



Title	Abstrcts & Titles, No.58-No.61
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 13(2), 157-187
Issue Date	1972-03
Doc URL	<a href="http://hdl.handle.net/2115/37883">http://hdl.handle.net/2115/37883</a>
Type	bulletin (other)
File Information	13(2)_157-188.pdf



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## Appendix

Abstracts & Titles, No. 58—No. 61

BULLETIN  
OF THE  
FACULTY OF ENGINEERING  
HOKKAIDO UNIVERSITY

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## Studies on Traffic Characteristics at Intersection

Chuzo ITAKURA    Shinji OGASAWARA  
Terutoshi KAKA    Shinzo KON  
Seiichi HORIE

### Abstract

Intersections are very important areas for traffic operations in urban streets. But it is difficult to observe traffic characteristics and vehicular behaviour, only a few reports concerning the traffic flow in winter can be found.

Thus the present authors made an attempt to observe traffic characteristics at the intersections in Sapporo under summer and winter conditions.

The intersection traffic characteristics based on observed data obtained at certain main intersections in Sapporo were deduced and a comparison was run between the traffic characteristics in summer and winter.

The possible traffic capacity in green time, the degree of acceleration and deceleration, the vehicular speed, the headway, the right-turn maneuver and the difference between the traffic characteristics in summer and winter condition were discussed.

## Effects of Niobium on the Grain Size of 0.15% and 1.4% Carbon Cast Steels

Fujitaka KAWANO    Yukio TOMISAWA  
Mitsunori FUNAZAKI    Kaichi MATSUBARA

### Abstract

Niobium (up to 0.6%) as a possible cast-grain-refiner and/or a modifier of austenitic graincoarsening, was added to steels containing 0.15% and 1.4% carbon, respectively.

Both additions of 0.14% niobium to 0.15% carbon steel and of 0.13% niobium to 1.4% carbon steel, proved to be an effective cast-grain-refiner. But in the later, brittle eutecticniobium-carbides were precipitated at the cast grain boundaries by an addition of 0.07% niobium or over as mentioned in the previous paper with eutectoid steel. This brittleness may be relieved by shortening of proeutectoid cementite in the hypereutectoid steel with an addition of niobium.

Niobium was a more powerful modifier of austenitic grain-coarsening for 0.15% carbon steel than aluminum, but no further effect of additions above 0.14% niobium was seen on the austenitic grain-coarsening.

Because of the lowering of solidus temperature of 1.4% carbon steel by additions of niobium, the grain-coarsening temperature of the niobium steel decreased markedly.

## Characteristics of an Eccentrically-Pivoted Small Butterfly Valve

Hisataka TAMURA

Mikio ARIE

### Abstract

It is well known that a butterfly valve in flow is usually subjected to a moment in the direction to be closed. In some applications such as the aortic valve, the unbalance moment must be as small as possible in order to ensure its smooth operations. An eccentrically-pivoted butterfly valve is expected to give a smaller unbalance moment than an ordinary one. In this respect, an experimental study of an eccentrically-pivoted butterfly valve was performed to measure the unbalance moment and loss of head introduced by the valve. The results for the case of four eccentricities 0, 10, 20 and 30% are reported in this paper. It was found from the experiment that the unbalance moment is reduced by a considerable amount in the case of the eccentrically-pivoted butterfly valve as compared to a conventional butterfly valve. It was also found that the loss of head showed the same tendency.

## A Study on the Evaluation of the Performance of a Heat and Power Generating Plant

Takashi SONODA

Takeshi SAITO

### Abstract

An analysis of the performance of a heat and power generating plant was considered in order to determine the qualitative difference of two types of energy generated by the plant, namely, heat and power, based on the 2nd law of thermodynamics, as compared against the methods investigated previously. An application of the concept of exergy, i. e. the maximum effective work of energy was presented.

The heat and power generating plant dealt with in this paper was a combined plant consisting of a gas turbine with an exhaust heat recovery boiler. The gas turbine cycle was 'simple open' or 'regenerative open' and the exhaust heat recovery boiler generated hot water.

The influence of the main parameters of the plant under optimum design conditions of the gas turbine was described. The factors considered here were ambient temperature, inlet gas temperature of the gas turbine exhaust gas temperature of exhaust heat recovery boiler, and effectiveness of gas turbine regenerator etc.

## Study on Thermodynamical External Work (1st Report)

—The Influence of External Heat Exchange  
and Internal Heat Generation from Friction—

Hiroshi TANIGUCHI  
Kazunori WAKAI

### Abstract

In a study of the thermodynamical performance of a heat engine, the calculation of the external work is of considerable importance. Generally, this calculation of external work is done by considering the external heat exchange or the internal heat generation arising from friction. In small type heat engines or large type gas turbines with internal cooling systems, in which a considerable amount of external heat exchange and internal friction exists, the above-mentioned factors should be considered at the same time.

In this paper, the authors have dealt with external heat exchange and internal heat generation from friction separately to study their respective influences on the external work. For the purpose mentioned above, a non-dimensional factor  $x$  is introduced to express the external heat exchange and also, in the case of a steady-flow process and a non-flow process, the relations among the external work, the external heat exchange and the internal heat generation from friction was analyzed by utilization of an ideal gas as a working medium.

## Nonlinear Phenomena of a Vibro-Impact System

Ken-ichi FUKAYA  
Toshihiro IRIE

### Abstract

The impact vibration arising when a mass collides with a rigid wall under the action of an exciting force has been studied in recent years. However, subharmonic and superharmonic impact vibrations appearing in such mechanical systems have not been dealt with sufficiently.

In this paper, a theoretical study on nonlinear phenomena of these vibro-impact systems was made and the conditions for maintaining a stable periodic vibration were obtained. From the results of the numerical calculation, it was found that the superharmonic impact vibration arises only in systems with small clearances, while the subharmonic vibration appears when the clearance and excitation frequency become large, and that some types of impact vibrations exist together in a narrow domain of system parameters.

