oxidation of pyrrole by photogenerated Ru(bpy)_{3}^{2+} through the oxidative electron transfer process. The fine conducting pattern about 10 \mu m width of polypyrrole was formed on organic membrane such as Nafton which adsorbed Ru(bpy)_{3}^{2+} by this method.

B-4 Hybridized Patterning by the Photo-electrodeposition Coating and the Photo-polymerization of Pyrrole

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A hybridized micro-pattern formation, combining photo-electrodeposition (PED) of insulating resin and photo-polymerization of pyrrole (PPy), was demonstrated on an illuminated TiO\textsubscript{2} film electrode. PED patterning was overlaid on a PPy pattern, and vice versa. PED film can be deposited on PPy due to the photoelectrolysis of water even on the PPy under a given experimental condition. On the other hand, PPy coating was almost suppressed on PED because of the electrical insulation of the PED film. Upon controlling the applied bias and the duration of the illumination, a multi-layered hybridized pattern can be obtained.

B-5 Coloring and Bleaching Behaviors of Electrochromic Display Based on Polymeric Solid Electrolyte

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Polymeric solid electrolyte having high ionic conductivity of about 10\textsuperscript{-4} S/cm is applied to construct all solid state WO\textsubscript{3}-PB based electrochromic device (ECD). Poly[oligo(oxyethylene) methacrylate]/LiClO\textsubscript{4} hybrid thin film is prepared and sandwiched between WO\textsubscript{3} and PB coated ITO glass electrodes in a dry argon atmosphere. The increase of the applied voltage from 1 to 3 V results in the increase of an optical density change between coloring and bleaching processes for this ECD. This optical density change is about 50% larger than that for WO\textsubscript{3} based ECD. The charge can be injected 3 times larger than that for WO\textsubscript{3} based ECD. The optical density at 800 nm for this ECD is proportional to the injected charges. Namely, effective charge conversion is carried out with PB film as counter electrode because no charge-up effect is found by the reverse reaction of counter electrode against working electrode. Cycling of coloring and bleaching is carried out for more than several hundred times without any decay in the activity and efficiency.

B-6 Electrochromism of Electropolymerized Film (I)

Electropolymerization of Phenanthroline Derivatives and Electrochromism of The Prepared Film

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Amino phenanthroline is illuminated as the monomer of electropolymerization, and its electropolymerizability and characteristics of obtained film are evaluated. For 5-amino phenanthroline, polymer is not obtained as a film on an electrode. Tris(5-amino phenanthroline)Ruthenium(II) complex is prepared in order to change electronic structure of 5-amino phenanthroline and to facilitate electropolymerization. Electroactive thin film is obtained on a Pt electrode with the electropolymerization of this complex in LiClO\textsubscript{4}(0.1 M)/acetonitrile solution. This film shows electrochromic characteristics, which have the color change between yellow and colorless. This electrochromic behavior is revealed to be due to the redox of central ruthenium ion.

B-7 Electrochromic Display (IX)

Electrochromism and Electronic Structure of Benzoxazole Derivatives

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Electrochromism of benzoxazole derivatives is discussed with their electronic structure calculated from the omega-technique as a simple LCAO-MO theory. In benzoxazole derivatives, calculated total π-electron energy is revealed to be correlated with the experimental value about electronic state, which is obtained by the redox potential and absorption spectra. Namely, the reversible half-wave potential of these derivatives is evaluated from the difference in total π-electron energy between the neutral state and the anionic state. Furthermore, the energy for π-absorption band spectra of these derivatives is evaluated from the difference in total π-electron energy between the catonic state and the anionic state. Consequently, in the electrochromism of benzoxazole derivatives, the energy for absorption of color species is revealed to be
estimated from value of total pi-electronic energy of anion.

B-8 Properties of RbX : T1 (X=Cl, Br, I) Photo-stimulable Phosphors

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We are developing an X-ray image capturing unit, the Konica Direct Digitizer (KDD), which uses an X-ray detector composed of RbBr : T1 photostimulable phosphor.

