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The Second International Conference
on Microzonation for Safer Construction-Research and Application, Nov.
26-Dec. 1, 1978, San Francisco, California, U.S.A.

Deep Shear Wave Velocity Measurement for Evaluation of 1-10 sec Seismic Input Motions

N. GOTO^I, Y. OHTA^{II} and H. KAGAMI^{III}

Deep shear wave velocity loggings were planned at two sites in the Tokyo area from an earthquake engineering point of view, and actually carried out down to 3500 m and 2300 m temporarily using earthquake observation wells. The purpose of these surveys is to elucidate experimentally the relation of detailed deep site structure to ground motions with 1~10 sec period during an earthquake.

Shear waves are produced by means of ordinary small explosions and a specially designed SH wave generator. A set of three component seismometers was installed in a capsule having a clamping device to the borehole wall. Sequent measurements were conducted at different depths to the bottom at intervals of 100~500 m.

The velocity structures completely agree with the known data such as sonic logs, density distributions, geologic sections and so on.

Engineering seismological importance of shear wave measurement for thick soil deposits is stressed upon rough estimations of amplification between ground surface and bedrock.

The Tenth International Congress of
Anthropological and Ethnological Sciences, 10-16 December, 1978, New Delhi, India

A Study on the Estimation of Local Muscle Energy Metabolism Value in Human Static Postures

Shintaro YOKOYAMA

Department of Sanitary Engineering

Estimation of local energy metabolism values of 5 muscle groups —Posterior crural m. (M_1), Posterior femoral m. (M_2), Anterior femoral m. (M_3), M. of the buttock (M_4) and M. erector trunci (M_5)— was performed with Japanese males aged 20~28 from simultaneous measurements of total energy metabolism and bipolar surface integrated EMG values.

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M_1 - M_5 are known to play a very important role in standing and half rising postures and to be very big muscle groups. Selecting various postures which might not cause extreme changes in each muscle length and which have the similar total energy metabolism value, we can decide the coefficient that may convert an integrated EMG value into a local energy metabolism value and then can estimate local muscle energy metabolism values by the coefficient of each muscle group and the integrated EMG of each posture.

Mean estimated values of M_1 were 20.56 in standing on tiptoes, 7.90 in stiff standing and 11.61 [kcal/h] in half rising with knee bending at 120° . These of M_5 were 6.71 in standing on tiptoes, 6.45 in stiff standing and 42.61 [kcal/h] in half rising 120° . In the same manner, local muscle energy metabolism values in 11 static postures could be estimated.

Symposia of Requirements and Processes for Hydrogen Generation at The ACS/CSJ Chemical Congress, 1-6 April, 1979, Honolulu

Thermochemical Decomposition of H_2S with Metal Sulfides or Metals

H. KIUCHI, T. IWASAKI, I. NAKAMURA and T. TANAKA

Department of Metallurgical Engineering, Hokkaido University

The following two methods were investigated for the purpose of thermochemical decomposition of H_2S from direct reduction of sulfide ores with H_2 . (1) Decomposition of H_2S by a combination of the following two reactions in which M denotes a metal; sulfurization ($MS + xH_2S = MS_{1+x} + xH_2$) and thermal decomposition ($MS_{1+x} = MS + xS$). It was found that the utilization of non-stoichiometric composition of berthollide sulfides such as FeS_{1+x} is suitable for the above cycle. Better results were obtained by using a double sulfide $CuFeS_{2-x}$ which thermally decomposed into FeS and Cu_5FeS_4 under reduced pressure and these products were proved to return to their original state $CuFeS_{2-x}$ by sulfurization with H_2S . (2) Decomposition of H_2S by metals. As a fusible metal, molten Pb was used to prevent the formation of a dense film which tends to cease the generation of H_2 . Two tests were made, in which the bubbling of H_2S into molten Pb and the soft blowing at the surface of the melt were examined. Experimental results revealed that the presence of minute Ni or Cu in molten Pb serves to catalyze the formation of H_2 . It was also shown that the Pb regeneration is possible by the oxidation of the formed PbS under low partial pressure of O_2 and the this regeneration is due to the reaction of sublimated PbS.

The ACS/CSJChemical Congress, Hawaii, April 1-6, 1979

Mechanism of Reduction of Metal Sulfates with Hydrogen

R. SHIBAYAMA, K. KANEKO, T. TANAKA

An investigation on hydrogen reduction of cobalt, and copper sulfates are presented and the reduction mechanism is discussed.

The results obtained are as follows:

1) In the reduction of cobalt sulfate, metallic cobalt or Co_9S_8 is not directly formed from CoSO_4 , but CoO is formed first, which is then reduced to metallic cobalt. On the other hand, SO_2 evolved in the course of reduction is reduced to H_2S by the catalytic action of metallic cobalt and then the H_2S formed, forms Co_9S_8 . Therefore, the cyclic reaction in which the Co_9S_8 reacts with the unreacted CoSO_4 and forms CoO , is dominant in hydrogen reduction of CoSO_4 .

2) In contrast to this, the conclusion is that, H_2S is not produced and only metallic copper is obtained in the reduction of CuSO_4 , because the lack of the catalytic action of metallic copper minimizes the formation of H_2S .

The American Chemical Society and
Chemical Society of Japan Chemical
Congress, April 1-6, 1979. Honolulu,
Hawaii, U. S. A.

Corrosion Inhibition of Copper with Potassium Octylhydroxamate

Takenori NOTOYA and Tatsuo ISHIKAWA

The inhibitive effect of potassium octylhydroxamate (P-OHO) on the corrosion of copper in both acidic and neutral NaCl solutions has been investigated by means of corrosion tests, electrochemical polarization and infrared spectroscopy.

The P-OHO was found to be a good inhibitor in the chloride environments. The inhibition efficiency was determined from weight loss measurements by using a "spinner" test assembly. The corrosion rate of copper decreased with the increasing P-OHO concentrations at concentrations more than 0.1 m mol/l in neutral solutions. Corrosion tests revealed that the maximum inhibition efficiency was 98% at the concentration of 1 m mol/l in the solutions of pH 6.0~8.6. The polarization curves indicated that P-OHO was a cathodic inhibitor rather than an anodic one. Reflection-absorption infrared spectra of surface films formed on copper in the NaCl solutions in the presence of P-OHO were identified as Cu^{II} -octylhydroxamate. It is concluded that the inhibition action is mainly due to the formation of adherent films of the Cu-octylhydroxamate complex on the surfaces of copper and/or copper oxide.

Alcohol Fuels Technology Third International Symposium May 28-31, 1979, Asilomar, California, U. S. A.

Formaldehyde Emissions from a Spark Ignition Engine Using Methanol

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With the aid of derivative spectrophotometry, emission characteristics of formaldehyde from a S.I. engine using methanol were obtained. The single cylinder, water cooled 4 stroke cycle engine was operated with wide open throttle at engine speed of 1500 rpm. Formaldehyde, unburned methanol and other trace species were measured at several distances along the exhaust tube for various equivalence ratios and ignition timings.

The results indicate that formation of formaldehyde from unburned methanol already begins in the cylinder or within the exhaust port, and then, formaldehyde accumulation occurs at a temperature ranging roughly 400~500°C in the exhaust tube. This is remarkable in lean mixture, for example, the formaldehyde concentration becomes 1.7 times the initial levels. Dominant oxidation of unburned methanol is obtained at a temperature about or above 400°C. An amount of unburned methanol oxidation is proportional to the formaldehyde concentration in lean mixture including stoichiometric.