## On the Effectiveness of Regenerative Heat Exchangers

—The Effect of Thickness of Heat Storage Materials—

Nobuhiro SEKI

Hiroyuki KŌNO

### Abstract

In general, heat storage materials of regenerative heat exchangers are moderately thick when applied in industry furnaces. Therefore, it seems necessary to take the transversal temperature variations in materials into account to predict the effectiveness of these heat exchangers. In this report an attempt was made to show an extended analysis by including the effect of such variations. It was further shown that the analytical results agree fairly well with the experimental results.

From the above it may be concluded that the transversal temperature variations in materials should be taken into account to estimate the effectiveness of these heat exchangers composed of thick materials.

## Azimuthal-Current-Prebunching Effects on Electron-Wave Interactions

Ichiro SAKURABA

Takeo SUZUKI

### Abstract

In the case where  $b=0$ ,  $d=0$ ,  $Q=0$ ,  $\beta_e \approx 20$  and  $C \approx 0.05$  and the azimuthal current variation was applied at the input, the expressions for the small-signal forward-wave output and the equivalent resistance were given. The power output is due to growing- and decreasing-waves and the effect of characteristic ripple is negligible.

## Bildung von Piperidon-derivaten durch Isomerisierung der Monocyanäthylketonen

Itiki MURASE  
Yoshiyuki TAKATA

### Zusammenfassung

In Gegenwart von Cyclohexylamin und Essigsäure lässt man Acrylnitril auf Cyclohexanon einwirken, so bildet sich zusammen mit Monocyanäthylcyclohexanon [I] der Krystalle [II], dessen Fusionspunkt 145°C ist. Wir haben festgestellt, dass [II] Octahydro-2-oxo-chinolin ist. Ueber die Isomerisierung von [I] nach [II], haben wir versucht die katalytische Wirkung von Gemische aus Amin und Carbonsäure. Erhitzt man [I] um 180°C in Gegenwart von primärem oder sekundärem Amin und Essigsäure, so entsteht [II] mit guter Ausbeute.

Konzentrierte Schwefelsäure und Phosphorsäure ebenfalls haben die katalytische Wirkung in Isomerisierung von [I] nach [II].

Monocyanäthylierungketonen aus Cyclopentanon, Cycloheptanon, Aceton, Methyläthyketon und Acetessigsäureäthylester bilden durch die oben erwähnten Katalysator die entsprechenden Piperidon-derivaten.

## Monocyanäthylierungsreaktion der Ketone in Gegenwart von Katalysator des Gemisches von primärem Amin und Kabonsäure (I)

—Monocyanäthylierungsreaktion des Cyclohexanons—

Yoshiji NISHIMURA    Tadao YATU  
Itiki MURASE        Yoshiyuki TAKATA

### Zusammenfassung

Es wurd unter Verwendung des Cyclohexanons als Keton, die katalytische Einwirkung des Gemisches von Amin und Karbonsäure auf eine Erzeugungsreaktion des Monocyanäthylketon aus Keton und Acrylnitril untersucht.

Monocyanäthylcyclohexanon entsteht bei der Umsetzung von Cyclohexanon mit Acrylnitril in Gegenwart des Gemisches von primärer Amin und Karbonsäure in höherer Ausbeute.

In Amine als Katalysator sind aliphatische primäre Amine wirkungsvoll, während aromatische primäre Amine, aliphatische und aromatische sebundäre Amine und tertiäre Amine keine katalytische Wirkung zeigen.

Primäre Amine selbst zeigen die schwache katalytische Einwirkung, während sie durch den Zusatz von Karbonsäure die stärkere katalytische Wirkung darstellen.

Gegenwart von Wasser oder Alkohol verhindert die Monocyanäthylierungsreaktion.

**Monocyanäthylierungsreaktion der Ketone in Gegenwart von  
Katalysator des Gemisches von primären Amin  
und Karbonsäure. II.**

Yoshiji NISHIMUR    Tadao YATU  
Ichiki MURASE      Yoshiyuki TAKATA

**Zusammenfassung**

Es wurde Cyanäthylierungsreaktion von Ketonen mit Acrylnitril in Gegenwart von Mischkatalysator [I], der bestand aus einem Gemisch von Cyclohexylamin und Eisessig, untersucht.

Aus Cyclopentanon, Cycloheptanon, Aceton, Methyläthylketon, Methylisobutylketon und Acetophenon entstand Monocyanäthylketone allein. Aber die Ausbeute an Monocyanäthylketonen waren weniger als Monocyanäthylcyclohexanon.

Aus Acetessigsäureäthylester und Acrylnitril in Gegenwart von Mischkatalysator [I] entstand Monocyanäthylverbindung nicht.

**Reaction of Carboxylic Acid Hydrazides with Acids (I)  
Formation of N, N'-Diacylhydrazine by the Reaction of  
Aliphatic Acid Hydrazide in Aqueous Inorganic Acids**

Toshiro TIBA  
Hiroyuki OHMORI  
Yoshiyuki TAKATA

**Abstract**

Capric acid hydrazide [I] was heated in an aqueous solution of strong acid such as sulfamic acid, hydrazinium sulfate, ammonium bisulfate, sulfuric acid, hydrochloric acid, potassium bisulfate and phosphoric acid to give N, N'-didecanoylhydrazine [II] in high yields.

In the case of sulfamic acid, the yield of [II] was maximal when the molar ratio of acid to [I] was 0.3. The yield of [II] with other acids were nearly the same when the molar ratio of the acid to [I] was 1-0.5, or maximal at the ratio of 0.5. It was assumed that one mole of [II] is formed by the reaction of two moles of carboxylic acid hydrazide with one equivalent of strong acid. [II] was also obtained, though in a low yield, by heating [I] with aqueous potassium dihydrogen phosphate, ammonium chloride or ammonium sulfate.

## NOTICE

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## **Angular Selectivity and Acoustic Sensitivity in Optical Heterodyne Ultrasonic Image Converters**

Ichiro SAKURABA

### **Abstract**

In the optical heterodyne system for acoustic image detection proposed by Massey, the effects of angular selectivity on the measurable acoustic intensity are discussed.

