liquor due to the insoluble nature of the electrode material results from the use of lead dioxide coated anodes. Two tables on cel-performances and 11 references.

53. **Thermodynamics in chemical process design**

P. K. Bishnoi (Chem. Age of India, **16**, 506, 1965). Thermodynamics works as a powerful tool to avoid the searching of some fantastic possibility and belps by indicating likely occurrence in understanding research for new and interesting synthesis of products. This discusses these aspects; 9 references.

54. **Electrochemistry makes new organometals—**

(Chem. and Engg. News, **43**, No. 16, 46, 1965). Organometallic anions and radical-anions serve as electron transfer sources.

55. **Fresh water from the sea —**

E. Marcar (Copper, No. 24, 3, 1965). Introduction, water desalting processes, the place of copper metals; bibliography.

56. **Electrolytic chromatography —**

T. Fujinaga, C. Takagi and S. Okazaki (Intenational Chem. Engg., **5**, 374, 1965). Development of a new chromatographic separation method, combining the use of electrolytic deposition as an elutiou method for separation and determination of small amounts of metal ions.

—T. L. R.

(B) Electro-Organic Chemistry

ORGANIC REDUCTIONS & OXIDATIONS

1. Study of the processes of reduction and electro-reduction of organic substances on a Pd electrode. A. V. Shashkina and I. I. Kulakova, Zh. Fiz. Khim. 37, 1718-25 (1963).

The paper deals with the processes of reduction and electro-reduction of a series of organic substances on a palladinized Pd electrode in O. 1N H_2SO_4 and KOH.

2. Effect of functional groups on the process of electroreduction of unsaturated organic substances — A. V. Shashkina and I. I. Kulakova, Zh. Fiz. Khim. 37, 1726-32 (1963).

The functional groups affect the electroreduction by the electron mechanism. This has been discussed by a systematic study of the reduction of a number of organic substances on a Pd electrode in O. 1N H_2SO_4 and KOH.

3. Electrochemical oxidation of 9-arylamino anthracences in non-aqueous medium and (formation) complexes by charge transfer —Georges Cauquis, Jean Pierre Billon. Jacques Raison and Yves Thiband, Compt, Rend **257**, 2128-30 (1963).

Discusses the formation of free radical intermediate in the oxidation of 9-arylamino annthracene, which is identified by its electron para magnetic resonance spectrum.

4. Catalytic hydrogenation and electrochemical reduction of dimethyl acetylene carbinol on dispersed Pd-Ni alloys. P. A. Karpova and I. P. Tverdovskii, Tr. Gos. Inst. Prikl. Khim. No. 49, 230-3 (1962). C. A. **60**, 1153 (1964).

The effect of increasing the nickel content in the binary alloys of Pt-Ni and Pd-Ni on the catalytic hydrogenation of a solution of dimethyl acetylene carbinol is discussed.

5. Catalytic hydrogenation and electrochemical reduction of maleic acid on Pd-Pt alloys. R. A. Karpova and I. P. Tverdovskii, Tr. Gos. Inst. Prikl. Khim. No. 49, 215-23 (1962). C. A. **60**, 1155 (1964).

The catalytic properties of Pt-Pt alloys for the reduction of maleic acid is compared with their hydrogen overvoltage.

6. Mechanism of the electrochemical oxidation of formic acid in acid electrolytes — A. Kutschker and W. Vielstich, Electrochim. Acta, **8**, (12), 985 (1963).

Current-voltage plots with formic acid in acid electrolytes at noble metal electrodes show in general three anodic peaks. The first peak represents the splitting of the acidic H atom. At second and third peaks, non-specific electrochemical or chemisorbed reactions occur.

7. Comparative voltammetric study of methanol oxidation and adsorption on noble metal electrodes in $HClO_4$ solutions — M. W. Brieter, Electrochim. Acta, **8**, (12), 973 (1963).

8. Electrochemical studies of reducible aromatic compounds — Robert Edward Visco (Univ. of Illinois, Urbana), Dissertation Abstr. **24**, 489 (1963). C.A. **60**, 3714 (1964).

9. Electrochemical study of kinetics of a chemical reaction coupled between two charge transfer reactions — G. S. Alberts and Irving Shain, Anal. Chem. **35** (12), 1859 66 (1663).

The reduction of p nitrosophenol was studied by potentiometric, polarographic and

chronopotentiometric techniques. The coulometry confirmed that the overall reaction involves 4 electrons and the product was identified as p-aminophenol.

10. The anodic oxidation of methanol and formic acid and the reductive adsorption of CO_2 — J. Giner, Electrochim. Acta, **9**, 63-77 (1964).

The study is done by following the anodic fast potential-sweep method made on platinized Pt in acid solutions containing MeOH and HCOOH.

11. Kolbe electrolytic synthesis IV. Theoretical investigation of the mechanism by standard potential calculations — Linnart Eberson, Acta. Chem. Scand. **17**, 2004 (1963).

From the standard potential calculations, the primary electrode reaction in the Kolbe electrolysis was assumed to be $RCOO^- \longrightarrow R^{\cdot} + CO_2 + e$ followed by $R^{\cdot} \longrightarrow R^+ + e$ if the ionisation potential of $R^{\cdot}$ is less than 8 eV.

12. Electro-organic preparations: XIV: Reduction of a chlorinated cyclohexane derivative—Henning Lund, Acta. Chem. Scand. 17, 2139 (1963).

The cyclic ester ketal of 2-methyl-4, 5, 6 trichlorocyclohex-2 en-1 one was reduced in acetate buffer at pH 5 containining 45% EtOH at a cathode potential of –1.2V vs SCE and this reduction was shown to consume 4 electrons per mole.

13. Ethyl alcohol oxidation at platinum electrodes—R. A. Rightmire, L. L. Rowland, D. L. Boos and D. L. Beals. J. Electrochem. Soc. **111**, 242 (1964).