1978 International Symposium on Antennas and Propagation, Sendai, Japan, August 29-31, 1978

Investigation of an Antenna System Composed of Slot and Wire Antennas

Kiyohiko ITOH, Ichiro SHIBAZAKI and Tadashi MATSUMOTO

This paper deals with the theoretical analysis of the mutual coupling between slot and wire antennas, and its experimental verification. An antenna system composed of a slot and a wire has been analyzed King et al. and Butler et al., and actually applied by Clavin et al. It is obvious from these papers that the mutual coupling between the slot, that is, a magnetic current antenna, and a thin wire, that is, an electric current antenna is very strong. A concept of the mutual coupling between antennas is formulated clearly in the form of the mutual impedance and the mutual admittance for the electric and magnetic current antennas, respectively. However, a concept of mutual coupling between the slot and the thin wire has not been grasped clearly as the above-mentioned quantities. This paper clarifies this concept in the form of a matrix representation by using the technique of reaction matching.

1978 International Symposium on Antenna and Propagation, Sendai, Japan, August 29-31, 1978

Microstrip Line Array Antenna and its Application

Kaijiro NAKAOKA, Kiyohiko ITOH and Tadashi MATSUMOTO

In this paper we have proposed a Microstrip Line Array Antenna (hereafter referred to as MSAA). It consists of a group of series of slots which are positioned on the ground plane along a microstrip line. There are two basic types of MSAA; the resonant array when the transmission line is terminated in an open-circuit at a distance L beyond the last slot and the nonresonant array when terminated in a matched load.

The resonant array is designed for broadside operation, while the nonresonant array can be designed to have the main lobe at any angle except the broadside direction. We describe the design procedure, the radiation pattern and the gain of the resonant array. Also we have succeeded in building a 16 by 20 MSAA of which the gain is about 28 dB at 12 GHz band, based on this design procedure with a uniform aperture distribution. This array is applicable to the direct receiving antenna for the broadcasting satellite.

ACS/CSJ Joint Chemical Congress,
Div. Fuel Chemistry, Hawaii, (1979)

Effect of Hydrogen Pressure on the Reaction of NaOH-Alcohol-Coal

Masataka MAKABE and Koji OUCHI

Faculty of Engineering, Hokkaido University

The effect of pressure of nitrogen and hydrogen on the reaction of NaOH-alcohol-coal was examined by measuring the solvent extractivity. Up to 8 MPa the extract yield in pyridine under hydrogen and nitrogen atmospheres have nearly the same values, namely 95~98%. Ethanol extraction yield under hydrogen atmosphere showed larger values than that under nitrogen atmosphere. This may be ascribed to some catalytic hydrogenation effect. The extraction yield in both solvents increased with the increase of pressure, which means that the reaction proceeds with nascent hydrogen because under higher pressure the nascent hydrogen produced may remain in liquid form for a longer time, which may contribute to the higher chance for reaction.

The rise of temperature also increases the extraction yield. The yield of extraction with ethanol under hydrogen pressure invariably has higher values than those under nitrogen. The yield of extraction with benzene under nitrogen has higher values than those under hydrogen at lower temperature, but at higher temperature the yield of extraction under hydrogen becomes higher. This can not be explained well.

ACS/CSJ Joint Chemical Congress,
Div. Fuel Chemistry, Hawaii, (1979)

Structural Analysis of Quinoline Extracts and Hydrolysis Products of Coals

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and Hironori ITOH

Faculty of Engineering, Hokkaido University

The quinoline extraction yield of some bituminous coals attains almost nearly 100%. In younger coals and strong coking coals it decreases. The decrease in the former is caused by the ether linkages to make macromolecules and that in latter may come from the large aromatic nucleus contained in them.

Alcohol-alkali treatment of coals gives nearly 100% of dissolution of the products in pyridine up to the coals of 85%C.

Structural analysis using NMR method was carried out for these extracts. Both products have quite similar structural indices except that the hydrolysis products have a somewhat larger aliphatic characters because of the slight hydrogenation in this reaction.

The younger coals have a benzene or naphthalene nucleus and the strong coking coals have nearly 5 aromatic rings in their unit structure. The former have also many ether linkages and in the latter, ether linkages decrease and methylene linkages are dominant.

American Chemical Society-Chemical
Society of Japan Chemical Congress
1979, Honolulu, U. S. A., April 1-6, 1979

Some Aspects of Organic Synthesis Using Organoboranes

Akira SUZUKI

The ready availability of organoboranes has led to extensive studies of their chemistry and to the development of many reactions of great value in synthetic organic chemistry. Since 1965, our research group continuously studied the use of organoboranes as synthetic intermediates and found that organoboranes are versatile as alkyl radical, carbanion and carbocation sources for the synthetic reactions of a wide variety of organic compounds, which include preparations of aliphatic ketones, ω -hydroxy-ketones, α , β -unsaturated ketones, α -bromoketones, alkyl aryl ketones, γ , δ -unsaturated ketones, saturated alcohols, olefinic diols, β , γ -unsaturated alcohols, allenic alcohols, alkyl halides, alkyl acetates, alkyl methyl ethers, alkyl azides, a selective synthesis of secondary amines, preparations of alkanenitriles, nitroalkanes, saturated and α , β -unsaturated carboxylic acid esters, a direct synthesis of carboxylic acids, and various syntheses of alkanes, alkenes, alkynes and alkylarenes.

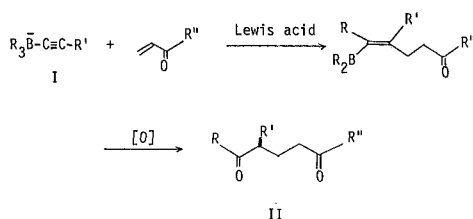
Some recent developments of such novel synthetic reactions employing organoboranes performed in our laboratory will be presented. (Lecture by Invitation)

American Chemical Society-Chemical
Society of Japan Chemical Congress
1979, Honolulu, U. S. A., April 1-6, 1979

Reaction of Lithium 1-Alkynyltrialkylborates with α , β -Unsaturated Carbonyl Compounds in the Presence of Lewis Acids

Shoji HARA, Kotaro KISHIMURA, Tetsuya HARA
and Akira SUZUKI

Lithium 1-alkynyltrialkylborates (I) prepared from alkynyllithium reagents and trialkylboranes are well known to react with electrophiles such as alkyl halides and iodine to give corresponding organic compounds. However, there are no reports in which α , β -unsaturated carbonyl compounds react with such borates to form the Michael type addition products. We found that 1-alkynyltrialkylborates (I) react with α , β -unsaturated carbonyl compounds such as methyl vinyl ketone and acrolein in the presence of Lewis acids, followed by the usual alkaline hydrogen peroxide oxidation to give δ -dicarbonyl compounds (II). For instance, the borate complex obtained from lithium phenylacetylide and tri-*n*-butylborane reacted with methyl vinyl ketone in the presence of TiCl_4 to give the corresponding δ -diketone in a yield of 83%. This Lewis acid-catalyzed reaction of organoboranes provides a novel route for the synthesis of δ -dicarbonyl compounds from organoboranes.

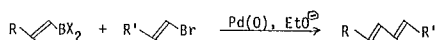


American Chemical Society-Chemical
Society of Japan Chemical Congress
1979, Honolulu, U. S. A., April 1-6, 1979

Cross-Coupling Reaction of Vinylboranes with Vinyl Halides in the Presence of Palladium Catalyst

N. MIYaura and A. SUZUKI

In the course of our studies on organic synthesis using organoboranes, we found that B-vinyl-1, 3, 2-benzodioxaboroles or B-vinyl-disiamylboranes undergo cross-coupling reactions



$X_2 = \text{Disiamyl or}$



Vinyl halide		Yield (%)
I	R = Butyl	80
II	Butyl	81
II	Phenyl	52
III	Butyl	86
III	Hexyl	83



I



II



III

with vinyl halides in the presence of palladium catalyst as shown in the following equation.