Results of the analysis show that the measurable acoustic density is strongly affected by the angle of wavefronts between the local-oscillator beam and the reflected signal beam frequency-modulated by sound waves and if the optical devices are in good alignment for all positions of scanning the signal beam, the optical heterodyne method has a minimum measurable acoustic density comparable to that obtained using the best of practical alternating methods now available.

## **The Distribution of Effective Quantum Efficiency and Directional Characteristics in Optical Heterodyne Detection**

Kojiro KOYANAGI

Akira ABE

Ichiro SAKURABA

### **Abstract**

The effect of the distribution of effective quantum efficiency on directional characteristics in optical heterodyne detection of uniform plane waves was presented.

When the optical wavelengths, the optical input, and the maximum values of effective quantum efficiency are kept constant in the case where the effective quantum efficiencies are uniform, triangular, trapezoidal and Gaussian in distribution, the less angular selectivity, the lower the detection power of precisely parallel and normal incident beams. This is closely related to Siegman's antenna theorem of optical heterodyne detection.

## **Some Considerations on Energy Density Mobile Radio Antenna**

Michio KASHIWAGI

Kiyohiko ITOH

Tadashi MATSUMOTO

### **Abstract**

This paper deals with an analysis of the fading phenomenon in a mobile radio field by using a reflector model and a simple statistical model and a new type of energy

density radio antenna which is helpful in overcoming this fading.

The energy density antenna is an antenna which samples the energy density, that is,  $1/2(\epsilon|E|^2 + \mu|H|^2)$  of a mobile radio field, rather than the electric field only. J. R. Pierce proposed the energy density antenna systems which samples  $E$  field by a monopole antenna and  $H$  field by a loop antenna. This paper proposes a new type of energy density antenna system which samples  $H$  field by a slot antenna or a magnetic current antenna and  $E$  field by a conductor antenna or an electric current antenna.

When only one component of the  $H$  field is to be received in the statistical model, the component which is perpendicular to the direction of motion should be chosen, that is, when the slot antenna is set normal to the motion.

### Shallow-Cavity-Backed Slot Antenna for Energy Density Antenna

Michio KASHIWAGI  
Kiyohiko ITOH  
Tadashi MATSUMOTO

#### Abstract

In order to reduce the effect of signal fading of a mobile radio field the authors proposed a different type of energy density antenna proposed by Pierce. This antenna receives the  $E$  field with a unipole antenna and the  $H$  field with a slot antenna instead of a loop antenna.

In this report a slot antenna backed by a rectangular cavity was devised in such a way as to be made smaller inasmuch as the shallow-cavity-backed slot antenna is favorable for a paste-on or fluso-mounted-type receiver to be mounted on a mobile vehicle.

The experimental results of the input impedance characteristics of the above mentioned slot antennas are also described.

### Development of Transistor Logic Circuit Configurations

Teiichi KUROBE

#### Abstract

Generally configurations of transistor logic circuits are developed empirically. The author has attempted in this paper to establish order systematically in the usual circuits and as a result arrived at a new method to arrange or otherwise systematize the various circuits.

Logic circuits are divided into six classes which are grounded-emitter gates, grounded-collector gates, grounded-base gates, unsaturated circuits, speed-up circuits and large noise margin circuits.

## Additivity of Delay Time and Rise Time in Multistage Transistor Circuits

Teiichi KUROBE  
Krzuhiko AZUMI

### Abstract

The delay time and the rise time for a step input in multistage circuits which isolate each stage satisfy the additivity. However, since transistors are bilateral, it seems that the additivity does not hold good in multistage transistor circuits. The authors have obtained results by calculating the numerical examples of various circuits consisting of two stages in which the additivity holds good when the after stage is a common emitter configuration or a common collector configuration and does not hold good when the after stage is a common base configuration.

## Frequency Response of the Transport Factor in Double-diffused Transistors

—In Consideration of Variable Mobility—

Yoshihiko OGAWA

### Abstract

The excess minority-carrier distribution in the base region and the frequency response of the transport factor in double-diffused transistors are calculated in consideration to the fact that the mobility is dependent of the density of impurity in the base region. As a result, it is shown that the denominator of the transport factor can be expanded in a series of the frequency and the terms higher than the fourth order of the series can be approximately omitted. The phase characteristics shows an excess shift which is nearly forty-five degrees. If an effective mobility, which is constant, is used approximately instead of the variable mobility, the amplitude characteristics in this case is almost consistent with the above result, but on the phase characteristics it makes a difference between both results.

## On Hybrid Trees

Masakazu SENGOKU  
 Yoshihiko OGAWA  
 Teiichi KUROBE

### Abstract

In this paper *hybrid trees* in a linear graph which consists of two kinds of edges are defined and some of their properties are presented.

The properties are represented by set-theoretical binary operations (e. g.  $\cup$ ,  $\cap$ ,  $\oplus$ ,  $-$ ,  $\frac{\partial}{\partial e}$ , and  $\int de$ ). And a method of *hybrid tree* generation is also given by using the above. These results are available for topological analysis and synthesis of active networks.

## A FORTRAN Program for English-Japanese Translation

Tadayuki NAKAMURA    Nobuo MORI  
 Mitsuru SUDO         Koji TOCHINAI  
 Yoshimasa NAKAMARU

### Abstract

In this report we describe an experimental computer program written in FORTRAN language for the translation of English into Japanese.

The program of the "unpack" operation which divides the contents of one word into words, or the "pack" operation which gathers the contents of some words into one word, can not be written directly in FORTRAN. Accordingly, we developed programs executing such operations by the use of exponentiation and have completed the program with FORTRA.

We also compared the execution time and the length of the program written in FORTRAN only, with those of the program using machine language for the unpack or pack operation, and we may conclude that the former is more practical.

The method of syntactic analysis used here, is based on the immediate constituent theory, and in this experimental program we used 160 English words. 190 Japanese equivalents, and about 120 gramatical patterns. There are 1090 computer words used in this whole program, and it seems to be but a small number considering the complexity of processing.