The oxidation of EtOH at Pt electrodes was studied by a.c. differential capacitance measurements, current density measurements, rate of change of c.d. with time, constant current, voltage-time tracer and product analysis.

14. The kinetics of the electrolytic reduction of nitrobenzene. 1. Progess with time of the nitrobenzene decrease at various current densities and temperatures determined by polarographic measurements — Th. N. Skulikidis, K. Sarropoulos and S. Chanos, Kolloid. Z. 193, 45 (1963). C.A. **60**, 6480 (1964).

The reduction of nitrobenzene in alcoholic HCl is a first order reaction which increases with increase in c.d. upto 2.35 amp/dm² and then remains constant. The activation energy for the reduction is 2.28 Kcal/mole at 7-60°C.

15. The scheme of anodic condensation of monomethyl adipate. M. Ya. Fioshin and L. I. Kazakova. Dokl. Akad. Nauk. S.S. S.R. **152**, 1132 (1963).

The formation of ester of sebacic acid from the electrolysis of sod. salt of monomethyl adipic acid is studied. The maximum yield is obtained at c.d. of 5-7 amp/dm² in an alc. medium.

16. The use of insoluble anodes in the electrochemical synthesis of organic substances—M.Ya. Fioshin and L.I. Kakakova, Khim. Prom. 1963 (10), 760-2. C.A. **60**, 6481 (1964).

The use of Pt, PbO_2, Ti, Ta and graphite anodes in the synthesis of organic substances is reviewed.

17. The electrolysis of some nitro-substituted mono and diphenylacetic acids—B. Wladislaw and A. Giora, J. Chem. Soc. (1964), 1037-1040.

With the exception of 4,4′ — dinitrodiphenyl acetic acid all the nitrophenyl acetic acids give the corresponding nitrobenzaldehydes and nitrobenzyl alcohols.

18. Electrochemical nitration of benzene to nitrobenzene. R. Babic and T. Markovic, Kem. Ind. **11**, 476 (1962). C.A. **60**, 7680 (1964).

The optimum conditions for the electrochemical nitration of benzene was: for 44 g of benzene a reaction time of 50 minutes with 73.7 g H_2SO_4, 30% excess of HNO_3 and a c.d. starting from 0.055 amps/cm² (yied 85%).

19. The electroreduction of aromatic nitrocompounds in non-aqueous solutions. I. The reduction of nitrobenzenes in acid liquid ammonia solutions — W. S. Harris and G.B. Matson, U.S. Dept. Com. Office Tech. Serv. AD 293, 446 (1962) pp. 27. C.A. **60**, 8891 (1964).

The paper deals with the reduction of nitrobenzene at low rate using a Hg cathode in acid liquid ammonia and provides a scheme of reaction mechanism.

20. Comparative study of the reduction of aromatic aldehydes at stationary and rotating amalgamated cathodes — H. V. K. Udupa, G. S. Subramanian, K. S. Udupa and K. Natarajan, Electrochim. Acta, **9**, 313 (1964).

The two different courses for the reduction of benzaldehyde, salicylaldehyde and anisaldehyde has been studied by using the cathode polarisation vs. current density plots.

21. Electrochemical oxidation of some reducing agents on rotating Pt disc electrodes. L. S. Reishakhrit and N. S. Sukhobokova, C.A. **60**, 10,218 (1964).

The diffusion coeffts. of some of the reducing agents like hydroquinone, metol, p-aminophenol and p-phenylenediamine has been calculated by oxidation in O.5N Na_2SO_4 + 10^{-5}N H_2SO_4 at 15°–45° using Levich equation.

22. Dual cathode technique for the electrolytic reduction of m-dinitro-benzene to 2:4-diaminophenol — K. S. Udupa, G. S. Subramanian and H. V. K. Udupa, Bull. Acad. Polon. Sci. Ser. Chem. **9**, 419 (1961).

By using two cathodes namely monel till the reduction of $-NO_2$ to -NHOH and copper from -NHOH to $-NH_2$ stage, the yield of 2:4-diaminophenol increased from 51% to 64%.

23. Coulometric oxidation of hydroquinones —K. S.V. Santhanam and V. R. Krishnan, Z. Physik. Chem. **39**, 137 (1963).

The quantitative oxidation of hydroquinone has been obtained in N H_2SO_4 as electrolyte at a controlled potential of + 1.3V vs. SCE.

24. Anodic oxidation of formic acid at platinum electrodes. M. H. Gottlieb, J. Electrochem. Soc., **111**, 465 (1964).

Open circuit potential of the system HCOOH, H_2SO_4, Pt is a mixed potential determined by the direct oxidation of formic acid and cathodic reduction of H ion. The value for exchange current for formic acid oxidation is calculated to be less than 10^{-10} amp/cm².

25. Influence of adsorption of neutral molecules and organic cations on the kinetics of electrode process. A. N. Frumkin, Electrochim. Acta, 9, 465 (1964).

The dependence of the kinetics of electrode process on the adsorption of the reacting particles at small coverages as well as at coverages approaching unity is discussed.

26. Electrolytic production of metanilic acid. II. Application of cells with the flowing electrolyte. N. E. Khomutov and T. N. Skovnyakov. Zh. Prikl. Khim. 36, 1772 (1963).

Current yields of 85% were obtained in the electro-reduction of a flowing solution of sodium m-nitrobenzene sulphonate (O.O4M) in O.25M H_2SO_4 using Pt, Pb and graphite anodes and Fe and Zn cathodes at 80°.

27. Influence of the electromechanical and adsorption characteristics of graphites on the direction of the process of electrohydrogenation of some ketones—V. A. Smirnov, M. G. Smirnova, L. A. Demchuk and D. P. Semchenko, C. A. **60**, 12,698 (1964).

The electro-reduction of acetone was studied on different types of graphite, which were investigated by X-rays. The main products were iso-PrOH and pinacol. Their relative yields depend on the graphite used, the temperature and the current density.