The following procedure is representative. The reaction of (E)- β -bromostyrene (5 mmol) with B-1'-hexenyl-1, 3, 2-benzodioxaborole (5 mmol), 2 N-EtONa/EtOH (5 ml) and Pd (PPh₃)₄ (0.05 mmol) is carried out under reflux for 2 h in benzene. The product isolated was confirmed to be 1-phenyl-1, 3-octadiene (80%). Some of other results of the reaction are summarized in the Table. The present procedure provides a simple method for the synthesis of unsymmetrical dienes in good yields.

American Chemical Society-Chemical
Society of Japan Chemical Congress
1979, Honolulu, U. S. A., April 1-6, 1979

Electrophilic Alkylation of Benzenes with Strongly Electron-Withdrawing Groups in Super Acid Media

N. YONEDA, Y. TAKAHASHI, H. SUZUKI,
T. FUKUHARA and A. SUZUKI

Electrophilic alkylation on the aromatic rings with electron-withdrawing groups such as -COR, -COOR, -CN, and -NO₂ was studied in the presence of FSO₃H-SbF₅, HF-SbF₅ or SbF₅-SO₂ClF at temperatures of -50° to 50°C under an atmospheric pressure. Alkyl phenyl ketones having an alkyl group of five or more C-atoms underwent ring closure to produce 1-tetralone derivatives.

Alkyl phenyl ketones with an alkyl group of carbons less than five, benzaldehyde, trifluoroacetophenone, benzonitrile, benzoic acid and its ester all reacted with alkyl halides to give the corresponding nuclear alkylation products under such conditions. The relative reactivities of alkyl halides followed the order EtX > iso-PrX > tert-BuX.

It was found that alkylation of nitrobenzene with iso-PrX is fairly difficult, but EtX reacts with the aromatic substrate to give the alkylated product in a relatively good yield. On the other hand, *p*-methylnitrobenzene reacted readily with iso-PrX under the same conditions to afford the nuclear alkylation product.

American Chemical Society-Chemical
Society of Japan Chemical Congress
1979, Honolulu, U. S. A., April 1-6, 1979

Synthesis of Dicarboxylic Acids by the Reaction of Lactones with Carbon Monoxide in Super Acid Media

N. YONEDA, Y. TAKAHASHI, Y. SAKAI and A. SUZUKI

Recently, we have reported that diols with four or more C-atoms, except their vicinal derivatives, give the corresponding carboxylated products in good yields by the reaction of carbon monoxide in the presence of HF-SbF_5 . In the course of our studies on such carboxylation reactions, we examined the reaction of lactones with carbon monoxide in super acid media and found that γ -butyrolactones give the corresponding dicarboxylic acids. For instance, γ -methyl- γ -butyrolactone reacted with carbon monoxide in the presence of HF-SbF_5 (HF/SbF_5 molar ratio, 5) at 0°C under an atmospheric pressure, followed by hydrolysis to give 2-methylpentanedioic acid in quantitative yield.

ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979

Esterification of Cellulose by BF_3 Complex

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Acetic anhydride was saturated with BF_3 gas to form a precipitated complex A, $(\text{Ac}_2\text{CHCO})_2\text{O} \cdot 3\text{BF}_3$, and complex B, $\text{BF}_3 \cdot 2\text{AcOH}$. A saturated solution was added to acetic anhydride until the precipitation was dissolved. Totally used acetic anhydride to BF_3 was 6.7 in weight ratio. Ramie pretreated by acetic acid was acetylated by the solution.

Cellulose triacetate was obtained within 2 minutes at 70°C or 5 minutes at 55°C in a fibrous state. However the mixture of the complex A isolated from the saturated solution and acetic anhydride acetylated hardly any cellulose. On the other hand, the isolated complex B or acetic acid absorbed BF_3 had a high ability of the acetylation.

If a dehydrating reagent such as P_2O_5 was present in the acetylation system, the complex B acetylated cellulose without acetic anhydride. The mixture of the complex B and propionic anhydride or propionic acid gave a mixed ester of cellulose acetate and propionate. The complex A, B acetic anhydride and acetic acid were equilibrated in the solution and the most desirable mixture ratio for acetylation of cellulose were present. Cellulose esters of other fatty acids could be obtained in the same way. The mechanism of the reaction was considered as follows, $\text{BF}_3 \cdot 2\text{RCOOH}$ was dehydrated to form $\text{RC}^+=\text{O}$ which attacked the OH groups of cellulose.

ASC/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979

Alkali-Oxygen Pulping of Rice Straw

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To rice straw alkali was added in the following three manners and oxydized in an autoclave by oxygen gas of 5~10 kg/cm² at 120°C for 1 hr. (a) Rice straw was immersed in an alkaline solution at 10~120°C for 1 hr and then compressed to twice weight of rice straw. (b) To rice straw alkaline solution was added by spraying and allowed to stand for 0~4 hr at 20~60°C (c) Rice straw was pretreated in water at 100°C for 1 hr and an alkaline solution was added by spraying. The principal results are shown in Table 1. The pulp obtained at high yield of 45~50% showed excellent paper strength comparable to KP and high brightness of about 60. The pulping saved 70% energy in alkaline pulping of the straw.

Table 1. Yields and Properties of the Pulps

Method	Concent. of NaOH soln.	NaOH % (based on straw)	Screened Yield %	Brightness	Breaking Length (km)	Burst Factor	Tear Factor
a	1.0 (80°C)	(1)	44.5	45.5	7.3	4.5	75
	2.0 (40°C)	(2)	47.6	61.2	6.8	3.7	72
b	3.0	10	48.9	60.1	4.2	2.0	48
	6.0	20	49.9	59.0	6.3	4.4	63
c	5.0	17.5	46.9	64.1	5.5	3.9	65
	6.0	20	44.2	67.0	5.3	3.7	67

ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979

Biosynthesis and Spherulites of Bacterial Cellulose

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Two-dimensional spherulites are formed in the pellicle of bacterial cellulose by static cultures of *Acetobacter xylinum*. These spherulites are much larger than those usually observed in other natural or synthetic polymers. Evidence by polarizing microscopy indicates that the cellulose microfibrils in the spherulites of bacterial cellulose are oriented radially or tangentially.

If the larger refractive index is in the radial direction, the spherulite is termed positive, whereas, if it is tangential, it is termed negative.

Also, the orientation may be limited to only a fraction of the thickness of the pellicle. The degree of orientation of the birefringent elements in a spherulite of bacterial cellulose varies vertically within the pellicle as well as horizontally. The vertical variation is particularly significant because of disc-like formation of the spherulite with a ratio of axes of about 1 : 10. The tangential or radial deposition of some of the microfibrils to form a two-dimensional analog of a spherulite may have been induced as follows. If a weakly soluble substance which inhibits or retards the crystallization of cellulose diffused radially from a point on the surface of the medium, then a circular gradient of inhibition of the growth of the microfibrils would be established around the point. It is suggested that initial stage of nucleation may be induced by a fraction of the intermediate lipid-carbohydrate compound.

ACS/CSJ Chemical Congress, Honolulu, Hawaii, U. S. A., April 1-6, 1979

Catalytic Activities of Methanol Reforming Catalysts and the Preparation of Catalysts

H. KOBAYASHI, N. TAKEZAWA, C. MINOCHI and K. TAKAHASHI

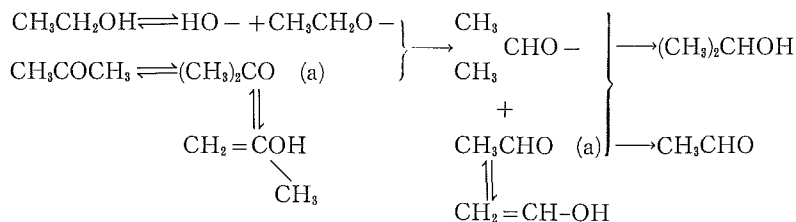
Methanol reforming reaction $\text{CH}_3\text{OH} + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}_2$ occurs with high selectivity over copper-containing catalysts, in such a way that hydrogen atoms in the water molecules are effectively converted into gaseous hydrogen as well as those in the methanol molecules. In the present work, the effect of the preparation of the catalyst upon the reaction was studied. The catalysts were prepared by kneading copper compounds with various metal oxides or by the exchange between surface hydroxyls on the oxides with the copper ion under various conditions. The catalytic activity per weight of copper and its crystal size were strongly dependent upon the starting material used, pH of the solution employed for the preparation of copper compounds and the copper-support ratio. It was found that the reaction is structure sensitive when the crystal size of copper is smaller than $100 \text{ \AA}$, whereas it is insensitive over the catalyst having a larger crystal size and the effect of the support is practically negligible.