## A Method of Discrimination between Japanese Vowels Based on Spectral Analysis

Seiichi IDO      Katsuo SAIKAWA  
Koji TOCHINAI   Yoshimasa NAKAMARU

### Abstract

In this paper we deal with a method of discrimination between Japanese vowels pronounced separately by means of spectral distributions. It is said that it is necessary to process a large amount of data for the recognition of vowels by means of spectral distribution, but the amount of data processed are so large that it is impossible to execute real-time operations. According to decrease processing data, we have attempted a method of discrimination using about ten maximum values of time-varying amplitudes of the outputs from each band pass filter. We could determine any type of Japanese vowels in this manner, with the aid of a digital computer in a very short time.

In this experiment we used average values of Vowels pronounced separately by several speakers as reference patterns, and recognized an input vowel by comparing its pattern against these references.

The results obtained in this study are as follows.

1. Vowels could be discriminated from others sufficiently by this method.
2. There is a correlation between the results of this experiment and Kullback's divergence.
3. It seems to be suitable to introduce this method in processing on real time.

## A Study on Uniaxial Magnetic Anisotropy in Nickel-Iron and Nickel-Iron-Phosphorus Thin Films Electrodeposited on Scratched Surfaces

Kôichi MUKASA  
Masayoshi SATÔ  
Masao MAEDA

### Abstract

The uniaxial magnetic anisotropy constant,  $K_u$ , of nickel-iron thin films electrodeposited on surfaces scratched in one direction was measured. A simple model is proposed to explain the observed anisotropy, and it is found in this work that  $K_u$  is composed of the shape anisotropy and magnetostrictive anisotropy.

A study on the effect of average internal stress,  $\sigma$ , on uniaxial magnetic anisotropy was made and the effect of  $\sigma$  on  $K_u$  is found to be well explained by the proposed model. In the composition range of thin films in which the shape anisotropy plays a significant role, it is found that  $K_u$  is eliminated by intermediate copper or thin gold layers between films and deposition substrates, since the depth of the scratches on the substrate will be eliminated by these intermediate thin layers. In the study of correlation between

the profile of surface scratches and  $K_u$  a more good agreement of the measured values of  $K_u$  with those calculated from the demagnetizing field of thin films was obtained in the case of rougher scratches than finer scratches. The effect of hypophosphite ions in the plating bath on  $K_u$  was also investigated. It is observed that the presence of hypophosphite ion results in a decrease of  $K_u$ . This decrease of  $K_u$  was explained by considering the decrease of saturation magnetization of nickel-iron-phosphorus thin films.

### Studies on the Deterioration of Integrated Circuits

Masao MAEDA  
Tutomu TSUJI  
Nobutake KONISHI

#### Abstract

An investigation on the chemical reaction occurring at the contact interface between  $\text{SiO}_2$  and metal-electrode were carried out. Aluminum, tantalum, and titanium have a strong affinity with oxygen as compared with silicon and it is expected that oxidation of metals and reduction of  $\text{SiO}_2$  occurs at the contact interface. In the present experiment, aluminum, tantalum, titanium and nickel were used as the metal-electrodes.

It is found that oxidation of metals and reduction of  $\text{SiO}_2$  at the contact surface between  $\text{SiO}_2$  and metal-electrode occur in similar fashion with anodic oxidation. Processes of oxidizing reaction were found to depend on the affinity of metals with oxygen and good ohmic characteristics were obtained at the interface where  $\text{Al}_2\text{O}_3$  was formed.

After the heat treatment of samples for 30 min at  $542\sim 555^\circ\text{C}$  in argon atmosphere, it was observed that metal oxide grew dendritically and there were hillocks on the aluminum film. The Growth of hillocks seems to be related to the dendrite growth. It was observed by X-ray microanalyser that elemental Si was produced on  $\text{SiO}_2$ .

### The Measurement of Plasma Parameters with a Fabry-Perot Resonator

Takeaki ENOTO  
Michio SUZUKI

#### Abstract

The input admittance of the Fabry-Perot resonator coupled to a waveguide by means of a grating, in which an anisotropic dielectric sheet or a plasma sheet is inserted, is derived using the network formulation of the electromagnetic field. The reflection coefficient vs. frequency characteristics are calculated for some values of strip widths.

The formula which determines the dielectric constant from the reflector movement necessary to shift the resonant frequency back to its original value is derived. This formula is applicable to the case of a thick dielectric sheet, and this case can not be treated as a quasioptic treatment. The change of the value of  $Q$  due to the dielectric loss is calculated. Lastly, the formula which determines the electron densities of the plasma from the reflector movement is derived.

## Optimum Reflecting Mirrors of the Fabry-Perot Resonator filled with Anisotropic Medium and its Application

Toshiki TANAKA

Michio SUZUKI

### Abstract

The confocal Fabry-Perot resonator is known as a resonator with considerably low diffraction loss. However, in the case where the medium in the resonator is anisotropic, the diffraction loss increases to a large amount, because the path of the extraordinary light is different from that of the ordinary light in the isotropic medium.

In this paper, we consider a confocal Fabry-Perot resonator which is constructed by two counter reflecting mirrors in the anisotropic medium, and have obtained theoretically optimum shapes of the reflecting mirrors which restrain the diffraction loss from increasing. We have also estimated the conversion efficiency of the second harmonic generator for laser light, as one of its applications.

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## Discussions on the Permeability Test for Size Measurement

Yoji NAKAJIMA

Tatsuo TANAKA

### Abstract

The Kozeny-Carman equation derived from Kozeny's permeation model is the basic equation for determining the fineness of powders from the permeability test. This paper deals with some discussions on the validity of Kozeny's model, particularly on the physical meaning of the Kozeny constant,  $K$ , appearing in the basic equation. It was revealed that the constant,  $K$ , originates from many sources and not from a single source, depending upon the packing structure; in other words,  $K$  does not necessarily change even when the packing structure changes. This information may explain the apparent contradiction in which  $K$  is virtually constant regardless of the packing structure when the powder bed is isotropic. Hence Kozeny's model was revealed to be reasonable as a macroscopic model.