We are making efforts to increase the sensitivity, shorten the operating period and improve the image quality.

We have found that the subjects could be considerably resolved by several methods as follows: 1) Adopting RbI : T1 in exchange for RbBr : T1. 2) Increasing the output power of laser diode. 3) Producing the X-ray detector by evaporation.

B-9 Valence Control in Epitaxial Si Thin Film Grown at Low Temperature by HR (Hydrogen Radical Enhanced)-CVD

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Crystalline Si films formed on conventional glass substrates are promising as semiconductor films for thin film transistor (TFT) of large-area display devices. A new preparation method termed HR (Hydrogen Radical enhanced)-CVD had been proposed to make crystalline Si thin film at low substrate temperature.

In this report, an attempt has been made to prepare crystalline Si thin films grown epitaxially on (110)Si substrate at low temperature by HR-CVD. In addition, influences of foreign elements for valence control have been studied in respect of the growth of Si networks.

B-10 Epitaxial Growth of ZnSe at Low Substrate Temperature by HR-CVD

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Extensive efforts have been devoted for developing preparation techniques of II-VI compound semiconductors, i.e., ZnSe, ZnS and others, at low substrate temperature for the purpose of the valence control by mixing foreign elements, which is essential for application to electric devices.

We proposed a novel technique termed “HR-CVD” (Hydrogen Radical Enhanced CVD) and made successfully ZnSe with high quality at about 200°C by this technique.

A systematic study has been carried out for the purpose of understanding the chemical reactions in the growth of ZnSe epitaxially at such low temperature. Additionally, preliminary attempts were made for the valence control by adding PH3 as a doping material to make a “P-type ZnSe” films on GaAs substrate.

B-11 Functional Pattern Formation in Photosensitive TiO2 Colloid Layer

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A new imaging process was proposed which was able to form functional patterns with photosensitive TiO2 colloid whose surface was modified with unsaturated polyester chains. In the exposed area, TiO2 colloids were deactivated by being covered with polymerization products of modifiers. While the photoactivity was unchanged in the unexposed area of TiO2 colloid layer. We have found that the polymerization process of modifiers on the TiO2 colloid was accelerated by a heat treatment, which followed the UV irradiation. In order to emphasize this effect, we synthesized a TiO2 colloid whose surface was modified by unsaturated polyester chains that were terminated with a nonreactive saturated polyester part. These grafted chains improved the photoinitiated polymerization efficiency. It was found that the polymerization of modifiers was amplified by a heat treatment below 100°C, following the UV irradiation. No polymerization products were formed by the heat treatment in the unexposed area of TiO2 colloid layer.

B-13 Electroluminescence at SiC in Aqueous Electrolyte Containing Persulfate Ions

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Electroluminescence (EL) as n- and p-types of SiC (crystals) electrodes was studied in aqueous solution containing redox species. For species generating strongly oxidizing intermediates, such as peroxysulfate bright luminescence was observed during cathodic polarization. n-SiC shows greenish-yellow emission and the peak occurs at 565 nm indicating the role of dopants or impurities in the recombination process. The luminescence of p-SiC shows emission in the violet-blue region with a peak at 415 nm showing band transition and also giving evidence for the formation of inversion layer. EL rise time at n-SiC has also been studied using a pulsed potential technique.

B-14 Synthesis and Its Ionic Conductivity for New Polymeric Solid Electrolyte with Variable Ionic Conductivity by Light Irradiation

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Polymer containing anthryl group is newly prepared at the matrix of polymeric solid electrolyte. Anthracene is well-known to show reversible dimerization by light and heat treatment. The polymeric solid electrolyte composed of this polymer and LiClO₄ shows the conductivity of about 10⁻⁶ S/cm under dark. This conductivity gradually decreases with light irradiation (500 W, Xe Lamp). This is revealed to be due to light-induced dimerization of anthryl group covalently onto polymer. This dimer is also revealed to show reverse reaction to the monomeric state by heat treatment. The ion conduction behavior of this polymeric solid electrolyte is discussed with photochemical reaction of anthryl group and segmental motion of polymer.