28. Electrohydrogenation of adiponitrile. V.G. Khomyakov and D. Ya. Gusakova. C. A. **60**, 12,698 (1964).

The hodrogenation of adiponitrile to hexamethylenediamine is described using a nickel electrode prepared by electrolysis of Ni $(NH_4)_2(SO_4)_2$ at a c.d. of 3.6 or 20 amp/dm².

29. Electrochemical oxidation of formic acid on Pt. C. W. Fleischmann, G. K. Johnson and A. T. Kuhn, J. Electrochem. Soc., **111**, 602 (1964).

Discusses the anodic oxidation of formic acid on Pt black electrodes in 5N H_2SO_4.

30. Electrochemical processes in the quinone-hydroguinone system. Liu-An Yao, Yu. B. Vasilev and V. B. Bagotskii, Zh. Fiz. Khim. **38**, 205 (1964).

The electro-oxidation of hydroquinone and reduction of quinone were studied on rotating Pt electrodes by determining the polarisation curves both in acid and alkali solutions.

31. Mechanism of electroreduction of some organic substances on Rh. IV. T. M Grishina, G. P. Khomchenko and G. D. Vovchenko. C. A. **60**, 14123 (1964).

The effect of As and Hg poisoning of Rh-electrode catalyst on the electroreduction of eroton-and butyraldehydes and acetone in O. 1N H_2SO_4 is described.

32. Effect of the material of an electrode on the electro-reduction of streptomycin to dihydrostreptomycin. N. E. Khomutov, V. V. Skornyakov and T. P. Fadeeva. Zh. Fiz. Khim. **38**, 102 (1964).

The cathode materials studied are Pb, Sn, Cd, Zn graphite and Zn-Hg in the form of perforated cylinder. The anodes are also cylindrical and the electrodes are separated with a diaphragm.

33. Electrochemical and catalytic hydrogenetion of nitromethane on Pt. G. A. Bogdano-

vskii, G. P. Khomchenko and A. I. Shlygin. C.A. **60**, 14123 (1964).

Catalytic and electrochemical hydrogeneration of nitromethane on platinized Pt electrode was studied in acidic and alkaline media.

34. Reduction of unsaturated compounds on Pd electrode in acidic, basic and alcohol-acidic media. I. I. Kulakova and A. V. Shashkina. C.A. **60**, 14124 (1964).

Processes of adsorption and reduction of allyl chloride, allyl cabinol, acrolein, acrylic acid, methcrylic, acid, vinyl acetate, methly acrylate and vinylethly ether were studied using Pd electrode in O. 1N H_2SO_4, KOH and in 50% ETOH.

35. Electrochemical reduction at controlled potential of some para substituted nitrobenzenes — Michel Le Goyader, Compt. Rend. **258**, 947 (1964).

Electrochemical reduction of substituted nitrocompounds in H_2SO_4 at a Hg cathode occurs either by a single 6 electron stage or leads to the formation of hydroxylamine and of amine. The potential for the controlled potential reduction and other conditions of electrolysis of various p-substituted nitro compounds are given.

36. Electro-organic preparations XIII. Reduction of isonicotinic amide and related compounds. Henning Lund, Acta. Chem. Scand. **17**, 2325 (1963).

The various reduction products of isonicotinamide in different buffer solutions at controlled potentials is described.

37. The mechanism of the electrochemical oxidation of oxalic acid. J. W. Johnson, H. Wroblowa and J. O. 'M. Bockris, Electrochim. Acta, **9**, 639 (1964).

The oxidation of oxalic acid on platinized Pt was studied at 80 C in a solution of H_2SO_4, Na_2SO_4 and NaOH. The suggested mechanism of the oxidation is: undissociated acid is the reacting species; both electrons are supplied by organic species and the rate determining step is the second charge transfer.

38. The electrolytic oxidation of simple aldehydes and alcohols at platinum electrodes. C. Liang and T. C. Franklin. Electrochim. Acta, **9**, 517 (1964).

A study of the electrolytic oxidation of MeOH, EtOH, iso-PrOH, CH_2O etc. in the potential region between 0.3V (SCE) and oxygen evolution by using cyclic voltammetary, chronopotentiometry, potential decay and controlled potential teechnique is disscussed.

39. Engineering aspects of scaling-up electro-organic processes — Robert B. MacMullin, Electrochem. Technol. **2**, 106 (1964).

A methodical approach to electro-organic process development is outlined. Applications for such products as dialdehyde starch, p-aminophenol, adiponitrile etc., are discussed in the light of the same.

40. The mechanism of oxidation of low molecular weight organic compounds at platinum electrodes in aqueous solutions. Thomas C. Franklin and Charles Liang, U.S. Dept. Comm. Office. Tech. Serv. AD 286,472, pp. 146 (1962). C.A. **61**, 280 (1964).

Electrode processes for the oxidation of some low molecular weight organic compounds at Pt electrodes in 2N H_2SO_4 and 2N NaOH has been described.

41. The relative electrocatalytic activity of noble metals in the oxidation of ethylene. Harald Dahms and John O'M Bockris, J. Electrochem. Soc., **111**, 728 (1964).

Electrocatalytic activity of 5 noble metal electrodes (Au, Kr, Pd, Pt and Rh) are compared by a study of the oxidation of C_2H_4 with these electrodes in N H_2SO_4 at 80°C.

42. The electrochemical oxidation of ethylene, an experimental study. Mino Green, Jan Weber and Vera Drazic, J. Electrochem. Soc., **111**, 721 (1964).

Both steady state and time dependent current-voltage curves of the anodic oxidation of C_2H_4 were studied at the electrode Pt (Pt)/M NaOH, C_2H_4 (dissolved). The partial pressure of C_2H_4 had no effect on the steady state current voltage curve in the Tafel region. The authors have concluded that the discharge of OH-ion plays the important role in the rate determining step.

43. The electrochemistry of diphenyl picryl hydrazyl. Emanuel Solon and Allen J. Bard, J. Am. Chem. Soc., **86**, 1926 (1962).