ACS/CSJ Chemical Congress, Honolulu, Hawaii, U.S.A. April 1-6, 1979

The Reaction Between Ethanol and Acetone over Magnesium Oxide

N. TAKEZAWA and H. KOBAYASHI

The mechanism of the reaction between ethanol and acetone was studied over magnesium oxide with the aid of IR and GC-MS. From the kinetic data, the amount of adsorbed species



Midland Macromolecular Meeting
"Symposium on Application of ESR
to Synthetic Organic Polymers" 21-25
August, 1978 Midland, Michigan, U.S.A

Kentaro MURAKAMI and Junkichi SOHMA

Molecular motions of spin labeled PMMA in benzene solutions were investigated by ESR. Similar motions of nonlabeled PMMA in deuterated benzene solutions were also studied in order to check whether the hidden assumption, which is a slight difference of the labeled system from the nonlabeled one, is valid in this system. The rotational correlation times of the polymer side chain as well as their temperature dependences were measured in both systems. A comparison of the correlation times determined by either ESR or ^{13}C NMR indicates that the environment around the labeled molecule is nearly the same as that around the nonlabeled one and the only factor affecting the correlation times is the difference in the molecular size of the foreign group. It was found that the activation energies of the rotational motion of the nitroxide and methoxy group in the side chain were 4.4 and 2.8 kcal/mol, respectively. This inequality is explained again by the difference in the molecular size.

The 6th International Congress of Radiation Research May 13-19, 1979, Tokyo, Japan

Spin Trapping Studies of Radiolysis of Polymer Solutions

Junkichi SOHMA, Tetsuo MIYAZAWA and Masayoshi TABATA

Unstable radicals produced in liquid phases by γ -irradiation of solutions of several polymers (Polysoprene, Polypropylene, Polymethylmethacrylate and Poly- α -methylstyrene) were detected by ESR combined with the spin trapping method. Based on the analyses of the ESR spectra of the spin-adducts the radical species were identified. It was found, for example, in PMMA-benzene solution that methyl radicals were present after γ -irradiation and these methyl radicals were released from the ester group in the side chain. New radical species of PMMA, $\sim\overset{\text{CH}_3}{\underset{\text{R}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot$, which is a counter part of the well-known radical, $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CH}_3}{\underset{\text{R}}{\text{C}}}\cdot$, of PMMA, was identified in radiolysis of PMMA in the liquid solution. The former radical was very unstable and decomposed themselves into CO_2 , methyl and a double bond at the chain end. The released radicals abstract hydrogens from main chains to form main chain radicals and these main chain radicals undergo β -scission. This process provides a slow degradation initiated by γ irradiation. Details of the radiolysis mechanism of PMMA were discussed.

13th International Congress on High Speed Photography and Photonics, 20-25 August, 1978, Tokyo

High Speed Holography Relaxing the Restriction on Object Velocity

T. SATO, K. MURATA and H. FUJIWARA

Department of Applied Physics, Faculty of Engineering

In high speed holography the motion of an object during the exposure causes a modulation of the interference pattern to be recorded on a hologram plate. Therefore the velocity of an object is limited. This limitation on the allowable velocity of a moving object can be relaxed by the use of a frequency chirp of the laser pulse. The applicability of this principle is examined experimentally. The result shows that the limited velocity increases several times. Furthermore, employing a new arrangement similar to Michelson interferometer, a two-frequency holography is simulated for high speed objects. This arrangement is applied to the holography of balloon breaking.

13th International Congress on High
Speed Photography and Photonics, 20-
25 August, 1978, Tokyo

Restoration of Motion Blurred Images Using the Projection Iterative Method

Junji MAEDA and Kazumi MURATA

Department of Applied Physics, Faculty of Engineering

If there is a relative motion between the imaging system and the object, the recorded photographic image is degraded. We often experience such phenomena in high speed photography, in aerial photography as well as in conventional photography. This paper describes the digital restoration of photographic images blurred by a linear relative motion during exposure between the camera and the object. At first, the point spread function (PSF) of the blurring system is digitally estimated from the smeared image itself. It is shown that the sufficient information about the PSF is derived utilizing the power cepstrum method. Then the projection iterative method is employed to restore the degraded images by using the knowledge of the estimated PSF. The usefulness of this method is confirmed by experiments with a real photograph as well as by computer simulations.

ICO International Conference "Optica
Hoy y Mañana" Madrid, Spain, 10-17
Sept. 1978

Observation of Aberrated Diffraction Patterns Using Computer Generated Holograms

Yukihiro ISHII and Kazumi MURATA

Department of Applied Physics, Faculty of Engineering

Many studies have been carried out in order to display the diffraction patterns having third-order aberrations. However, it is difficult to show a single aberration independently in a practical lens system.

The computer generated hologram (CGH) is suitable for recording the wavefront having either a particular or a combined aberration. The corresponding diffraction patterns can be observed at the Fourier transformed plane of the hologram and also at different planes with a shift of focus. Furthermore, the diffraction patterns having the desired amount of wavefront aberration can be obtained by varying the size of the aperture of a hologram. We use the modified Lee type hologram which consists of equispaced resolution cells with four by four sections to increase the diffraction efficiency. It has the advantage that CGH itself shows the contour lines of the recorded wavefront aberration. The various kinds of third-order aberrations, the combined ones or the Pfeilfehler are demonstrated.

ACS/CSJ Chemical Congress, Honolulu, Hawaii, U. S. A. April 1-6, 1979

Kinetics of Hydrogen Absorption (and Desorption) and H_2 - D_2 Exchange Reaction by Activated $LaNi_5$

S. TANAKA and T. B. FLANAGAN

Since the activated state of $LaNi_5$ is of great interest with regard to practical energy (hydrogen) storage, it is important to study the kinetics of hydrogen absorption and desorption by activated $LaNi_5$. The rate of hydrogen absorption by activated $LaNi_5$ is many times faster than that of unactivated $LaNi_5$. The hydrogen absorption and desorption rates were found to be dependent upon ΔP in the α phase and α/β two-phase region of activated $LaNi_5$ where $\Delta P = (P_{\text{initial}} - P_{\text{eq}})$; P_{eq} is the equilibrium pressure over the sample before the run was commenced. The rates were found to be independent of n (H g -atom to the formula weight of $LaNi_5$) along the two-phase co-existence region provided that they were compared at the same value of ΔP . In addition, the rates of absorption and desorption were nearly equal when determined at the same value of ΔP . A small amount of helium ($P_{He} = 0.5$ Torr) in the hydrogen gas ($P_{H_2} = 15$ Torr) surprisingly decreased the hydrogen absorption and desorption rates on activated $LaNi_5$. Electron micrographs reveal that the activated $LaNi_5$ particles have a popcorn-like appearance. These observations eliminate the reaction controlled by slow process of the α/β phase transition, the solid diffusion-controlled slow step and the surface-controlled slow step. These suggest that mass transport through cracks within the sample particles is the slow step. This rate determining step is different from that for unactivated $LaNi_5$ in the α -phase region, which was found to be a diffusion of hydrogen through the bulk of the sample. The rate determining step of hydrogen exchange reaction between H_2 and D_2 by activated $LaNi_5$ was also argued.