As may be inferred from Kozeny's model, the specific surface area based on particle volume is the average surface area of the envelopes which cover particles smoothly divided by the average volume of the envelopes. As a natural consequence of this suggestion, the concept of effective particle density was introduced and experimentally examined. The results indicate that the concept, and hence the suggestion as to the meaning of the specific surface area, are reasonable.

## Theoretical and Experimental Studies on Fluidized Catalytic Reactors

H. KOBAYASHI

T. CHIBA

### Abstract

This paper describes a theoretical and experimental study on gas-solid fluidized beds as a chemical reactor.

A new theoretical model, a generalized two-phase model, was constructed for the estimation of the degree of chemical conversion in a first-order reaction. The parameters, involved in the model were correlated to the bubble characteristics and operational factors such as the activity of catalyst, the height of bed, the velocity of reactant gas, etc., according to the results obtained from the measurements of the bubble behaviour, gas mixing, gas concentration profiles, and chemical reaction rates in the fluidized beds.

Good agreements were obtained between the calculated values from the model and the experimental values obtained by the authors and other workers over a wide range of operational conditions.

## Nature of Catalytically Active Sites on BF<sub>3</sub>-treated Alumina

Mitsuomi ITOH  
Kanjiro MATSUURA  
Akira SUZUKI

### Abstract

An account was given on the surface acidic properties of a series of BF<sub>3</sub>-treated alumina ranging in precalcination temperature from 300° to 1000°C. It was found that alumina dehydrated at around 400–500°C were converted by BF<sub>3</sub> adsorption to solid acids with strong Brønsted sites indicative of the maximum total acidity for each acid strength. Their catalytic activities in carbonium ion-type reactions did not correspond to the n-butylamine acidities as a function of precalcination temperature.

The Lewis acidity of a series of BF<sub>3</sub>-alumina was measured by means of a spectrophotometric study of chemisorbed triphenyl chloride and an ESR study of adsorbed perylene. The influence of the preheating temperature on the Lewis acid composition in total acidity was examined with respect to the reaction activity and selectivity for dehydration of n-butyl alcohol, and isomerization of 1-butene. From a quantitative comparison of the two types of acid sites with the selectivity in the above reactions, it was indicated that the Lewis acidity observed by the former method provided a better coincidence with the reaction profile.

It was concluded that the acid sites on the BF<sub>3</sub>-aluminas differ, depending on the precalcination temperature of alumina. Whereas Brønsted sites exist mainly on the surface of catalyst calcined at relatively low temperatures up to around 600°C, the Lewis acid sites became of important portions in total acidity when preheated above 700°C. The concentration of hydroxyl groups and the Lewis acid sites as aluminum ions partially exposed at a few special sites in the surface were discussed as important factors contributing to the existence of the two different types of acid sites.

## “Photochemical Reactions of $\alpha$ , $\beta$ -Unsaturated Acids and Esters”

Mitsuomi ITOH      Masao TOKUDA  
Masanori HATAYA   Akira SUZUKI

### Abstract

Photochemical reactions of  $\alpha$ ,  $\beta$ -unsaturated acids and esters, including  $\beta$ ,  $\gamma$ -isomerization, the addition reaction of formamide and aniline, and Fries rearrangement, were described.

Irradiation of several  $\alpha$ ,  $\beta$ -unsaturated acids and esters, such as *trans*-crotonic acid, *trans*-methyl crotonate, *trans*-ethyl crotonate, *trans*-ethyl 2-pentenoate, *trans*-ethyl 4-methyl-2-butenate, ethyl tiglate and ethyl 3-methyl-2-butenate, with a 500 watt high pressure mercury vapor lamp gave the corresponding  $\beta$ ,  $\gamma$ -isomers in almost quantitative

yields. On the other hand, irradiation of ethyl 2,3-dimethyl-2-butenate and ethyl  $\alpha$ -methyl cinnamate produced but a small amount and no  $\beta$ ,  $\gamma$ -isomer, respectively. The reaction mechanism clearly indicated that the *trans*-derivative was isomerized photochemically to the *cis*-isomer, which seemed to be the precursor of the  $\beta$ ,  $\gamma$ -isomer.

Photochemical addition of formamide and aniline to crotonic acid and its esters were also discussed. For example, light-induced amidation of *trans*-crotonic acid and its esters gave  $\alpha$ -,  $\beta$ - and  $\gamma$ -adduct in a yield of 60–77%. The formation of  $\gamma$ -adduct was elucidated as an addition product to  $\beta$ ,  $\gamma$ -isomer, which was photochemically obtained from the *trans*-isomer.

Finally, photo-Fries rearrangement of *trans*-phenyl crotonate was reported. An irradiation of *trans*-phenyl crotonate produced *cis*-isomer, chromanone, *ortho*-crotonyl phenol and phenol in low yields.

## Reaction of Organoboranes with $\alpha$ , $\beta$ -Unsaturated Carbonyl Compound

—Convenient New Syntheses of Saturated and  $\alpha$ ,  $\beta$ -Unsaturated Carbonyl Derivatives from Olefins *via* Hydroboration—

Akira SUZUKI  
Mitsuomi ITOH

### Abstract

Studies on the reactions of organoboranes with  $\alpha$ ,  $\beta$ -unsaturated ketones, which provide convenient new syntheses of saturated and  $\alpha$ ,  $\beta$ -unsaturated ketones from olefins *via* hydroboration were described. Trialkylboranes, readily available *via* hydroboration, undergo a remarkably fast 1,4-addition to methyl vinyl ketone. Hydrolysis of the initially formed intermediate, produces the corresponding methyl ketone. The cyclic organoboranes obtained from dienes also undergo the 1,4-addition to produce  $\omega$ -hydroxy ketones after alkaline hydrogen peroxide oxidation. At the beginning, this interesting reaction seemed to proceed through a co-ordination process [2]. However, it was recently confirmed that the reaction is catalyzed with oxygen, and goes on through a radical chain mechanism [6]. According to the latter mechanism, it is expected that organoboranes would react with acetylacetylene. Actually, 4-alkyl-3-buten-2-ones were obtained from the corresponding trialkylboranes in good yields by such oxygen-induced reaction.