The electroreduction and oxidation of diphenylpicryl hydrazyl, a stable free radical, at a Pt electrode in methyl cyanide solution were investigated by using voltametry, chronopotentiometry and controlled potential coulometry.

44. Controlled potential electrolysis of hindered half-esters. W. H. Harwood, R. M.

Hurd and E. S. Snavely Jr. Ind. Eng. Chem., Prod. Res., Develop. 3, 105 (1964).

Half esters of malonic, succinic and glutaric acids are electrolysed with Pt electrodes in MeOH solutions at various controlled anodic potentials. The ultimate yield from coupling of half-esters does not depend much on the anodic potential.

45. Adsorption of organic substances on hydrogen-adsorbing metals as dependent on the elctrode potential. A. N. Frumkin, Dokl. Akad. Nauk SSSR, **154**, 1432 (1964).

A relation has been derived for dependence of adsorption of the organic substances on hydrogen adsorbing metals on the electrode potential.

46. Significance of the critical potential in the Kolbe reactions. B. E. Conway and M. Dzieciuh, Proc. Chem. Soc., **1962**, 121-2.

At Pt, Au or Pd electrodes in anhydrous CF_3COOH containing CF_3COOK and saturated with CO_2, 96% of C_2F_6 is obtained and no oxygen is evolved. In this reaction a critical potential is reached at a limiting current density of 10^{-5} amp/cm^2 with N CF_3COOK in CF_3COOH and 10^{-1} amp/cm^2 with N HCOOK in HCOOH or H_2O. This has been explained on the basis of the formation and removal of a metal 'carboxylate' on the electrode.

47. Electrochemical reductions, by potential control of some para substituted nitrobenzenes. Michel Le Guyader and Maurice Le Demezet, Compt. Rend. **258**, 3046 (1964).

The reduction of p-nitrophenol, p-nitrophenetole, p-nitrophenylacetate, p-nitrophenylbenzoate, p-nitro-N-phenylaniline, p-nitroacetanilide and p-nitrobenzanilide on a Hg cathode in H_2SO_4 has been studied at various controlled cathodic potentials.

48. Effect of As on catalytic and electroreduction of crotonic and maleic acids on Pt. L. Ya. Krasinikova, G. P. Khomchenko and G. A. Vovchenko, C.A. **61**, 1509 (1964).

Discusses the decrease of the rate of catalytic and electroreduction of crotonic and maleic acids due to arsenic poisoning of Pt.

49. Oxidation-reduction potentials of heteroannularly disubstituted ferrocenes. E. G. Perevalova, S. P. Gubin, S. A. Smirnova and A. N. Nesmeyanov, Dokl. Akad. Nauk. SSSR, **155**, 857 (1964).

The effect of the two substituents in different rings of ferrocene on the redox potentials was found to be additive. The value of the redox potentials are also given.

50. Electrochemical reduction of polynuclear carboxylic acids. Walter Fuchs and Ansgar Schiffers, Chemiker Zg. **88**, 188 (1964).

The study of the reduction of phenanthrene-9-carboxylic acid in alkaline medium is discussed.

51. Low temperature electrochemical oxidation of hydrocarbons. G. J. Young and R. B. Rozelle, Fuel Cells, **2**, 216 (1961) (Pub. 1963).

Polarization behaviour of electrodes of porous graphite impregnated with Pt in electrolytes of 6M H_2SO_4 and 6M KOH at 90° was studied and the importance of this study for employing in fuel cells examined.

52. The electrochemical oxidation of hydrocarbons in fuel cells. C. E. Heath and C. H. Worsham, Fuel Cells, **2**, 182 (1961) (Pub. 1963).

This paper deals with the study of the electrochemical oxidation of C_2H_6 in a cell employing specially developed catalysts.

53. Adsorption and oxidation of formic acid on smooth Pt electrodes in perchloric acid solutions. S. B. Brummer and A. C. Makrides, J. Phys. Chem. **68**, 1448 (1964).

The adsorption and oxidation of HCOOH on smooth Pt electrodes were studied in $HClO_4$ solutions by anodic and cathodic chronopotentiometry and by potentiostatic techniques.

54. The electrochemical generation and the visible spectra of free radical anions of the mononitronaphthalene and nitromesitylene in dimethylformamide. W. Kemula and R. Sioda, J. Electroanal. Chem. **7**, 233 (1964).

The electrochemical generation and the polarographic determination of the free radical anions of alpha-and beta-nitronaphthalenes and of nitromesitylene are discussed. The spectra of the free radical anions and the u.v. spectra of the nitrocompounds are correlated.

55. Electrochemical method of preparation of tetramethly ammonoum hydroxide with application of ion-exchange membranes. N. A. Dzbanovskii, V. V. Tsodikov, L. D. Borkhi and R. T. Khleborodova C.A. **61**, 3925 (1964).

The paper deals with the preparation of tetramethylammonium hydroxide by the electrolysis of tetramethly ammonium iodide solutions between graphite and iron electrode in an electrodialysis cell separated into three compartments by cation exchange membrane and by a ceramic daiphragm at a c.d. of 3 amp/dm^2.

56. Combined preparation of tetraethyl lead and tetramethly lead. H. Lehmukuhl, R. Schaefer and K. Ziegler. Chem. Ingr. Tech. **36**, 612 (1964).

A new synthesis of $PbMe_4$ from lead and methly chloride is described and the reaction mechanism equations are given.

57. Mechanism of the electro-oxidation of acetylene on Pt. James W. Johnson, Halina Wroblowa and John O'M. Bockris. J. Electrochem. Soc., **111**, 863 (1964).

The oxidation of C_2H_2 on platinized Pt was studied at 80°C in H_2SO_4 + Na_2SO_4 and NaOH solutions of constant ionic strength. A mechanism for the reaction has been proposed based on the adsorption of C_2H_2 with the OH radical.

58. Free radical reactions by organic electrode processes. VI. Electrolytic coupling of esters. Toshihiko Okube and Shigeru Tsutsumi, C.A. **61**, 6637 (1964).