16th International Conference on Coastal Engineering, August 27 to September 3, 1978, Hamburg

Behaviors of the Salt Wedge and the Salinity Distribution at Estuaries

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The salt wedge has been observed by ultrasonic method at estuaries of the Ishikari, Shiretoko and Rumoi River in Hokkaido, Japan. According to the records, behavior of the interface of salt and fresh water is strongly influenced by configurations of the water course and the river bed. Therefore, in this paper, a distance from the front of the salt wedge to

the river mouth is divided into two or three sections in accordance with behavior of the interface, and the salinity distribution in the upper layer is estimated in each section.

By solving the differential equation of two dimensional salinity diffusion, the distribution is represented by terms of flow velocity, diffusion coefficients, depth of the upper layer and salinity at the boundary. Where, diffusion coefficients are determined by comparing evaluated longitudinal distribution of surface salinity with observed one.

By estimating the rate of salinity entrainment into the upper layer, the entrainment coefficient E at the interface is evaluated as $E = 0.4 \times 10^{-5} \sim 0.8 \times 10^{-5}$ at three estuaries.

Japan-USA Joint Corrosion Meeting
for BWR and PWR, May 30, 1978,
Tokyo, Japan

Introductory Remark to High Temperature Water Corrosion of Iron Base Alloys

Norio SATO

Corrosion Research Group, Hokkaido University, Japan

This article reviews a few fundamental concepts which are of importance in the understanding of high temperature water corrosion of iron-base alloys. Firstly, the thermodynamic stability of iron and other alloying metals is illustrated in the potential/pH diagram, which is the basic standpoint of corrosion investigation. Secondly, the two apparently different corrosion mechanisms that are expected to operate on the metal surface in high temperature water are described; these are electrochemical corrosion and chemical corrosion. The third concept is the localization of corrosion which usually results from either local acidification or basification of environmental solution at particular places on the metal surface determined by thermal-hydraulic conditions, solid deposits, and non-homogeneous surface composition of alloys. Lastly, the effects of the metallurgical condition on corrosion are briefly discussed.

International Conference on Solid
Films and Surfaces (ICSFS), July 5-
8th, 1978, Tokyo, Japan

Differential Composition Profiles in Depth of Thin Anodic Oxide Films on Iron-Chromium Alloy

Masahiro SEO and Norio SATO

Faculty of Engineering, Hokkaido University

A differential method for obtaining the number of component atoms in surface atomic layers was applied to the analysis of thin anodic oxide films on Fe-30Cr alloy surfaces in

aqueous solutions. The surface excess, Γ_{Cr} , Γ_0 and Γ_s on the dividing surface with $\Gamma_{\text{Fe}} \approx 0$ was estimated from the measured in-depth composition profiles. The values of Γ_{Cr} and Γ_0 depend on the anodic potential and the electrolyte used for the film formation. Especially, the ratio of Γ_{Cr} to Γ_0 is higher in 0.5 M sulfuric acid solution than in borate solution of pH 6.48. Further, the validity and usability of the present method are proved by comparing the measured values of the number density of metal atoms in the anodic oxide films with the known values of stoichiometric oxides and hydroxides of iron and chromium.

The 7th International Congress on
Metallic Corrosion, October 4-11, 1978,
Rio de Janeiro, Brasil

Recent Progress in Techniques of Corrosion Study

Norio SATO

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The recent methodological advances in corrosion rate estimation, passivity, and stress corrosion cracking of metallic materials in aqueous environments are outlined. A critical comparison is made of three methods for electrochemical corrosion rate estimation: Tafel line extrapolation, polarization resistance, and charge transfer resistance. *In situ* and *ex situ* techniques for measuring passivity and passive films, such as ellipsometry, specular reflectometry, photoelectric potential, electron spectrometry, ion spectrometry, membrane potential, and mechano-electrochemical techniques, are described. In stress corrosion cracking, the major advances are the fracture mechanics approach, slow strain rate tests, and acoustic emission applied for detecting SCC.

7th International Congress on Metallic
Corrosion, October 4-11 (1978), Rio de
Janeiro, Brasil

Depth Profiles of Passive Films on Iron-Base Alloys

Masahiro SEO and Norio SATO

Faculty of Engineering, Hokkaido University

A differential method for obtaining the exact composition profiles in depth by use of AES and argon ion sputter-etching was applied to the analyses of Fe-30 Cr alloy, 304- and 316- stainless steels potentiostatically passivated in deaerated 0.5 M sulfuric acid solution. From the measured composition profiles in depth, the surface excess of components, Γ_{Cr} , Γ_{Ni} , Γ_0 on the dividing surface with $\Gamma_{\text{Fe}} \approx 0$ was estimated as a function of anodic potential. The surface excesses, depending on the species of alloys, are as follows: $\Gamma_{\text{Cr}} = 1 \sim 3 \times 10^{19}$ atoms/cm²,

$\Gamma_{\text{Ni}} = 4 \sim 8 \times 10^4$ atoms/cm², $\Gamma_0 = 3 \sim 6 \times 10^{15}$ atoms/cm² and $\Gamma_s = 2 \sim 8 \times 10^{14}$ atoms/cm². Specially, the values of Γ_{Cr} and Γ_0 on 316- stainless steel are smaller than those on 304- stainless steel, indicating that molybdenum promotes no enrichment of chromium in passive films. The corrosion resistivity of the alloys is discussed by taking into account both microbreakdown of the film and repassivation of the substrate alloy at breakdown sites. It is concluded that the beneficial effect of molybdenum on the corrosion resistivity can be attributed not to the stability of the film itself but to the acceleration of repassivation process at breakdown sites.

The 3rd Japan-USSR Seminar on
Electrochemistry, October 28, November 1, 1978, Kyoto, Japan

Ion Transport Through Lead Sulfate Film in Lead-Acid Battery

Norio SATO and Masao SAKASHITA

The ion selective property of PbSO₄ has been studied by use of PbSO₄ precipitate membranes produced artificially on cellulose sheets. From membrane potential measurements it was found that PbSO₄ is cation-selective in solutions of KCl, H₂SO₄ and NaSO₄, whereas it is anion selective in Pb(NO₃)₂ solution. When a PbSO₄ membrane separates a Pb(NO₃)₂ solution from a H₂SO₄ solution, it changes to a bipolar membrane exhibiting rectification of ion transport through the membrane. In the discharge process of lead-acid batteries, PbSO₄ formed on Pb anodes also act as a bipolar membrane and tends to suppress the anodic ion transport. In order to ensure a good discharge performance, it is important to reduce the degree of bipolarity established in PbSO₄ layers on the anode.

Symposium on Zeolites. Application
of Zeolites in Heterogeneous Catalysis
and Related Fields. Szeged, Hungary
September 11-14, 1978

A Theoretical Study of the Site Selectivity of the Cations in Zeolite A. For Anticipation of Cation Sites and Catalytic Activity

Masahiro NITTA, Kiyoshi OGAWA and Kazuo AOMURA
Department of Chemistry, Faculty of Engineering

A theoretical approach was attempted for the interpretation of the site selectivities of the exchangeable alkali and alkaline earth metal cations in zeolite A. The cation-lattice interaction energies comprising the electrostatic, repulsion, polarization, dispersion, and charge transfer energies were calculated for the cation at the six- and eight-membered oxygen ring sites

in a simplified model of zeolite A structure. As a result, the site selectivities of the cations were determined as follows: Li^+ , Na^+ , Ca^{2+} and Sr^{2+} ions prefer the six-membered oxygen ring site, whereas K^+ , Cs^+ and Ba^{2+} ions prefer the eight-membered oxygen ring site. These results are in good agreement with those obtained experimentally.

