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EDITORIAL

The increasing importance attached to symposia as a means of fostering the exchange of scientific ideas is a development of great significance for the future of Indian science. The credit for giving the lead in this matter goes largely to the National Institute of Sciences, India. The National Chemical Laboratory, Poona has sponsored a series of symposia covering some of the major aspects of applied chemistry, which were instrumental in bringing a large number of industrialists into contact with the laboratory and in giving the laboratory an insight into the urgent practical problems of the various industries. The ultimate objective of these symposia has been to promote the utilization of scientific research by industry, and there is no reason to doubt that it will be possible to achieve this in large measure before long. The Council of Scientific and Industrial Research has sponsored symposia on a variety of subjects in the other National Laboratories also; and a symposium on "Electrochemical Processes and their Applications to Indian Industry" was held in this Institute on the 27th and 28th March, 1954. It may therefore be opportune to consider the role that symposia can play in the advancement of science in this country.

Professor Conant[1] has pointed to the fundamental role which the organization of individual scientists in close communication with each other has played in the recent growth of the experimental sciences. The existence of such an organization has helped in the rapid dissemination of new ideas. Discoveries have given rise to more discoveries, and erroneous observations and illogical notions have been corrected in time. In India to-day we are on the threshold of a new era of scientific progress and a tradition of co-operative effort in science has yet to be built up. No better means of achieving this can be contemplated than the holding of regular symposia and conferences which would bring scientific workers into closer mutual contact.

A scientific symposium serves the dual purpose of stimulating creative thinking on the subject of the discussion, and providing an outlet for the results of a completed investigation. The reporting of completed work is however of secondary importance under present day conditions of the enormous multiplication of scientific and technical periodicals publishing original work. Symposia encourage further research not so much by making unpublished information available as by stimulating productive mental effort to which discussion is an incentive. Professor Beveridge[2] has considered at length the ways in which the discussion of a problem with colleagues or even with lay persons may be helpful and we cannot do better than quote some of his conclusions here.

'The other person may contribute a useful suggestion. With a different background of knowledge he may see the problem from a different aspect and suggest a new approach. Even a layman is sometimes able to make new suggestions. The introduction of agar for making solid media for bacteriology was due to a suggestion of the wife of Koch's colleague, Hesse... A new idea may arise from the pooling of information or ideas of two or more persons. Discussion provides a valuable means of uncovering errors. Ideas based on false information or questionable reasoning may be corrected by discussion. Discussion and exchange of views is usually encouraging, stimulating and refreshing. ... The most valuable function of discussion is perhaps to help one to escape from an established habit of thought which has proved fruitless, that is to say conditioned thinking... In explaining a problem to another person, and especially to some one not familiar with the field of science, it is necessary to clarify and amplify aspects of it that have been taken for granted and the familiar chain of thought cannot be followed. A new thought may occur while one is making the explanation without the other persons having said a word.'

It would be realized that these remarks apply with much greater relevancy to discussions of an informal nature than to discussions in a formal scientific session. There is a closer meeting of minds and more uninhibited intellectual intercourse when scientists congregate during after-hours and begin to talk shop in smaller groups. In fact, the success of a symposium may be said to depend, in the final analysis, on the provision of opportunities for such discussions. It is worth-while recalling at this stage the original meaning of the word 'symposium' which in Greek denoted an after-dinner drinking party with music, dancing and conversation. The Greeks with their practical genius for organization, realized long ago that an atmosphere of informality and relaxation is the best stimulant to intellectual conversation.

We have had an opportunity during the recent symposium in this Institute to appreciate the value of personal contacts in science. The symposium was conceived against the background of the industrial expansion being planned in India and the need to take stock of the potentialities for expansion of the electrochemical industries in the country. The subject of the symposium covered a wide field, and it was not the intention to discuss intensively the technical advances in any particular branch of electrochemistry. The promotion of intimate contact between workers in scientific laboratories and also between them and industrialists was our immediate objective, and in this, we believe, we have largely succeeded. Some of the papers presented at the symposium will be published in this and subsequent issues of this bulletin, and the July issue will contain an account of the proceedings of the symposium.

1. Conant, J. B., "Science and Common Sense" (Oxford Univ. Press, London, 1951).
2. Beveridge, W. I. B., "The Art of Scientific Investigation" (Heinemann, London, 1951).