The preparation of tetra ethyl ethane tetracarboxylate by electrolysing Na-diethylmalonate in non-aqueous alcoholic solutions is described and the mechanism of the free radical reactions are shown.

59. Electrochemical oxidation of hydrocarcarbons. Raymond Joseph Jasinski, J. Huff, S. Tomter and L. Swettle, C.A. **61**, 7935 (1964).

The electrochemical oxidation of some gaseous hydrocarbons, MeOH and HCOOH, all soluble in the acid electrolytes, which can be utilised in the fuel cell, has been described.

60. Electrochemical reduction of formaldehyde on a single crystal of zinc. V. N. Nikulin, Zh. Fiz. Khim. **38**, 1103 (1964).

Electrochemical reduction of formaldehyde on 2 planes of a single crystal and on polycrystals of zinc was studied polarographically in 0.1M KOH at a constant current of 30 mA.

61. The electrochemical oxidation of formic acid in the presence of dimethly formamide. Sidney D. Ross, Manuel Finkelstein and Raymond C. Petersen, J. Am. Chem. Soc., **86**, 2745 (1964).

The effect of $HCONMe_2$ on the electrolysis of $KHCO_2$ in H_2CO_2 and of KOAc in HOAc was studied in a cell with 1 sq. cm. Pt electrodes 0.6 cm. apart at 0.40 amp.

62. Electrochemical reduction of porphyrins. H. H. Inhoffen and P. Jaeger; Tetrahedron Letters. **1964** (21), 1317.

Mesoporphyrin di-Me ester when electrolysed in a deuterated solvent at a Hg electrode at a potential somewhat above the polarographic half-wave at 0.51 vs. Ag/AgCl, KCl (satd) gave the corresponding phlorine.

63. Mechanism of electrochemical reduction of alkyl bromides. John W. Sease, Patricia Chang and Joyce L. Groth. J. Am. Chem. Soc., **86**, 3154 (1964).

The observed electrochemical reduction of 1-bromobicyclo-(2.2.2) octane and 1-bromobicyclo-(2.2.1) heptane has been explained as to proceed by the displacement of Br to give an alkyl free radical and Br-.

64. Removal of inhibition to formation of Kolbe products by electrolysis of mixtures I. Propionic and 3-phenylpropionic acids —F. F. Rawlings, G. W. Thiessen, T. G. Lee, M. J. Murray Jr. & J. L. Seago, Electrochem. Technol. **2**, 217 (1964).

The benzenoid inhibition to aqueous Kolbe electrolysis of 3-phenylpropionate ion is removed by the simultaneous electrolysis of the uninhibited propionate ion. The products suggest both a free radical and a corbonium ion mechanism.

65. Electrochemical chlorination of n-dodecane. F. N. Ruchlen, G. B. Wills and H. M. Fox. J. Electrochem. Soc., **111**, 1107 (1964).

The paper deals with the chlorination of n-dodecane at a porous carbon anode in an electrolysis cell containing 20% HCl electrolyte. The ratio of the products of monochloro dodecane to dichlorododecane is correlated with the calculated statistical distribution assuming a free radical mechanism.

66. Behaviour of some organic compounds on ruthenium electrode catalyst — T. N. Stoyanovskaya, G. P. Khomchenko and G. D. Vovchenko, C.A. **61**, 11617 (1964).

The effect of acetone, butyraldehyde and crotonaldehyde on the potential of an electrolytically deposited (from alk. solution) Ru electrode in 0.1N H_2SO_4 has been discussed.

67. The Becquerel effect of dissolved organic compounds I. The electrochemical nature of the effect — Heinz Mauser and Ulrich Sproesser, Ber. **98**, 2260 (1964).

The potential of a metal electrode immersed in an organic solution can change due to radicals which are formed in photochemical reactions of dissolved organic compounds. The Becquerel effect of such solutions may be obtained by this phenomenon and the possibility of using this effect for a study of photochemical reactions is discussed.

68. Electro-oxidation of ethylene glycol in an alkali medium. V. S. Daniel-Bek and G. V Vitvitskaya, Zh. Prikl. Khim. **37**, 1724 (1964).

The mechanism of the oxidation of ethylene glycol has been studied in 6.5M KOH with electrodes of C containing 30 % Pd and electrodes of skeleton Ni. The process of oxidation is mainly consisted of liquid phase catalytic dehydrogenation.

69. On the anamalous gas evolution in the electro-oxidation of absolute methanol — Kazuo Saski, Chisato Hamaguchi and Shigeo Nagaura — Bull. Chem. Soc., Japan, **37**, 1086 (1964).

The number of CH_3O radicals formed at the anode which subsequently disproportionate to HCHO and H, has been found to account for the accumulation of the gas in the anode compartment.

70. Electrochemical reduction of acrylonitrile in dimethylformamide — Stefan Lazarov, Assen Trifonov and Todor Vitanov— Z. Physik. Chem. (Leipzig) **226**, 221 (1964).

The formation of dianion of acrylonitrile as the intermediate product and further reaction of this with a molecule of acrylonitrile or two hydrogen ions has been given as the probable mechanism for the formation of adiponitrile or propionitrile respectively.

71. Preparation of sorbitol by electrolytic reduction of glucose III. — Gheorghe Weiss, C.A. **61**, 12951 (1964).

The optimum conditions for obtaining maximum current yield values has been studied in detail. The method of recovery of sorbitol is also discussed.

72. Hydrogen transfer IV. Reductive fission of quarternary ammonium salts at a lead or mercury cathode—Leopold Horner and Anton Mentrup, Ann. **646**, 49 (1961), C.A. **61**, 12952 (1964).

The electrolysis of aqueous solutions of 30 quarternary ammonium salts using lead cathode has been studied and the mechanism for the formation of hydrocarbon or the tertiary amine is discussed.