B-15 Properties of Photovoltaic Devices Using Semiconducting Polymers

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stacking mode of molecules in the crystals are understood as dipole interaction.

B-17 Fluorescence Photochemical Behavior of Phenylpyrroloanthrone Derivatives

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Phenylpyrroloanthrone derivatives were synthesized by a novel reaction of 1-aminoanthraquinones with benzyl chloride in the presence of KOH in dimethylsulfoxide, followed by a treatment with AlCl₃. The pyrroloanthrone derivatives are highly fluorescent with quantum yield of fluorescence to be 0.3-0.65. Radiative and non-radiative rate constants of the excited pyrroloanthrones were estimated from fluorescence lifetime measurements. The former rate constant was revealed to be nearly the same in each solvent of ethanol, acetonitrile, and benzene, while the latter in benzene was ten times as large as that in ethanol, indicating a close proximity between \( n\pi^* \) and \( \pi\pi^* \) levels. Pyrroloanthrones were stable enough even on prolonged light irradiations to the 1st absorption band (\( \lambda = 420 \) nm) and the 2nd one (\( \lambda = 365 \) nm), while irradiation to the 3rd absorption band (\( \lambda = 313 \) nm) induced fading of the compounds to produce 1-benzoylaminoanthraquinone. Reaction mechanism of the production of 1-benzoylaminoanthraquinone involving singlet oxygen formation via an intersystem crossing from the upper excited singlet state of pyrroloanthrones was proposed.

B-18 Photo-Controlled Injection of Charge Carriers at Polyaniline/Polyvinylcarbazole Interface

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Photo-induced injection of charge carriers from polyaniline into polyvinylcarbazole was found to occur by light absorbed by polyaniline electrochemically prepared from a neutral aqueous solution of aniline and lithium perchlorate.

Electrophotographic mode measurements were performed on samples consisting of a multilayer of the structure: ITO/polyaniline (7000 A)/polyvinylcarbazole (10 microns). The photosensitivity was two orders of magnitude higher compared to samples consisting of polypyrrole/polyvinylcarbazole. The sensitivity was found to be higher in positively charged cases than negatively charged cases. The influence of substituted groups at \( p \)-position of aniline was examined. A polymer derived from \( p \)-fluoroaniline gave the best result. The illumination memory was observed, that indicates a long life of the photomodified state.

B-19 Photo-rechargable Solid State Secondary Battery

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We have made "Photo-rechargable Secondary Battery". This battery has a capability of self-charging under sun or fluorescence illumination, converting photo energy with a high efficiency. This system is made of all solid state materials, so it is expected to have no photo-corrosion problem on energy conversion. Photo-charge and discharge characteristics are discussed.

B-20 The Photochemical Behavior of Azobenzene Derivative in Langmuir-Blodgett Film

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A spectroscopic and photoelectrochemical behavior of 4-octyl-4'-(5-carboxypentamethyleneoxy) azobenzene in Langmuir-Blodgett film was studied. The LB film on a quartz substrate showed a reversible behavior in absorption spectra when irradiated with UV and visible light in turn. This was observed after a gradual red-shift of the 318 nm band to 338 nm upon preceding UV irradiation. Cyclic voltammetry of the LB film modified SnO₂ electrode in contrast to a bare SnO₂ electrode gave an UV light responsible oxidation wave at 0.13 V vs. Ag/AgCl when the electrode biased at \(-0.2 \) V was irradiated with UV light. This characteristic phe-
nomenon is now under investigation in connection with the isomerisation of the present azobenzene derivative LB film.