* THE DEVELOPMENT OF THE CARBON ELECTRODE INDUSTRY IN INDIA

by

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INTRODUCTION

With the industrial progress and the establishment of hydro-electric stations that is now taking place in the country, the development of electrochemical and electro-thermal industries will receive great attention. In other countries such industries are established near the site of the power stations, as these consume large amounts of power with a sufficiently high load factor. The success of these industries depends on the availability of cheap electric power. In most of these industries such as in the manufacture of aluminium, steel, ferro-alloys, calcium carbide, phosphoric acid, caustic alkali, chlorine, and dry cells, carbon electrodes (the word 'carbon electrode' is used here in a generic sense to include both carbon and graphite products) are used. In some cases like the production of aluminium the consumption of electrodes is quite high being about 0.6—0.7 ton of electrodes per ton of aluminium produced.

In addition to the above applications carbon products find use also in other electrical, metallurgical, chemical and mechanical fields. Table 1 shows some of the important applications of the carbon products in these various fields.

A few of the industries listed above namely, the production of aluminium, caustic alkali, electric steel, ferro-alloys, and dry cells are already in existence in the country. It is understood that the manufacture of calcium carbide has also been undertaken recently. The production of the above industries is not sufficient to meet the total requirements of the country. Some of these industries are also essential for defence purposes. It will be seen from the above that the carbon electrode industry which supplies one of the important basic raw materials in various shapes and sizes to most of the electrochemical, electro-thermal, metallurgical, electrical, mechanical and chemical industries is an equally important industry. It is highly essential therefore, that this industry be developed in the country at an early stage:

TABLE 1

Electrochemical:	(1) Caustic Soda and Chlorine. (2) Dry Cells.
Metallurgical:	(1) Aluminium. (2) Electric Steel. (3) Pig Iron. (4) Ferro-alloys.
Electro-thermal:	(1) Calcium carbide. (2) Silicon carbide. (3) Electro-graphite. (4) Phosphoric Acid.
Electrical:	(1) Carbon brushes. (2) Switch gear contacts. (3) Telephone parts. (4) Collector Contacts. (5) Projector, Search light and Welding carbons. (6) Vacuum tube parts.
Mechanical:	(1) Gilseal Rings. (2) Piston Rings. (3) Bushes.
Chemical:	(1) Raschig rings. (2) Acid & alkali resisting parts. (3) Acid Pumps. (4) Heat Exchangers.
Miscellaneous:	(1) Structural parts. (2) Furnace refractories.

It was Sir Humphrey Davy's poineer work which formed the basis of the carbon electrode industry of the present day. In the year 1800, Davy showed that an arc could be formed between two pieces of charcoal connected to the two

*Paper presented at the Symposium on 'Electrochemical Processes and their Applications to Indian Industry', March 1954.

poles of a battery. With a powerful battery Davy was able to strike an arc about 4 inches long, the arc emitting a most brilliant light.

This was the invention of the arc light and the electric arc furnace. Platinum, quartz, sapphires, magnesia, and lime were fused in this arc, and charcoal, plumbago and diamond were observed to disappear.

Davy named the charcoal pieces positive and negative poles depending upon whether they were connected to the positive or negative poles of his battery. It was Faraday who named these poles as "electrodes".

The ensuing 150 years after Davy's invention have seen the development of the carbon electrode industry. Giant carbon electrodes 45 in. in diameter and weighing a few tons and graphite electrodes 24 in. in diameter and 110 in. in length each, are being manufactured at present for furnace work. [1]

The development of the carbon electode industry has kept pace with the development of the aluminium, electrochemical and electrical industry. The developments of these industries were often running parallel and supplementing each other. Some of the landmarks in the development of the carbon industry may be put down as:

(1) Use of carbon arc for street, projector and search lights.

(2) Use of carbon as conducting brushes in electric motors and generators.

(3) Use of carbon as furnace electrodes and refractories.

(4) Graphitization of carbon products by Acheson.

(5) Development of self-baking continuous Soderberg electrode.

(6) Use of carbon as an inert, electrically conducting material in electrochemical industries.

(7) Manufacture of porous and impervious carbons.

The development of this industry got great impetus due to the two World wars. In the first war, the electric furnace industry and in the second war the electrochemical industry were pushed up.