73. The electrochemical oxidation of acetic acid in the presence of aromatic hydrocarbons — Sidney D. Ross, Manuel Finkelstein and Raymond C. Peterson, J. Am. Chem. Soc., **86**, 4139 (1964).

The electrochemical oxidation of acetic acid in the presence of benzene, ethylbenzene, tert-butylbenzene, mesitylene, naphthalene and phenylacetate is studied. The many paths by which non-gaseous products of acetoxyl and methyl derivatives with substitution occurring in both the ring and side chain are discussed.

74. The electrochemical oxidation of methanol in fuel cells — M. Pringent — C.A. **61**, 14178 (1964).

75. A methanol fuel cell with an invariant alkaline electrolyte — E. J. Cairns, D. C. Bartosik, J. Electrochem. Soc., **111**, 1205 (1964).

76. The electrolytic reduction of halogen compounds. The electrolytic reduction of triphenyl phosphine and related compounds — John Henry Wagenknecht, Dissertation Abstr. 25, 856 (1964). C.A. **61**, 14181 (1964).

77. Chronopotentiometric oxidation of H_2, C_2O_4 and oxalate ions at Pd anodes.—Thomas R. Blackburn and Peter C. Campbell, J. Electroanal. Chem., **8**, 145 (1964).

The suggested mechanism for the oxidation is the formation of PdO_2 as an intermediate.

78. Preparation of dichloroacetic acid from trichloroacetic acid — Noriake Urabe, Tetsuro Seiyama and Wataru Sakai — Denki Kagaku **28**, 152 (1960) — C.A. **61**, 14186 (1964).

Electrochemical reduction conditions are studied in order to employ a constant current electrolysis method so as to reduce selectively trichloro to dichloro acetic acid.

79. Rotating cathode type cell for reduction of o-chloronitrobenzene to 2-2'dichlorohydrazo-benzene — K. S. Udupa, G. S. Subramanian and H. V. K. Udupa — Bull. Acad. Polon. Sci. Ser. Sci. Chim. **9**, 541 (1961) C.A. **61**, 14187 (1964).

The optimum conditions to get a good

yield of 2-2' dichlorohydrazobenzene has been discussed and the effective depolarisation even at high current density facilitates the use of rotating cathode in contrast to a stationary one.

80. Electrolytic oxidation of uric acid: Products and mechanism — William A. Struck and Philip J. Elving — U.S. At. Energy Comm. TID—20253, 35 pp. (1964). C.A. **61**, 14187 (1964).

Study of the electrolytic oxidation of uric acid indicates the presence of a common path which later diverges to produce both alloxan and allantoin in comparable amounts. The mechanism of the formation of these two products are discussed.

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The formation of quinone and MeOH in the oxidation of p-methoxyphenol in 2M H_2SO_4 has been explained on the basis of the formation of the p-methoxysemiquinone which later undergoes the hydrolysis giving rise to these products.

82. The effect of the amount of added solvent in the electrolytic reduction of azobenzene —Taro Sekine. Denki Kagaku 28 (8) 1960; C.A. **61**, 14187 (1964).

The effect of the amount of benzene added in the reduction of nitrobenzene to hydrazobenzene has been discussed.

83. Stereospecificity of 2-butene-1, 4-diol prepared electrochemically — Masatoshi Sakuma, Denki Kagaku **28**, 164 (1960) — C.A. **61**, 14188 (1964).

Electrochemical reduction of 2-butyne-1,4 diol to 2-butene-1,4 diol is studied using various cathode materials. The product obtained is stereo-specific i.e., if cathodes of Au, Cu, Ni, Co, Pt-black, Au-Cu, Fe or Pd black are used cis form is formed while trans form is got when Pb, Sn, Cd or Hg-Cu cathodes are used

84. Anodic oxidation of aliphatic acids at carbon anodes — W. J. Kochl Jr. J. Am. Chem. Soc., **86**, 4686 (1964).

Electrolysis of simple aliphatic acids at carbon anodes produced high yields of product for which carbonium ion-like intermediate has been suggested.

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The influence of an amalgamated rotating Pb cathode on the current efficiency at various current densities has been studied and compared with that obtained under stationary conditions.

86. Kolbe's electrosynthesis mechanism by the method of measuring the capacitance of the Pt anode in aqueous acetate solutions —G. P. Girina and M. Ya. Fioshin — C.A. **61**, 15663 (1964).

The mechanism of the Kolbe's synthesis by measuring the capacitance of the double layer at different potentials and the corresponding change of the coefficient 'b' in Tafel equation has been explained.

ORGANIC POLAROGRAPHY

1. Polarographic study of the kinetics for the recombination of the anions of trimellitic acid with hydroxonium ion. Ya. I. Turyan and Yu. A. Vakhrushev. Zh. Fiz. Khim. **37**, 1921 (1963).

The rate constant for the recombination of the anion of trimellitic acid with hydroxonium ion has been polarographically studied in the universal buffer medium at a constant ionic strength of 0.25. Equations are obtained for the waves which are supported by the experimental data.

2. Electrochemical behaviour of nitrosobenzene in dimethyl formamide — W. Kemula and R. Sioda, J. Electroanal. Chem. **6**, 183 (1963).

Reduction of notrosobenzene in a solution of 0.2N $NaNO_3$ in dimethylformamide gives 2 polarographic waves. The first one is due to the formation of free radical anions which react with the reductant to form azoxybenzene. The second wave has a complex character.

3. Studies on the polarographic behaviour of nitrophenols. I. O-and m-nitrophenols: R. S. Phadke, R. S. Subrahmanya and M. R. A. Rao, Proc. Ind. Acad. Sci. Sect. A. **57**, 315 (1963).

The paper deals with the measurements of diffusion coefficients by the diaphragm cell method and its superiority over the viscosity and conductivity methods.

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heterocyclic compounds. I. Variations of the polarographic waves and half-wave potentials with pH. — L. Vignoli, B. Cristau, F. Gouezo and C. Fabre, Chim. Anal. (Paris) 45, 439 (1963).