ACS/CSJ Chemical Congress, Honolulu, Hawaii, April 1-6, 1979

Infrared Spectroscopic Investigation for Catalytic Desulfurization of Organic Sulfur Compounds

Masatoshi SUGIOKA, Takayoshi KAMANAKA and Kazuo AOMURA
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The activities of various kind of zeolites for the cracking of ethanethiol and thiophene were examined in a helium stream. Zeolites such as NaY, HY and MeY showed a catalytic activity for the cracking of ethanethiol and the products were ethylene and hydrogen sulfide. HY and MeY except NaY showed the catalytic activity for the cracking of thiophene without gas phase hydrogen and the products were predominantly hydrogen sulfide.

The infrared spectra of ethanethiol and thiophene adsorbed on zeolites suggest that the adsorption states of ethanethiol and thiophene on zeolites depend on the acidic characteristics of zeolites and, in all cases, there is the interaction between these organic sulfur compounds and the surface hydroxyl group or surface oxygen anion of zeolites. It is, thus, concluded that the surface hydroxyl group or surface oxygen anion of zeolites play an important role for the adsorption and cracking of these organic sulfur compounds. Models of adsorption states and the cracking mechanism of ethanethiol and thiophene on zeolites were proposed on the basis of observed infrared spectra.

The 11th ICO Conference on Optics
Today and Tomorrow, Madrid, Spain,
September 10-17, 1978

Spatial Coherence Modulated by an Ultrasonic wave and its Application to Laser Speckle Reduction in an Image Plane

Y. OHTSUKA and Y. IMAI

An ultrasonic wave is found to act as a coherence modulator of light. When a quasi-monochromatic light beam is modulated in phase by a progressive ultrasonic wave, its mutual intensity is expected to vary along an exit plane of the ultrasonic column. This fact has been proven theoretically and experimentally. The experimental results are in good agreement

with the theoretical predictions. It was shown that such a phase-modulated laser beam is applicable to the problem of laser speckle reduction.

11th ICO Conference on Optics Today
and Tomorrow, Madrid, Spain, Sep-
tember 10-17, 1978

Complex Spatial Coherence Measurement by Sinusoidal Phase-modulation

Kazuyoshi ITOH and Yoshihiro OHTSUKA

A method for spatial coherence measurements is demonstrated, which utilizes phase-modulation of light in a wave-front folding type of interferometer. Either wave-front of light in the interferometer is modulated sinusoidally in phase in order to facilitate signal processing as well as servo-signal generation. The interferometer is stabilized well by a servo system. Experimental results are presented which are obtained across phase-fluctuating fields simulated by two kinds of rotating lacquer-coated glass disks.

4th International Thin Film Congress,
Loughborough, U. K., 11-15 September
1978

Composition Dependence of Photo-Induced Refractive Index Changes in Amorphous As-S Films

K. TANAKA and Y. OHTSUKA

Department of Engineering Science, Faculty of
Engineering, Hokkaido University

In many kinds of amorphous chalcogenide films, band-gap illumination produces various structural transformations. This report presents an investigation of the changes in refractive index in connection with compositional variations of $\text{As}_x\text{S}_{100-x}$ films.

Refractive index and thickness of an As-S film were determined from measurements of effective refractive indices of guided optical wave of a wavelength 633 nm. Accuracies of this measuring method are about 0.001 and 10 Å for refractive index and film thickness, respectively.

It was found that reversible temperatures were not always equal to glass transition temperatures in the excess-chalcogen compositions. The irreversible photo-induced change has a fairly sharp maximum at $x=40$. Compositional characteristics of the reversible changes are distinctly different from those of the irreversible; $\text{As}_{40}\text{S}_{60}$ films reveal greater changes in the refractive index than those of $\text{As}_{40}\text{S}_{60}$ films, and the changes are nearly independent of compositions between $x=10$ and 30. A tentative model which accounts for these features by structural properties is proposed.

16th International Conference on
Coastal Engineering, Hamburg, Fed-
eral Republic of Germany, Aug. 27-
Sept. 3, 1978

Outflow Dynamics at a River Mouth

Masakazu KASHIWAMURA and Shizuo YOSHIDA

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When river water flows out onto the sea surface, its dynamical behavior is very singular due to the buoyant force exerted by the sea water and rapid widening of stream lines. Temporal acceleration of the surface flow, an abrupt increase of mixing between the fresh water and the sea water, various types of outflow patterns which are responsible for the discharge amount, etc. are always observable within a near-shore area around a river mouth.

The authors present a development of dynamics which can explain all of these singular phenomena, from a view point of the theory of density current, under the assumption of the flow immiscibility and stationariness. The dominating equation is the same as that of a transonic gas flow, with the exception that the Mach number is replaced by the interfacial Froude number. Two examples show horizontal distributions of numerical values of the interfacial Froude number in the neighbourhood of the mouth of the Ishikari River.

In addition, three types of mixing mechanism occur between the fresh water and the sea water, inside and outside of a river mouth. Those types are classified mainly through experiments, partly accompanied by a theoretical consideration.

6th International Congress of Radia-
tion Research, Tokyo, Japan, May 13-
19, 1979

Relaxation of Trapped Electrons in Hydrocarbons and 2-Methyltetrahydrofuran Irradiated at 4.2 K

Masaaki OGASAWARA and Hiroshi YOSHIDA

The absorption spectra of trapped electrons in 3-methylpentane, 3-methylhexane, and 2-methyltetrahydrofuran matrices γ -irradiated at 4.2 K were examined before and after thermal annealing at 77 K. The annealing causes the blue-shift of the absorption maxima by $1 \sim 2 \times 10^3$ cm^{-1} , the increase in intensity of the absorption maxima, the disappearance of the long-wavelength absorptions, and the decrease in intensity of the short-wavelength absorption tails. Thus the spectra are narrowed without loss of the integrated intensity. These results indicate that the spectral change is not due to the redistribution of the trapped electrons into more stable traps but to the relaxation of them. Difference in chemical nature of the trapped electrons

corresponding to two absorption peaks, at 1200 and 1330 nm, in the MTHF matrix at 77 K is also indicated by the selective scavenging of the their precursors at 4.2 K.

6th International Congress of Radiation Research, Tokyo, Japan, May 13-19, 1979

Two Classes of Trapped Electrons in Glassy Alcohols Irradiated at 4.2 K

Masaaki OGASAWARA, Kunio SHIMIZU and Hiroshi YOSHIDA

Absorption spectra of trapped electrons in γ -irradiated methanol, ethanol, 1-propanol, 2-propanol, 2-buthanol, and 1-pentanol were studied at 4.2 K. The trapped electrons produced at 4.2 K can be divided into two classes: one is ir-adsorbing electrons (e_{ir}) and the other is visible-adsorbing ones (e_{vis}). The apparent large shift of the absorption maximum from ir to visible on annealing at 77 K can be attributed primarily to the selective decay of the e_{ir} and blue-shift and narrowing of the e_{vis} band. Thus the large spectral-shift does not correspond to a progressive solvation of the trapped electrons by the matrix molecule reorientation. It is concluded that the e_{ir} is trapped in alkyl moiety of the alcohol matrices, whereas the e_{vis} electrons is closely associated with the hydroxyl groups.