IMPORTS

The imports of electrical carbons including furnace electrodes upto the beginning of World war II were more or less steady. The review of the "Sea-borne Trade of India" does not indicate the quantity of the imported materials but gives only the total value and this stands approximately at Rs. 2.5 lakhs per year. About half of this was for carbon blocks used for making brushes for electric motors and generators. On the start of World war II these figures increased by leaps and bounds, mostly to meet the requirements of electric furnace and electrochemical industries then being established in the country. The present value of the imports is between Rs. 35—40 lakhs per year. About 65% of the imports are from U. S. A., about 25% from U K. and the balance from other countries. The import figures are given in Table 2

TABLE 2 Imports of Carbon, Electricals (including furnace electrodes) into India.

Year	Value in Thousand of Rupees.	Year	Value in Thousand of Rupees.
1929-30	292	1941-42	726
1930-31	258	1942-43	570
1931-32	282	1943-44	842
1932-33	323	1944-45	646
1933-34	317	1945-46	1115
1934-35	195	1946-47	778
1935-36	215	1947-48	1050
1936-37	193	1948-49	2015
1937-38	217	1949-50	2000
1938-39	273	1950-51	3485
1939-40	380	1951-52	5148
1940-41	645		

MANUFACTURE OF CARBON ELECTRODES

The process of manufacture of carbon electrodes and the raw materials used in their manufacture are generally well-known, and have been described in vari aus technical articles by workers in the field and by Mantell in his book 'Industrial Carbon'. It is not proposed to deal with this aspect here, except for the part which applies especially to this country.

The raw materials may be divided into two main categories namely, the body materials and the binding materials.

The body materials used are anthracite coal, metallurgical coke, retort carbon, pitch coke, petroleum coke, graphite and lamp black. India is deficient in anthracite coal but has enough of bituminous coal. Low ash coke prepared from this coal after suitable treatment may serve as a good raw material for this industry. A paper dealing with the "Cleaning of Coal for electrode manufacture" was read by the authors at the recent Symposium on "Coal Washing" held at the Fuel Reseach Institute Dhanbad and the position regarding the availability of raw materials was discussed in the paper.

Retort carbon is available from gas works in limited quantities. Petroleum coke, at present available from Assam refineries is mostly used for the production of aluminium. Three new petroleum oil refineries are being started in the country, and the petroleum coke available from these refineries could be utilised for manufacture of carbon articles. Binding materials which are coal tar and coal tar pitch would be available in sufficient quantities for this industry.

MANUFACTURE

Knowing the importance of the industry, the Council of Scientific & Industrial Research sanctioned a scheme for undertaking research and development work with a view to manufacturing carbon articles in the country. The authors had been working for the past few years on this subject. After completing laboratory work on the manufacture of carbon electrodes for dry cells, the authors are now busy in manufacturing carbon brushes of various types and sizes on a pilot plant scale. These are now being supplied to Goverment Departments and private concerns. Efforts are being made to put this work on a commercial basis. Apart from brushes, carbon articles of special types such as oil seal rings, switch gear contacts etc., are being manufactured. Efforts are being made to manufacture big size electrodes required for electro-chemical industries.

Not only the products are made from indigenous materials but also with machinery designed and made in the laboratory. The equipment made is capable of handling quantities for pilot plant production. The same units could be used for regular manufacture, or bigger units could be made. The authors feel confident that machinery required for this industry could be designed and made in the country. For the development of this industry in the country, one need not depend on imported raw materials or equipment and technical knowhow.

ECONOMICS

With the development of this industry, some of our important industries using carbon in various forms as a basic raw material will be independent of imports. This aspect is very essential in times of emergency. In addition, it will give employment to a number of people.

It is understood that in U. S. A. there were over 40 factories manufacturing carbon electrodes of various descriptions and employing over 6000 men in actual production work.

In Germany during war time there were about 8 — 10 factories employing over 3000 workers.

The cost price of the different raw materials varies from about Rs. 200—Rs. 300 per ton, while big size electrodes are sold at about Rs. 2000—Rs. 3000 per ton. The brush blocks which require a lot of processing are sold at Rs. 10—Rs. 15 per lb.

It will be seen that the cost of the manufactured articles depends considerably not on the cost of the raw materials but on the cost of processing. Electric baking used for graphitization generally consumes a good amount of power. It is for this reason that it is essential to have cheap electric power. These furnaces are of the continuous type and have a sufficiently high load factor and it should be possible to arrange for cheap power.