## Ueber die Umsetzung von Karbonsäurehydraziden mit Säuren. II.

Entstehung von N, N'-Diacylhydrazinen durch Umsetzung  
von aromatischen Karbonsäurehydraziden mit  
wässriger Lösung von Mineralsäuren

Toshiro CHIBA  
Hiroyuki ŌMORI  
Yoshiyuki TAKATA

### Zusammenfassung

Die Umsetzung von aromatischen Karbonsäurehydraziden mit wässriger Lösung von Mineralsäuren wurden untersucht.

Beim Erhitzen von Benzoesäurehydrazid oder *p*-Nitrobenzoesäurehydrazid mit wässriger Lösung von Sulfaminsäure oder Salzsäure entstanden N, N'-Diacylhydrazine. Aber die Reaktivität beider aromatischer Karbonsäurehydrazide war schwächer als höherer Fettsäurehydrazide und die Ausbeute an N, N'-Diacylhydrazinen waren nicht hoch. Die Ausbeute an N, N'-Diacylhydrazinen war niedriger in folgender Reihenfolge: Caprinsäurehydrazid > Benzoesäurehydrazid > *p*-Nitrobenzoesäurehydrazid.

## Copolymerizations of *p*- and *m*-substituted phenyl vinyl ketones with styrene

Kazuaki YOKOTA    Tuguaki SUZUKI  
Syunji NAKAZAWA    Kyoshi NAKAMURA  
Yoshiyuki TAKADA

### Abstract

The copolymerizations of substituted phenyl vinyl ketones ( $M_1$ ) having *p*-CH<sub>3</sub>O, *p*-CH<sub>3</sub>, H, *p*-F, *p*-Cl, *p*-CH<sub>3</sub>CO, *m*-Cl, *m*-CH<sub>3</sub>, *m*-CN substituents with styrene ( $M_2$ ) were studied. From the results obtained the monomer reactivity ratios and the  $Q_1$ ,  $e_1$  values were determined. The relative reactivities of the substituted phenyl vinyl ketones toward the styryl radical were plotted against the Hammett  $\sigma$  constants of the substituents and concave curves were obtained. But in this case a linear relation was obtained in the region corresponding to the electron acceptor substituents in the *p*-substituted ones. The effects of the substituents on the reactivities differed with these polarities. In addition the ultraviolet absorption bands of the monomers and the dependence of  $\log r_1 r_2$  on the  $\sigma$  constants were estimated. From these results it may be concluded that the effects of the electron donor and acceptor substituents contribute respectively to the resonance and the polar structure in the transition state.

## Studies on the Reduction Reaction of Nitrobenzene and Its Derivatives with Aluminum, I

—The Reduction of Nitrobenzene in  
Alkaline Conditions. Part 1—

Kunihisa ŌIE            Junichi KOSUGI  
Hiroshi TAKAHASHI    Yoshiyuki TAKATA

### Abstract

The reduction reaction of nitrobenzene with aluminum in alkaline conditions was studied. It was found that this procedure is effective for the selective reduction of nitrobenzene. In aqueous alkaline solution, nitrobenzene was mainly reduced to aniline and azoxybenzene was isolated as a minor product. On the other hand, the dimeric reduction products such as azobenzene and hydrazobenzene were obtained in alcoholic aqueous alkaline solution. The necessary amount of sodium hydroxide was 0.05~0.8 mol. to 1 atom of aluminum in a concentration of less than 5 per cent. Hydrazobenzene was obtained in a 72% yield in methanolic solution and in a 85% yield in ethanolic solution.

## Resolution Enhancement of Electron Paramagnetic Resonance Spectra and Its Applications

Keiichi OHNO  
Isao TAKEMURA  
Junkichi SOHMA

### Abstract

A resolution enhancement technique of ESR spectrum was developed by using adigital computer on line. The theory of enhancement, on which the present experiments were based, is described in detail. The enhancement was applied to the ESR spectra obtained from the magnetic centers trapped in amorphous matrices, such as trapped electrons in alkaline ice,  $\gamma$ -irradiated polymers etc. The spectra treated by this technique had such a high resolution that the magnetic centers were clearly identified from the ESR spectra.

## Application of ESR to Catalysis

Y. OHNO            M. MOROZUMI  
M. SHIOTANI      S. MORIUCHI  
J. SOHMA

### Abstract

ESR was applied to study CuO catalyst, and the following conclusions were drawn from the ESR data; 1) ESR intensity was in parallel with the catalytic activity. 2) ESR spectrum obtained from the CuO catalyst was attributed not to  $\text{Cu}^{2+}$  but to the impurity of  $\text{Fe}^{3+}$ . 3) ESR spectrum obtained from the catalyst after the reaction was different from that obtained before the reaction. 4) Analysis of ESR data suggests that the impurity  $\text{Fe}^{3+}$  in the CuO catalyst plays an important role in the catalytic action. ESR spectra from  $\text{V}^{4+}$  in  $\text{V}_2\text{O}_5$  catalyst are found to be completely different in accordance with the difference of the catalytic activity caused by the different carriers. Microscopic conditions of the  $\text{V}^{4+}$  ion, such as the symmetric property around  $\text{V}^{4+}$  and the covalency of  $\text{V}^{4+}$ , were characterized by the ESR spectra. One of the big differences caused by different carriers was the difference in the aggregation state; one was homogeneously dispersed, the other was clustered. ESR was observed from the anion radical formed from Nitrobenzene adsorbed on surface of CaO catalyst and the concentration of the reducing points of the catalyst was quantitatively determined by the calibration of ESR intensities. Relations of the reducing points to the basic points of the catalyst as well as to the catalytic activity were discussed.

## Force on a sphere at maximum relative velocity and flow patterns around the sphere vibrating in liquid

Kazuo ENDOH  
Harumochi HIRANO

### Abstract

Experiments were performed to obtain basic information on force on a sphere and flow patterns in the vicinity of the sphere vibrating in liquid.