ACS/CSJ Chemical Congress, Honolulu, Hawaii, USA, April 1-6, 1979

Radiation-Induced Polymerization of Nitroethylene as studied by Low-Temperature Pulse Radiolysis

Masaaki OGASAWARA, Shigeyoshi ARAI and Masashi IMAMURA

A low-temperature pulse radiolysis of nitroethylene in 2-methyltetrahydrofuran was carried out to elucidate the polymerization mechanism of nitroethylene. Immediately after the pulse, an intense, broad absorption due to solvated electrons in ir region and a sharp absorption at 440 nm were observed. The latter consists of short-lived component and long-lived one. The short-lived component is assigned to nitroethylene radical anions resulting from the electron attachment to nitroethylene. With the decay of the nitroethylene radical anion, a broad absorption at 500-650 nm gradually grows. The spectrum is attributed to sigma-bonded dimer-anion or propagating anion produced from it. This is in contrast to the results obtained in the pulse radiolysis of other olefins such as fumaronitrile, maleic anhydride, and methyl acrylate, which have been found to give intense absorption in ir region due to charge-resonance-type dimer-anions. This type of dimer anion does not form from nitroethylene because of the high reactivity of nitroethylene in anionic reaction.

1978 International Conference on Cybernetics and Society, Tokyo-Kyoto, Japan, November 3-7, 1978

Some Non-Metrical Aspects of Visual Space

Masaru SHIMBO, Takahiro YAMANOI and Michiaki KAWAGUCHI

The possibility of a non-Riemannian geometrical formulation of visual space is outlined with reference to Luneburg's theory of Riemannian binocular visual space. Assuming physical and visual space to be an aggregation of microscopic elements, we define affine transformation between these elements. The coefficients of transformation represent the properties of psychophysical recognition by visual sensation. Metric and parameters of connection are introduced with reference to length and parallelism in one of the spaces, so that a general kind of invariants includes a non-Euclidean concept of torsion tensor as well as another non-Euclidean concept of Riemann-Christoffel curvature tensor, representing the indeterminacy of location and direction, respectively. The twisted cord illusion is an experimental evidence of torsion tensor. Hillebrand's parallel and Blumenfeld's distance alley curves, both of which are defined as straight lines in visual space, are explained as geodesics in non-Riemannian visual space under the restriction of teleparallelism, where the space has only torsion without curvature, and of Riemannian configurations, respectively.

The 11-th Symposium on Mathematical Physics, Toruń, Poland, December 4-7, 1978

On the Higher Order Space and Its Physical Interpretation

Michiaki KAWAGUCHI

The higher order space in multiple parameters with the fundamental function F is specially called the metric Kawaguchi space with multiple parameters. In this case, the L -dimensional area in a domain D is given by the integral

$$S = \int_D F du^1 du^2 \cdots du^L$$

for the parameters u^α ($\alpha=1, 2, \dots, L$). And the important Zermelo-Géhénian's condition was found.

For physical interpretation of the higher order space, we discuss the structure of the Solar System to which our planet, the Earth, belongs and of the Galactic System to which the Sun belongs. We shall present an interpretation of an *a priori* possibility of a certain characteristic aspect of such a structure from a mathematical standpoint.

From ancient times, in the history of astronomy, man believed in an obscure notion of the cosmical structure to have an infinite number of steps. A theory proposed by Immanuel

Kant in 1755 was followed thenforth. These are known as the so-called Lambert-Charlier Theory of the cosmolical structure of *infinite steps*. However, the observational reality of present days does not always seem to agree with what the theory seems to imply.

While the new view point we propose will retain to considerable extent the same feature as the classical one in that the ordered structure is not excluded, we need to remark that the steps exhibited by the solar and/or the galaxy are not infinite but finite in number. They are in fact not more than *three*. It seems that there is a theoretical ground for this which can be approached by a mathematical reasoning, that is to say, by the theory of higher order space.

The 11-th Symposium on Mathematical
Physics, Toruń, December 4-7, 1978

Asymmetric Features in Plasticity Space

Masaru SHIMBO

The possibility of a geometrical formulation of asymmetric features in plasticity is outlined in this paper within the framework of non-Riemannian theory of plasticity.

Fifth International Conference on
Positron Annihilation, Lake Yamana-
ka, Japan 8-11 April, 1979

Study of Neutron Irradiation Damage in V and V-C Alloys by Means of Electron Microscopy and Positron Annihilation

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Positron lifetime measurements, transmission electron microscopy and tensile test were carried out to study the annealing behavior of V-0.15 at% C, -0.3 at% C, -1.0 at% C alloys and a pure V. The V-C alloys were aged at 500°C for one hour before irradiation. Neutron irradiation was performed in JMTR up to a dose of 5×10^{20} n/cm² ($E > 1$ MeV) at 500°C.

From the results of positron lifetime measurements, it was found that long lifetime components due to the trapping of positron in voids appeared in all the as-irradiated specimens and the value increased as the annealing temperature was raised. The large voids, the mean

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diameters of which were in the range of 56–84 Å were observed, and further in the V-C alloys, thin platelike subcarbide phases could be seen in the transmission electron microscope (TEM). The void number density increased with annealing temperature and showed a peak number density at around 600°C. A comparison of positron annihilation results with the data of the TEM indicates that invisible microvoids coexist with visible voids.

Ninth International Congress on Electron Microscopy, Toronto, 1978, Vol. 1, 602

Observation of Initial Cracking in Hydrogen-Charged Pure Iron

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The aim of the present work was to investigate the microcracks and microvoids generated by the precipitation of hydrogen charged by cathodic method. Pure iron sheets of 0.5 mm thickness were charged with hydrogen by applying cathodic potentials in electrolytic cells containing 0.1 N-H₂SO₄ and were observed directly with the aid of a scanning and high voltage electron microscope at 650 kV.

The most obvious effect of introducing hydrogen by cathodic charging into iron specimens is the formation of surface blisters and internal cracks. It appeared that hydrogen gas was accumulating on a (100) cleavage or (110) slip plane and expanded to form observable crack, even in the absence of applied stress. The cathodic charging process causes an excess of hydrogen to be introduced into the specimen. Therefore, as the charging proceeds, hydrogen atoms will be absorbed on the inner surface of a cleavage or slip plane and hydrogen gas pressure will be built due to accumulation of the atoms, and then microcracks or microvoids are generated along these planes.

Ninth International Congress on Electron Microscopy, Toronto, 1978, Vol. 1, p. 380

The Voids Formation of Cu-1.5% Fe Alloy During Irradiation in HVEM

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This paper presents the effects of aging on void formation in Cu-Fe alloy during irradiation in the HVEM. After quenching into water from 1263 K and aging at 973 K at various

intervals, electron irradiation was performed at 523 K by using a 650 kV HVEM. Pure Cu was also irradiated to compare with the alloy.

A number of coherent and semi-coherent precipitates by aging the alloy and by electron-irradiation voids were observed in each specimen, but the behavior of void formation was different:

a) for the pure Cu, voids nucleated up to 1 dpa and further grew without changing the void number density, and the void swelling was the largest in this experiment.

b) for the aged specimens, void number densities were proportional to the pre-existing precipitate densities, on the contrary, void swelling were reduced with increasing pre-existing precipitate densities.

c) for the as-quenched specimen, the voids with low density nucleated after irradiation of about 3 dpa and then fine coherent precipitates were observed in the matrix and finally other voids with high density nucleated.

Fifth London International Carbon and
Graphite Conference 1978, September
18-22 London, U. K.

Application of Heavy Oil for Metallurgical Coke Manufacturing

— Fundamental Study on the Coking of Heavy
Oil Coexisting with Coal —

Yuzo SANADA

Coal Research Institute, Faculty of Engineering, Hokkaido University

The mesophase has been obtained successfully from selected reduced crudes and thermal tar pitches by processing and conditioning within a critical temperature range. The mesophase obtained shows coking behavior similar to that of coking coals. This critical mesophase is one of the synthetic coking coals. Based on the coking behaviors of the mesophase, the possibility of application of heavy oil to the metallurgical coke manufacturing by appropriate thermal conversion is recognized.

Various heavy oils are heat treated within a temperature range of 350–580°C to bring about aromatization and polymerization to such an extent that the volatile matter becomes 20–30%. It has become possible to change the quality of heavy oil to have a crucible swelling number of 2–7¹/₂.