The present imports stand at about Rs. 40 lakhs per year and with the industrial development that is now taking place in the country, the imports may go up still further. The development of the industry would help to stop this drain on our national finances, provide employment to a number of people and make the country independent of imports for a basic raw material.

CONSUMPTION OF ELECTRODES

The authors in their paper previously referred to in this article have roughly estimated the demand for carbon products required by the various industries in the country. The total quantity would come to about 10,000 tons per annum in the near future. Out of this, some demands may be met by the use of Soderberg self-baking electrodes which are produced *in situ* and are generally used by aluminium concerns. We may roughly take the present demand to be about 4 - 5 thousand tons per annum.

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*EFFECT OF SOME SURFACE ACTIVE AGENTS ON THE CAPACITY OF THE DROPPING MERCURY ELECTRODE

by

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INTRODUCTION

Surface active agents are of great importance in many industries. In the textile industry, they afford considerable help in processes like Kier boiling, dyeing and bleaching, by ensuring uniformity of treatment and increasing the speed of operation. The striking success of the first few synthetics has led to considerable scientific and commercial interest in them. The quantitative evaluation of surface active substances has become important both for the research worker who is discovering new compounds having surface active properties and for the consumer who has to choose his surface active agent from amongst the numerous commercial products. Several methods have been suggested from time to time for measuring their efficiency. A review of these methods is to be found in a former paper[1]. Amongst the physical properties taken advantage of for the purpose are: (a) the contact angle of the aqueous solution against a hydrophobic surface[2,3] (b) the surface tension of the aqueous solution[4], and (c) the spreading coefficient[5,6,7]

Our own interest in this problem has mainly arisen as surface active substances occur in cane juices and produce undesirable effects in processing. It is of interest to examine how far these are removed during the clarification process. In this connection an investigation was taken up as to the influence of surface active substances in general on the electrical double layer capacity. In the present paper the effect of some detergents on the capacity of the dropping mercury electrode has been measured which throws light on the possibility of using this as a tool for assessing surface activity.

EXPERIMENTAL

The commercial detergents lisapol, cerefak, aerosol O.T. and fixanol C were studied. Further a pure chemical compound lauryl-p-toluidine-2-sodium sulphonate having surface active properties and kindly prepared and supplied by Dr. K. Venkataraman, Director, Department of Chemical Technology, Bombay University was also investigated. The apparatus is the same as has been described in former communications[8,9,10,11] The principle of the method consists in applying a constant a.c. pulse of 45 mV. (r.m.s) over a d.c. potential and observing the a.c. component of the resulting pulsating current (vide fig. 1). The magnitude of the r. m. s. alternating current component is nearly a measure of the average differential capacity of the dropping mercury electrode. The constants of the dropping mercury electrode are as follows:-

CAPILLARY 1

(a) For Cerefak and lauryl-p-toluidine-2-sodium-sulphonate:

$m = 0.00438$ gm./sec.

$t = 0.70$ sec.per drop in 0.1 *N*-KCl open circuit.

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* Paper presented at the Symposium on 'Electrochemical Processes and their Applications to Indian Industry', March 1954.

CAPILLARY 2.

(b) For lisapol, aerosol O.T., fixanol C and lauryl-p-toluidine-2-sodium sulphonate;
m = 0.00154 gm/sec.
t = 1.50 sec. per drop in 0.1 *N*-KCl open circuit.

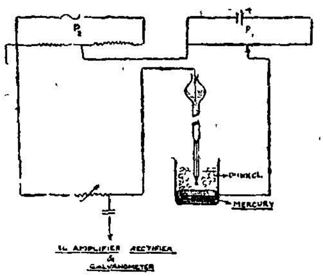


FIG. - 1

The studies were made with pure 0.1 *N*-KCl solution shaken up with mercury and mercurous chloride so as to avoid any further effect of the contact of mercury with the solution. The alternating current components of the pulsating current were recorded at different d.c. potentials from zero to about 2 volts. All the *D. C.* potentials were measured with reference to the mercury pool electrode and were converted as referred to the saturated calomel electrode, by measuring the potential of the pool electrode against the saturated calomel electrode. The alternating current components were then measured with 0.12% solutions of various detergents in the above solution (0.1 *N*-KCl shaken up with mercury and mercurous chloride). The percentage increase with sign of the alternating current component due to the presence of the surface active agents at the various corresponding d.c. potentials were calculated and the results have been plotted in graphs in figs. 2-6. A typical set of readings and the percentage increase in the alternating current component are given in table 1.