Results obtained were

1) Under conditions where the amplitude of vibration was smaller than the diameter of sphere, it was shown that the measured thickness of inner streaming  $\eta$  could be expressed by

$$\eta/d = f(d^2f/\nu)$$

where  $f$  is the frequency of vibration,  $\nu$  is the kinematic viscosity of liquid and  $d$  is the diameter of the sphere.

Moreover, under similar conditions and using the same liquid, flow patterns around a thin circular disk vibrating along the axis were investigated. The critical conditions for the direction of flow changes was expressed by

$$a^2f/\nu = 8.5(a/D)^{0.67}$$

where  $a$  is the amplitude of vibration and  $D$  is the diameter of the circular disk.

2) At a maximum relative velocity, the acceleration of liquid was neglected, and the force on the sphere was found to be expressed by

$$F = C_v \frac{1}{2} (a\omega)^2 \frac{\pi}{4} d^2$$

$$C_v = 180/Re_\eta$$

$$Re_\eta = \eta(a\omega)/\nu$$

Where  $\eta$  is the thickness of the inner flow in the vicinity of vibration sphere given by the experimental relation  $\eta/d = f(d^2\omega/\nu)$ .

From the results, together with the data obtained by Oder et. al., it was found that the force on a sphere at a maximum relative velocity was related with the thickness of the inner flow.

### Studies on Particle Size and Grinding Power Required for Wood Chips

Kazuo ENDOH                      Hiroshi SUZUKI  
Hiroshi TAKAHASHI              Harumochi HIRANO

#### Abstract

Experimental studies were made on representative particle size of wood fibres and power required for disk type refiners.

The results obtained were as follows:

- (a) It is reasonable to adopt the equivalent circular diameter based on the projected area of fibre to be representative which is related to the drag force. The behavior of the drag force measured by gravitational sedimentation of wood fibre, bears a close resemblance to Allen's law in screen opening from 125 to 1,190 microns.
- (b) Apparent physical properties of wood vary with wood species, but when wood is ground to comparatively small size fibres, the difference of botanical structure of wood have little or no effect on the physical properties of the fibre.
- (c) The power required for refiners  $M$  per unit volumetric feed rate of wood were found to be expressed by

$$M = \alpha f - 0.32$$

where  $f$  is the scanning area of fibre and  $\alpha$  is the constant determined by the type of refiner.

(d) Particle size distribution of ground fibre can be expressed by Rosin-Rammler's distribution. The values of slope of Rosin-Rammler's distribution  $n$  is related to wood species and the experimental correlation was

$$n \propto \rho_w^{-1.2}$$

Where  $\rho_w$ : apparent density of wood.

**Mass Transfer in Liquid Phase**  
—Diffusion Problem in Composite Media—

Toshiharu SHIBATA  
Masao KUGO

**Abstract**

A diffusion problem was discussed theoretically and numerically by a composite model which was composed of two liquid phases, namely a limited length phase and a semi-infinite length phase.

From the results obtained by solving the diffusion equations, the phenomena were elucidated by a modification of the truncated Higbie type where the values of  $\alpha$  is 0. As  $\alpha$  approaches unity, the increased rate of mass transfer may be calculated by the following equation

$$W \propto (l^{2r-1})(4D_1t)^r C$$

rather than the Higbie theory ( $r=0.5$ ).

**The Study of Equilibrium and Rate on the Liquid-Liquid  
Extraction Reaction of Organic Sulfer Compounds  
with Transition Metal Salt Solution**

—The Study of Sulfides—

Kazuo AOMURA      Takao YOTSUYANAGI  
Tamio KAMIDATE      Kuniichi OHUCHI  
Syozo HENMI

**Abstract**

In order to establish a new extraction method for the separation and the determination of individual sulfides ( $C_2 \sim C_6$ ) in petroleum, a preliminary investigation was conducted on the extraction mechanism with an aqueous solution containing transition metal ions and various anions. It was found that the  $d^9 \sim d^{10}$  metal ions ( $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$ ) formed stable complexes with the sulfides, and were applicable to the present purpose.

The extraction efficiency of metal ion was strongly influenced by the salting out reagents. This effect was well explained in terms of the cation effect, by which the activity of  $H_2O$  was decreased and the anion effect by which concentration of the metalanion complex was increased.

The absorption spectrum of these complexes indicated the peak, e.g., at 245 nm for  $Hg^{2+}$  and at 350~360 nm for  $Cu^{2+}$ ; the composition of  $[Me] : [sulfide] = 1 : 1$  was estimated from the results obtained by the Job's method as well as by the slope of the linear relation between  $\log D$  and  $\log [metal\ ion]$ . The distribution and extraction rate of the sulfides were enhanced by the presence of a particular anion in the aqueous phase in

the order of  $\text{CN}^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{ClO}_4^- \sim \text{NO}_3^-$  and this order corresponded well to that of the stability of the metal sulfide complexes. This effect of the anionic ligand seems to be attributed to the trans effect of the complex found in the substitution reaction of square planer complexes. The applicability of this extraction system to the separation of sulfides by the partition liquid-liquid chromatography was also predicted.

## NOTICE

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## A Study on Thermodynamical External Work (2nd Report)

—Application to the Brayton Cycle and the Sabathé Cycle—

Hiroshi TANIGUCHI

Kazunori WAKAI

### Abstract

In the calculation of heat engine cycles, it should be considered that the external heat exchange and the internal heat generation from friction renders a different influence respectively on the external work. These heats are not usually dealt with separately, but in our opinion some efforts must be made to separate these heats.

In the 1st report, we have already suggested one separating factor for the above-mentioned purpose and have analyzed the influence of it on the external work.

In this report, we introduced other separating factors by which analysis may be made easier and have analyzed the influence of these factors on the cycle performance by means of the Brayton cycle for a steady-flow process and the Sabathé cycle for a non-flow process.

## The Performance of a Gas Turbine Plant Combined with a Heat Supply-Part 1

Takashi SONODA

Takeshi SAITO

Hiroshi TANIGUCHI

### Abstract

The performance of a gas turbine plant combined with a heat supply was analysed on a part load demand for power, in which a gas turbine had a simple open cycle without a regenerator and with a hot water boiler for exhaust-gas heat recovery.