The compatibility of the heavy oil and the heat treated products thereof with coal in the course of coking were studied under a polarized-light microscope. Whereas non-coking coal shows no compatibility, it is recognized that between coking coal a compatibility was present.

American Chemical Society, Division
of Fuel Chemistry, Honolulu, Hawaii,
U. S. A. April 2-6, 1979

Temperature Dependence of ^1H n. m. r. Absorption in Coal and Pitch

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Coal Research Institute, Faculty of Engineering, Hokkaido University

^1H n. m. r. spectra of coals and pitches at high temperatures (350–750 K) were observed using a pulsed Fourier transform n. m. r. spectrometer with a high temperature probe. With the increasing temperature, the value of the line width at half-height ($\Delta H_{1/2}$) of a brown coal decreased and then increased rapidly. On the other hand, tar pitches indicated that the values of $\Delta H_{1/2}$ remained small over a wide temperature range. It is found that there is an excellent relation between temperature dependence of the line width and optical texture of the resultant coke.

In order to improve the resolution of a spectrum at higher temperatures, a home-built shim system was used. The n. m. r. spectra of ethylene tar pitch which shows two discrete lines corresponding to aromatic and aliphatic protons were observed.

Temperature dependence of hydrogen aromaticity (f_{Ha}) was obtained from the spectra at high temperatures. It is found that the value of f_{Ha} attains a minimum at about 610 K and increases drastically from 0.4 to 0.6 with the increasing temperature. Variation of f_{Ha} may be accompanied by the process of aromatization and/or the elimination of aliphatic chains from the aromatic ring system.

Chemical reactions such as pyrolysis, depolymerization, polycondensation and so on can be monitored directly by using the high-temperature technique. Moreover, application of the technique seems to be promising for studying the mechanism of mesophase formation as well as that of coal liquefaction.

14th Biennial Conference on Carbon
The Pennsylvania State University
June 25–29, 1979

Carbonization of Heavy Oil-Characteristics of Heavy Oils Heat Treated

Y. KUMURA*, H. YAMASAKI* and Y. SANADA**

The early stage of carbonization of heavy oils is one of the most important processes that affect the chemical and physical properties of the final carbon products.

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The behavior of β -fraction, the sizes of mesophase spherules and transformation patterns of the mesophase in relation to their fluidity have been studied to develop an understanding of the nature of this process.

In the early stage of the craponization reaction, the quantity of β -fraction depends on the aromaticity of the γ -fraction and not on the kind of heavy oil. The average sizing of mesophase spherules depends both on the aromaticity of the γ -fraction and on the type of heavy oil. The texture of mesophase is affected by the maximum fluidity of, and the type of heavy oil.

American Chemical Society, Division
of Fuel Chemistry, Honolulu, Hawaii,
U. S. A. April 2-6, 1979

Chemical Structure of Heavy Oils Derived from Coal Hydrogenation by Mass Spectroscopy

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Coal Research Institute, Faculty of Engineering

Coal liquefaction heavy oil derived from coal hydrogenation reaction obtained by the University of Utah's process was separated by liquid chromatography of modified USBM API 60 method into saturate (Fr-P), mono-(Fr-M), di-(Fr-D), tri- and tetraaromatic rings (Fr-T) and polyaromatic and/or polar compounds (Fr-PP). Then, the respective compound types were fractionated further by GPC according to their respective molecular size (Fr-M-1~7, D-1~7, T-1~7 and PP-1~7). Individual GPC fraction for compound type series were subjected to measurement of low resolution GC-MS analyses or by a direct insertion method using the low voltage ionization technique. Mass spectra were recorded repeatedly by multiscan operation and were estimated by computer to obtain the integrated mass spectra. Consequently, it was shown that Fr-M-1 to 7 consist mainly of alkylbenzenes and naphthenobenzenes and Fr-D-1 to 7 alkyl naphthalenes and naphthenonaphthalenes as the major components (fa: Fr-M < Fr-D < Fr-T), therefore it can be considered that the separation of LC into compound types was satisfactory. Considerable amounts of benzene ring and naphthalene ring compound series have one to three naphthenic rings joined to aromatic rings. The total numbers of carbon for alkyl group substitution attached to these aromatic and naphthenic rings have a distribution in a range from 0 to 31 for Fr-M and 0 to 21 for Fr-D, indicating a decrease of carbon numbers with the increasing elution volume of GPC.

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14th Biennial Conference on Carbon
The Pennsylvania State University
June 25-29, 1979

Carbonization of Heavy Oils-Chemical Constituents of the Residual Products Formed in the Early Stage of Carbonization

H. YAMASAKI*, Y. KUMURA*, T. FURUTA** and Y. SANADA***

The purpose of the present report is to present the characteristics of the chemical constituents of carbonaceous residue formed in the early stage of carbonization of various heavy oils.

The changes of hydrogen/carbon atomic ratio and chemical structural parameters of benzene soluble and quinoline insoluble were measured as a function of heat-treatment temperature. From these results, it would appear that the chemical constituents of the benzene solubles of cracked residues do not materially differ from the mesophase, because the fraction of aromatic hydrogen value of the mesophase (or quinoline insoluble) has nearly the same value of benzene insolubles. In the case of the straight run residues on the other hand, the increase of aromaticity is probably one of the remarkable features that takes place during mesophase transformation.

Sixth International Biophysics Congress,
September 3-9, 1978 Kyoto, Japan

Proton Magnetic Resonance Study of Living Mammals

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The motions of free water or water convertible to free water in biological bodies in the living state have been investigated by means of the "Temperature-Gradient Technique of NMR", and the intensity of the transient response spectra to the temperature change has been measured. The intensity of the spectra obtained for living mammals (mice) shows oscillatory behaviours as a function of temperature. On the other hand, for a mouse whose central nerve was anesthetized no such oscillatory behaviour was observed under the same experimental conditions. This means that the observed oscillations are due to the order-disorder transition of the orientational state of the water in voluntary muscles in the living mice. It may be concluded that the intensity of the spectra reflects the change of the motion of the contractile

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proteins in the voluntary muscles of the whole body of the mice. It is expected that the information on the activity or degree of health of the living body may be obtained from the pattern of the oscillation of the temperature-gradient spectra.

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Carbon-13 Spin Lattice Relaxation Study of Silk Protein

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Carbon-13 spin-lattice relaxation measurements of liquid silk protein in the silk gland have been made both in the native and denatured state. It has been found that the relaxation process consists of two exponential decays for the carbon of glycine in the native silk protein. On the other hand, a single exponential decay was observed for the denatured one.

From these results it has been suggested that the carbon of glycine in the native silk protein takes two different states. This may result from the difference in the position of glycine in the folded chain (fold A & B) of fibrous protein. This sort of difference in the conformation can not be detected by the carbon chemical shift.

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High Temperature PMR Study of Molten Polymer (PVC)

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The dynamic structure of molten polymer PVC (Poly-vinyl chloride) undergoing the process of pyrolysis has been studied using line shape and spin-lattice relaxation time in a homogeneous magnetic field in the temperature range from 100°C to 500°C. Well resolved spectra were observed for thermally decomposed molten PVC. The aromatization process was observed directly from the change in intensity of the aliphatic and aromatic protons. In order to obtain information on molecular motion at high temperature, the temperature dependences of spin-lattice relaxation times were measured. The variation of spin-lattice relaxation times (T_1) with temperature for PVC showed two minima, 65 msec at 140°C and 100 msec at 350°C, and

a maximum at 620 msec at 300°C under nitrogen atmosphere. From the measurements of the high resolution PRFT spectra, it is suggested that the relaxation process is influenced largely by free radicals produced during the pyrolysis. Also from the analysis of free induction decay, three components of the T_2 were separated and the growth of a liquid crystalline phase could be observed at 450°C.