TABLE 1.

Electrolyte: 0.1 *N* KCl-0.12% lauryl-p-toluidine-2-sodium sulphonate.
pH - 10.2.

CAPILLARY I.

D. C. Potential in Volts.	Current in μa. (r.m s.) with 0 1 *N* KCl, only.	Current in μa. (r.m s.) with 0.1 *N* KCl+ surface active agent.	%increase of current with sign.
0.07	62.2	24.1	-61
0.17	19.9	3.62	-81
0.27	8.78	2 70	-69
0.37	7.23	2.62	-63
0.47	5.80	2.75	-52
0.57	4 59	2.70	-41
0.67	4.04	4.21	+4
0.77	3.75	2.10	-43
0.87	3.53	1.63	-54
0.97	3.49	1.40	-59
1.07	3.67	1,30	-64
1 17	3.89	1.27	-67
1.27	4,12	1.50	-63
1.37	3.68	19.74	+437
1.47	3.55	3.77	+6
1,67	3.64	3.49	-4

TABLE 2.

Electrolyte: 0.1 *N* KCl-0.12% lauryl-p-toluidine-2-sodium sulphonate; pH-10.2.

D. C. potential in volts.	Capillary 1 %increase of current with sign-interpolated from fig 5.	Capillary 2 %increase of current with sign.
0.05	-58	-59
0.15	-78	-81
0.25	-71	-69
0.35	-64	-64
0 45	-55	-58
0.55	-45	-49.
0 65	-6	-36
0 7	-10	+7
0.75	-36	-40
0.85	-52	-54
0.95	-58	-60
1.05	-64	-65
1.15	-66	-67
1.25	-64	-69
1.35	+310	+ 92
1.40	+320	+548
1 45	+100	+12
1.65	-2	-2

With a view to find out the effect of the size of the capillary on the results, two capillary tips were tried on the system (0.12% lauryl-p-toluidine-2-sodium sulphonate in 0. 1 *N*-KCl at pH 10.2). The results are given in table 2. An examination of the table shows that the values are nearly independent of the size of the capillary or the drop time except at very high currents as met with at the desorption peaks. It is hoped that by having a suitable arrangement for parallel application of the a. c. and d. c. fields (instead of the present 'series' arrangement) it would be possible to further minimize this differential effect of the size of the capillary. With this improvement any difference yet noticed would be due to difference in drop time

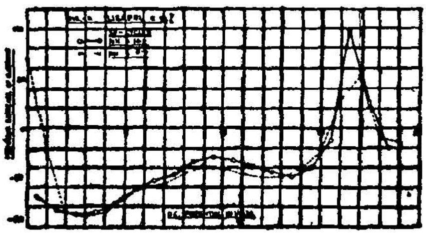
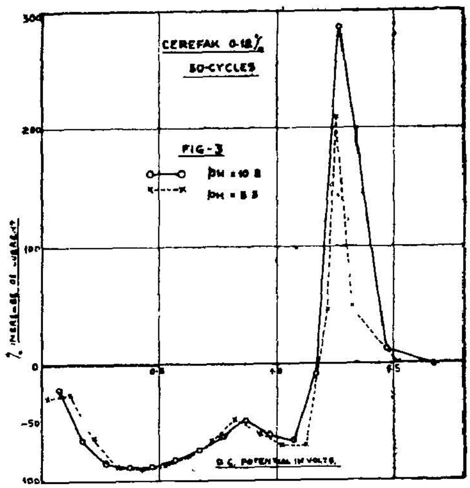
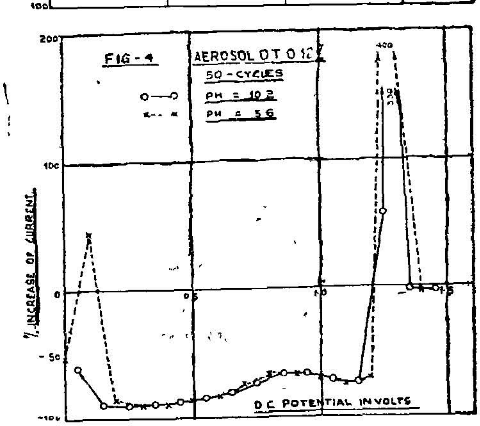
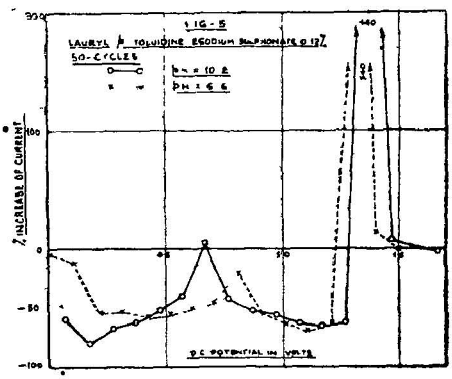
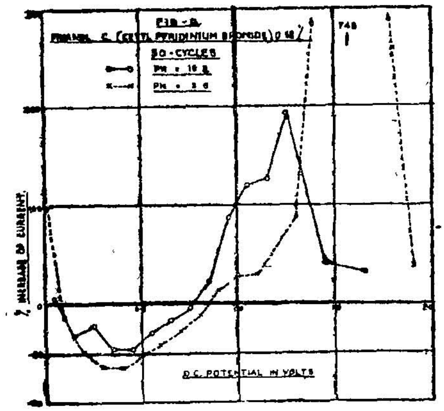