The authors presented a method of calculation for the determination of the inlet and exhaust temperature, pressure ratio, and air or gas flow rate of a gas turbine and heat output of a hot water boiler, using the design data and the heat consumption data of each load of a gas turbine.

Based on these calculated values, the performance of a heat and power generating plant was discussed with such efficiencies in which the electric power and heat were evaluated by the energy or the exergy respectively.

## The Magnification for Optical Parametric Image Conversion in Thin Nonlinear Materials

Ichiro SAKURABA

### Abstract

The relation between the longitudinal, transverse and angular magnifications in optical parametric image conversion was presented. These obey relations quite similar to the Maxwell elongation and Smith-Helmholtz formulas in geometrical optics. The fundamental equation for analyses of spherical aberrations was also given.

## Statistical Consideration of the Adsorption

Yoshio MOMOUCHI

Yasuki SEKIGUCHI

Masaji ONODERA

### Abstract

The adsorption behavior of gases was investigated by applying the asymptotic method. An adsorption isotherm was derived. Four types of critical temperature curves which depend on the coordination number  $Z$  was obtained. A stable area was determined by three of the above curves.

## REDUCTION TESTS OF SYNTHETIC CALCIUM FERRITES IN TERNARY SYSTEMS OF $\text{CaO-FeO-Fe}_2\text{O}_3$

Shuji SATO

Takeshi KIKUCHI

Chikao YOSHII

### ABSTRACT

Four calcium ferrites of a  $\text{CaO-FeO-Fe}_2\text{O}_3$  system were synthesized at  $1100^\circ\text{C}$ , while  $3\text{CaO}\cdot\text{FeO}\cdot 7\text{Fe}_2\text{O}_3$  and  $4\text{CaO}\cdot\text{FeO}\cdot 4\text{Fe}_2\text{O}_3$  were synthesized in an argon gas and  $\text{CaO}\cdot\text{FeO}\cdot\text{Fe}_2\text{O}_3$  and  $\text{CaO}\cdot 3\text{FeO}\cdot\text{Fe}_2\text{O}_3$  were synthesized in a gas mixture of  $\text{CO}/\text{CO}_2=30/70$ . Synthetic  $\text{CaO}\cdot 3\text{FeO}\cdot\text{Fe}_2\text{O}_3$  was not distinguished by one phase but rather at least by two phases, i.e. one was of an Asada-Omori type and the other was of a Cirilli-Burdese type. Reduction tests of these four compounds were carried out with various  $\text{CO-CO}_2$  gas mixtures by thermogravimetric balance.

Oxygen partial pressure equilibrated with each ternary ferrite at  $800^\circ\text{C}$  was roughly determined. Oxygen partial pressure ranges, where  $3\text{CaO}\cdot\text{FeO}\cdot 7\text{Fe}_2\text{O}_3$  and  $4\text{CaO}\cdot\text{FeO}\cdot 4\text{Fe}_2\text{O}_3$  were equilibrated, agreed with that of magnetite.  $\text{CaO}\cdot\text{FeO}\cdot\text{Fe}_2\text{O}_3$  and  $\text{CaO}\cdot$

$3\text{FeO}\cdot\text{Fe}_2\text{O}_3$  were stable in the same range of oxygen partial pressure as wüstite. All calcium ferrites were reduced to the assemblage of  $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ +metallic iron at  $800^\circ\text{C}$  with a gas mixture of  $\text{CO}/\text{CO}_2=80/20$ . Reducibility of each ferrite in this condition was nearly equal but  $\text{CaO}\cdot 3\text{FeO}\cdot\text{Fe}_2\text{O}_3$  of Cirilli-Burdese type had a very low reducibility. However, these ternary calcium ferrites were more reducible than wüstite.

### A Fortran Program for Ellipsometry of Surface Films on Metals

Kiyokatsu KUDO  
Norio SATO

#### Abstract

A Fortran computer program for ellipsometry to analyse multiple absorbing films on metals by means of single reflection and multiple reflection methods using an ellipsometer with a quarter-wave plate on the side of the incident beam is presented. This program makes it possible to calculate not only the theoretical reflection parameters as a function of optical constants of the substrate, film thicknesses of the uppermost and inner film and the angle of incidence, but also the optical constants and thickness of the surface film within a specified experimental error by comparing calculated reflection parameters with measured polarizer and analyser settings for a given surface. The program is applicable to any surface films particularly for the purpose of oxidation study of metals.

### The Reactions of Carboxylic Acid Hydrazides with Acids (III)

—The reactions of aliphatic carboxylic acid hydrazides with carboxylic acids—

Toshiro TIBA  
Hiroyuki ŌMORI  
Yoshiyuki TAKADA

#### Abstract

The reactions of acid hydrazides with carboxylic acids were investigated using capric acid hydrazide [I] as one of the carboxylic acid hydrazides.

When [I] was heated with formic, acetic, propionic, butyric, oxalic, succinic, pimelic and phthalic acid in aqueous solution, N, N'-didecanoylhydrazine [II] was produced. The reactivity of monobasic acids with [I] was in the following order: acetic < propionic < butyric  $\approx$  formic acid. When the reactions were carried out using more than 0.5 mole of formic acid to one mole of [I], [I] was formylated and the yields of [II] decreased. The reactivity order of dibasic acids in the reaction with [I] was as follows: oxalic > phthalic > succinic > pimelic acid. When more than 0.3 mole of phthalic acid against one mole of [I] were used, the yields of [II] were lowered, which are apparently due to

the formation of N-decanoyl-N'-phthaloylhydrazine as a by-product. Also phthalylhydrazide was produced as another by-product.

By heating [I] with anhydrous formic, glacial acetic, propionic, butyric and caproic acid, [II] was produced also. The reactivity order of acids in anhydrous conditions was as follows: acetic > propionic > butyric > caproic acid. When more than 0.3 mole of formic acid or one mole of other acids were used against one mole of [I], the yields of [II] were lowered because of the formation of N-acyl-N'-decanoylhydrazine as a by-product.