The half-wave potentials for each of the 2 waves obtained with the substances studied varies linearly with pH, exact values depending on the compound studied.

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The polarographic reduction of nitriles in various buffer solutions were studied and the probable intermediate in these reductions are discussed.

7. Preliminary report on N-N-dimethylacetamide as a polarographic solvent — L. O. Wheeler and D. W. Emerich. K. Miss. Acad. Sci. **9**, 63 (1963); C.A. **60**, 3729 (1964).

The possibility of using N-N-dimethylacetamide as a polarographic solvent is considered from the point of the shifts in half-wave potential by the addition of 5 volume percent of the solvent to the aqueous solutions.

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In N H_2SO_4 , di-2-imidazolyl disulphide reacts rapidly and quantitatively with Hg to form RSHg SR and its half wave reduction potential indicates a single reversible 2 electron process.

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The electrolytic reduction of benzyl chloride with uncontrolled potential gives toluene while at semi-controlled potential in the presence of CO_2, phenylacetic acid is obtained.

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The half-wave potentials of 20 halogenated derivatives of cyclohexane in aqueous EtOH are determined. The differences in $E_{\frac{1}{2}}$ are discussed as due to the steric effect, dipole-ment strengthening adsorption and chemisorption.

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The $E_{\frac{1}{2}}$ potentials of each of the hydrocarbon classes are shown to vary linearly with the thermal stability as determined by the p-band frequency.

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The reduction of o-phthalic acid in aqueous solutions (pH ≤ 4) shows kinetic limitations depending on pH and ionic strength μ.

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The aromatic character of nitroferrocene has been studied in buffered solutions.

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15. Electrocapillary behaviour of cis and trans forms of unsaturated acids — G. A. Korchinskii, Ukr. Khim. Zh. **29**, 1013 (1963). C.A. **60**, 7681 (1964).

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The stepwise reduction of benzylacetophenone, benzylacetone cinnamaldehyde and crotonaldehyde at the dropping Hg electrode in anhydrous dimethylformamide is described.

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The mechanism of reduction of several

diketones in aqueous and non-aqueous solvents is discussed including the reversibility of the electrode process.

18. Polarography of aromatic nitro derivatives in NH_4SCN-NH_3. Vincenzo Riganti and Teresa Soldi Gazz. Chim. Ital. **93**, 1308 (1963). C.A. **60**, 12896 (1964).

A study of the polarographic reduction of halo-nitrobenzenes, methylnitrobenzenes and halobenzenes in the sovent system NH_4SCN-NH_3 is discussed.

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22. Inhibitor activity of interface-active substances on polarographic reduction of azo-groups — L. Hollick, A. M. Shames El Din, R. M. Saleh and G. Holleck, C.A. **61**, 311 (1964).

Carboxymethyl cellulose and Ph_3PO cause a shift of polarographic wave of azobenzene towards more negative values at pH > 3. At pH > 7, the wave is split into two, the height of the more positive one decreased to a limiting value.

23. Polarography of anthraquinones and their nitroderivatives in dimethylformamide— E. S. Levin and Z. I. Fodiman, Zh. obshch. Khim. **34**, 1055 (1964). C.A. **61**, 1511 (1 64).

The mechanism of the reduction of the anthraquinone and its various nitroderivatives have been polarographically studied in dimethylformamide.

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The polarographic wave for xanthydrol occurs at -1.2V while that of xanthone occurs at -1.12 and -1.23 in 0.1M Me_4NOH and the sum of the wave heights of the latter is proportional to the concentration.

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Study of the compounds in various media and mechanism for the reduction has been proposed.

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The study of the reduction of acetonediperoxide gave a method of determination of the same in iso-PrOH and AcOH solutions.

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Two waves were observed in the pH range 4-6. The first wave was due to the reduction of cation and the second to the hydrated neutral molecule.

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The anodic oxidation wave of o-and p-isomers gave a well defined wave in a wide range of pH but that of m-derivative was not reproducible and often gave a maximum. By comparing the $E_{\frac{1}{2}}$ at the same pH, it was found that the oxidisability is of the order m-,o- and p-phenylenediamines.

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The stability of homogentisic acid and its lactone has been studied polarographically in acid and alkaline solutions.

30. Polarographic properties of 2-aryl derivatives of 1, 3-indandione. I. Microcoulometric studies on the reduction of 2-phenyl-1, 3-indandione in an alkaline medium— Adam Danek, C.A. **61**, 1515 (1964).

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The effect of various substituents on half-wave potentials of phenanthridizinium and acridizinium were explained qualitatively by means of inductive, steric and resonance effects.

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The polarographic study of the reduction of 6-nitro-6 (hydroxyimino) hexanoic acid showed that the diffusion current is dependent on the concentration and 4 electrons are involved in the reduction step.

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The polarographic study of the reduction of N-troponylglycine and N-troponylleucine in buffer solutions gave 2 electron reduction waves corresponding to the reduction of carbonyl group.

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The polarography of alpha-ammonio aldehydes is influenced by the hydration of the carbonyl group. This hydration is weak and depends on the steric hindrance of the ammonium group.

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The electrolysis of cytosine and its derivatives at the dropping Hg electrode is a 4 electron process and the reduction consists of splitting off of the amino group bound to C-4 and a reduction of the 3-4 double bond.

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Deals with the analysis of di-Meamino terephthalate in a solution buffered at pH 5.1 and that of di-Menitroterephthalate at a pH of 6.4. The range of concentration over which a good precision is obtained has been indicated.

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The above compound has been found to give 2 electron reduction waves in buffers from pH 1-9, whereas at higher pH hydrolysis occurred.

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The d.c. and a.c. polarography of terephthal-aldehydic acid was investigated in buffered solutions containing no EtOH over the pH range from 1 to 13.

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N-Nitroanabasine was reduced polarographically in a number of buffer solutions at

various pH values, and the best condition for the determination was found to be a pH 5.5 — 7.0.