B-21 Optimization of Single-Layered STN-LCD for High Contrast and Black-White Image
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For a super-twisted nematic liquid crystal display (STN-LCD) which is able to display a large content of information with a high contrast and wide range of viewing, it is necessary to get a black-white image in order to realize a full-color display. By means of a simulation of transmission spectrum and an experimental optimization of each parameter, we investigated a cause of coloration and its relation with contrast in a single-layered STN-LCD. As a result, we found that the extent of coloration is strongly dependent on the value of \( \eta \) and non-chromatic characteristics trades off with contrast ratio, and that by optimizing parameters we can realize a STN-LCD with a contrast ratio more than 100:1 under the driving condition of 1/200 duty multiplexing.

B-22 Control Factors of 3 Dimensional Si Network Propagation by HR-CVD
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A New method of preparation in Si films, in terms of HR-CVD (hydrogen radical enhanced CVD), is proposed. The network structure in Si films can be controlled intentionally by introduction of atomic hydrogens.

In this study, the roles of atomic hydrogens were systematically investigated in respect of propagation of Si networks.

B-23 Influences of Carbon and Germanium Atoms on Chemical Reactions in Propagation of Si Network
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Tokyo Institute of Technology

Influences of carbon and germanium atoms on chemical reactions in propagation of Si networks have been systematically investigated under controlling atomic hydrogens by a novel preparation technique termed Hydrogen Radical Enhanced CVD. Propagation of three-dimension network was greatly promoted when GeF was introduced for making SiGex alloy.

Whereas, network formation was obviously prohibited by addition of Carbon-related radicals due to their strong chemical interactions with Si-precursors in gas phase, leaving structural defects in the SiCx films.

By reducing between carbon radicals and Si-precursors in gas phase, the qualities of a-SiCx were greatly improved, films of less defects in silicon net-work and relatively high photo conductivity.

More over, the deposition was carried out at a considerably high rate.

B-24 Enhancement of Photosensitivity in Near-Infrared Region with a-Si Based Materials
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a-Si:H(F)/a-SiGex:H(F) stacked multilayers have been prepared by Hydrogen Radical enhanced Chemical Vapour Deposition (HR-CVD), in an attempt to design a material with high photoconductivity in the near-ir region. We set up the repeated distance and the ratio in thickness of the well layer to the barrier layer as parameters. The effect of space charges on carrier-transport was investigated by the steady state and transient photocurrent measurements.

B-25 Effect of Cu-Pc Layers Composition to Photovoltage
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Effect of binder resin and metal base to spectral
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B-26 Photosensitivity and Thermal Behavior of Vinylbenzylxoy-acetophenone Polymer and its Copolymers

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Photosensitive polymers with pendant acetophenone groups were prepared by the radical polymerization of 4-(4-Vinylbenzylxoy)acetophenone(4-(4-VBz)Ap), or 4-(3-Vinylbenzylxoy)acetophenone (4-(3-VBz)Ap).

P(4-(4-VBz)Ap, P(4-(3-VBz)Ap and its copolymers were crosslinked by the irradiation of UV-light in the film state.

These polymers were spectrally sensitized by Michler’s ketone and some kined of quinone compounds.

The P(4-(4-VBz)Ap was observed high resolution and high resolution and high thermal stability and can be utilized as a thermal stability nega-type photoresist.

B-27 Electrochemical and Spectroscopic Behavior of Dyes Incorporated into Electroconductive Polymers

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In order to improve the function of the organic conducting polymers, suitable dyes were incorporated into them by electropolymerization. The system were characterized by means of electrochemical and spectroscopic techniques and they appeared to show satisfactory electrochemical characteristics. The change in optical density of the dye/organic conducting polymer system was 1.5 times larger than that of a system consisting of only organic conducting polymer, and the color changed more clearly. This result comes from the fact that the dyes selected here have large absorption coefficients and change their color by redox reactions.