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Anodic polarographic waves are studied for a number of substituted phenols on graphic electrode and the $E_{\frac{1}{2}}$ are shown to obey the Hammett plot.

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12, 15-dihydro-12, 15 dioxo-13, 14 benzotryptycene is polarographically and chemically reversibly reduced in dimethylformamide (DMF) or in EtOH-PhMe mixtures with 0.1M LiCl as supporting electrolytes. The number of electrons taking part in the reduction process are one for each wave in DMF and 2 for the single wave in EtOH-PhMe.

46. Oscillographic polarography of nucleic acid purines and pyrimidine bases and their analogs — A. Humlova — C.A. **61,** 7949 (1964).

47. Investigations of the tautomerism and geometric isomerism of nitrogeneous derivatives of carbonyl compounds. XII. Polarographic investigation of semi and thiosemi carbazones of aliphatic aldehydes. — Yu. P. Kitalv and G. K. Budnikov — C.A. **61,** 7949 (1964).

The polarographic behaviour of acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde and isovaleraldehyde derivatives was investigated on a dropping Hg electrode in the conventional and oscillographic ploarography. These compounds formed a polarographically reducible complex with protons in the pre-electrode layer; the limiting process being the irreversible addition of one electron to the protonated species.

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Deals with the polarographic behaviour of 1, 26-trimethylpiperiodone-4, 1, 3, 5-trimethylpiperidone—4 etc in the pH range of 0-12.

49. Change of reactivity of polarizable molecules in the electric field of the double II. cis-trans isomerisation of stilbenediol —A. Vincenz-Chodkowska and Z.R. Grabowski—Electrochim. Acta, **9** 789 (1964).

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The adsorption of tert-amyl alcohol at the Hg solution interface was analysed and the theoretical treatment of these waves presented from the view point of the kinetic theory of adsorption.

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The effect of preliminary protonization during the reduction of aromatic ketones taking the specific case of the reduction of acetophenone in acid medium has been discussed.

58. Mechanism of the polarographic reduction of furfural — J. Stradins and V. Terands — C.A. **61,** 12953 (1964).)

The behaviour of urfural with regard to pH, ionic strength concentration, temperature in polarographic reduction has been discussed and compared with that of acetophenone and benzaldehyde.

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The polarographic behaviour of acrylonitrile in O M Et_4NI in the concentration of 5×10^{-5} to 10^{-2} M has been investigated. The reduction is irreversible and it is found that 1 electron takes part in the process.

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The $E_{\frac{1}{2}}$ of the 4 electron reduction wave of 4-nitropyrrole-2-carboxylic acid in HCl at pH 2 is unaffected by the addition of the 5-nitro isomer, but shifted to more negative value by the addition of phenylacetic acid. This has been explained on the basis of the adsorption of phenylacetic acid over the potential range 0 to 1.2V.

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The recombination rate of alpha-keto carboxylic acids is determined from polarographic limiting currents according to Brdicka and Wiesner in phosphate buffers and in a buffer solution from imidazole and imidazolium chloride.

64. Polarographic study of some methyl derivatives of acetophenone — V. D. Bezulglyi and L. A. Mel'nik — Zh. Obshch Khim **34,** 2495 (1964). C.A. **61,** 15665 (1964).

The half-wave potentials of a number of methylated acetophenone in 0.02N Et_4NI in 92% MeOH or 0.05N Et_4NI in 60% EtOH under various pH conditions are determined and the effect of sugstituents on the $E_{\frac{1}{2}}$ are discussed.

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67. Polarography of aromatic heterocyclic compounds XVI. Reducibility and ad-

sorption effects in isomeric benzoylpyridines — J. Volke and M. M. Amer — Collection. Czech. Chim. Commun. **29**, 2134 (1964).

The reduction of 2-, 3-, and 4-benzoylpyridines in NaOH and H_2SO_4 at a dropping Hg electrode has been found to occur at the CO group with 2 electrons taking part.

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The cleavage of isothiourea derivatives are followed polarographically in different buffers and found that the reaction is of first order with respect to the concentration of the compound under study and the base.

PATENTS

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Sebacic acid obtained electrochemically from sodium salt of the monoester of adipic acid in MeOH with a graphite anode.

2. Electrolytically manufactured tetramethyl lead. Karl Ziegler, Belg. 617,628 (1962), C.A. **60**, 3008 (1964).

The patent describes the large scale production of tetramethyl lead.

3. Electrosynthesis of sebacic acid — M. Ya. Fioshin et al. USSR Patent 156,938 (1963). C.A. **60**, 6492 (1964).

4. Electrolytic cell for the oxidation and reduction of organic compounds. R. W. Foreman and Franklin Veatch. U.S. Patent 3,113,760 (1964). C.A. **60**, 10221 (1964).

An electrolytic cell is described having a plurality of planar electrodes disposed in spaced laminar relation to each other, serially connected to receive a continuous flow of electrolyte there through and having no diaphragm.

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8. Electrolytic production of tetra alkyllead compounds — Jack Linsk, U.S. Patent 3,118,825 (1964) — C.A. **61**, 2736 (1964).

9. Electrolytic synthesis of organometal compounds — E. I. Du Pont de Nemours & Co., Brit. Patent 949,925 (1964) — C.A. **61**, 3935 (1964).

10. Electrolytic hydrodimerization of olefinic compounds especially of acrylonitrile to adiponitrile — Monsanto Co., Belg. Patent 631,302 (1963). C.A. **61**, 3935 (1964).

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12. Electrolytic cell having a sacrificial electrode for the manufacture of tetra ethyl lead and other organometallic compounds — David G. Braithwaite, Joseph S.D' Amico. Peter L. Gross and William Hanzel — U.S. Patent 3,141,841 (1964) — C.A. **61**, 323 (1964).

13. Continuous electrolytic polymerisation process — Erric O. Forster — U.S. Patent 3,140,276 (1964) — C.A. **61**, 12960 (1964).

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