B-28 Mechanism of Lates Ablation of Deposited Dyestuff Film

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A high speed and definition optical recording medium, which is deposited thin dyestuff film, for the heat-mode laser disc is studied. Its recording mechanism is based on the exothermic reaction of dyestuff and the thermal analysis of recording medium on laser irradiation was simulated. After the exposure there was induction period and the thermal degradation appeared at low irradiation energy. The effective reaction shows the high sensitivity compared with no exothermic reaction.

Degradation products by laser irradiation did not coincide with the products of pyrolysis or photolysis. The actual reactions on laser recording were not only exothermic decomposition but also some side reactions. As the result of the simulating thermal analysis, it is important to depress the side reactions for the further improvement of the sensitivity.

B-29 Control of Photofadog of Azo Dyet by Addition of Metallic Salts

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Azo dyes formed by coupling of p-substituted benzene diazonium salts with 1-naphthol-4-sulfonic acid are used for diazo copying procepts or thermal recording process. The photofading of the azo dye...
is controlled by addition of metallic salt. It was detected that metal ion combined with N=N combination and hydroxy group of azo dye [2-(p-substituted phenylazo)-1-naphthol-4-sulfonic acid (DBD-NW)] by I.R. spectrum. The remaining molecules of DBD-NW solution after photodecomposition were calculated by the measurement of absorbance of absorption maximum (523 nm) of DBD-NW. About 10% of photofading was controlled by addition of ZnCl₂. The photofading of DBD-NW-Zn was more controlled than DBD-NW-Mg.

B-30 Dissociation Equilibrium of Dimers of an Anionic Oxacarbocyanine Dye

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Dissociation constants and heat of dissociation of dimeric aggregates of an anionic oxacarbocyanine dye, potassium 3,3′-di-(3-sulfopropyl)-5,5′-diphenyl-9-ethyloxacarbocyanine, in aqueous ethanol solutions have been determined from the monomer band absorbance of the dye measured at different temperatures and dye concentrations at which the monomer is the major solute species and disturbances of monomer absorbance measurements by aggregated species is fairly small. In 10% ethanol, the dissociation constant was $2 \times 10^{-5}$ mol/dm³ (20°C) $\sim 7 \times 10^{-5}$ mol/dm³ (40°C) and the heat of dissociation was about 10 kcal/mol (42 kJ/mol), suggesting a higher dimer stability of this dye than that of typical cationic thiacarbocyanines.


Yoshiro Yonezawa, Kazuhiro Wataya and Hiroshi Hada

Dye monolayers composed of xanthene dyes or coumarin dyes with long alkyl chains and charged matrix molecules were prepared at the air-water interface and transferred onto the solid substrate (SiO₂, SnO₂) by the Langmuir-Blodgett technique. Absorption spectra of 5-(N-octadecanoylamino) fluorescein (OFL) monolayer consisted of monomer bands of acidic and basic forms of the dye, as well as the polymer band accordingly to the kind of matrix molecules and pH of the subphase. A comparison of absorption spectra of dye monolayer at the air-water interface with those of LB films revealed that positively and negatively charged matrix has a profound effect on the acid-base equilibrium of dye molecules at the lipid-water interface.

B-32 Observing Behavior of Interfacial Dyes by Means of Optical Waveguides

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Optical waveguides (OWG) were applied to studying behavior of interfacial dyes. Large electric field exists at the surface of OWG’s because light is confined to a thin surface film (a few microns in thickness). This causes large optical absorption due to surface species. Results are as follows. 1. Adsorption of methylneblue (MB) was monitored on a glass OWG; resultant optical density was 100-150 times larger than that in usual absorption measurements. 2. Electrochemical reduction and reoxidation of MB were observed on OWG electrodes (glass OWG coated with conductive SnO₂) with a high sensitivity. 3. Photoinduced reduction of MB was monitored at glass OWG/TiO₂ powder systems.