Fig. 2.









which would affect the amount of the detergent molecules accumulated at the interface in those cases wherein accumulation is slow.

The results obtained with the different detergents are presented in figs. 2-6.

DISCUSSION.

1. *Common structural features in surface active agents*

Any molecule showing high surface activity has two types of groups namely, water attracting and water repelling. Amongst the water attracting groups we have the ionized groups such as the sulphonates, sulphates. or quaternary ammonium. One can also have the non-ionized polyethers providing the water attracting portions. The water repelling portion is usually a hydrocarbon chain or aromatic nucleus. It is essential, however, that there should be a proper balance between two types of groups. If there is too much accentuation of the water attracting group, the wetting action goes down. If on the other hand the water repelling portion predominates, the solubility of the substance becomes too small The secret of getting a high degree of surface activity lies in striking a proper optimum balance. Such molecules with a proper balance between a hydrophilic and a hydrophobic group exhibit all the phenomena associated with surface activity.

The common basis for all surface active phenomena appears to be the tendency for the water repelling group to try to get away from water. At aqueous-air interfaces this tendency results in the adsorption of the molecules at the interface, and thereby the surface tension gets lowered. At oil-aqueous interfaces the water repelling group tends to get oriented towards the oil, leading again to adsorption at the interface causing lowering of interfacial tension and thereby helping emulsification. They act as good wetting agents by getting adsorbed on hydrophobic surfaces, orienting their own hydrophilic group towards water and thus rendering the originally hydrophobic non-wetting surface effectively hydrophilic and wetting. The same tendency is the cause of micelle formation in solution which helps the water repelling groups of a number of these molecules to join up to form a cluster in which all the water repelling groups are out of contact with water and the water attracting groups are in contact with water. The tendency again is the root cause of the errors that are caused in pH measurements by the indicator methods in solutions of the surface active substances [12]. Their power for protecting hydrophobic colloids can also be traced to the same tendency. Finally, the surface active agents tend to get adsorbed at mercury-aqueous interfaces the main factor bringing about adsorption being the tendency for the water repelling groups to get away from water. It is this last effect which is of interest in the present paper.

2. *The dropping mercury electrode*

The dropping mercury electrode in contact with solutions such as aqueous potassium chloride, behaves like an electrical capacity whose magnitude mainly depends upon the size of the drop and the d.c. potential applied. If a small alternating potential is applied to the dropping mercury electrode the magnitude of the current is mainly determined by the impedance due to the capacity of the dropping mercury electrode. Since the capacity is situated mostly in a very thin region near the mercury-solution interface, any adsorption on the mercury surface would affect the capacity. Any surface active substance present in aqueous solution would tend to get adsorbed owing to the hydrophobic group tending to get oriented away from water. This tendency, however, could be modified by electrical forces acting between the molecules of the adsorbent surface and the adsorbed molecule as well as the electrical forces between the molecules of the adsorbent and the solvent molecules. The forces may be between ion and ion, ion and dipole etc., depending upon the nature of the surface and the adsorbate. Near the electrocapillary zero these electrical forces would be a minimum, resulting in an intensification of adsorption of the surface active substance. a tremendous lowering of dropping mercury electrode capacity and the consequent lowering of the a. c. component of the pulsating current in the present technique. At potentials far removed from electrocapillary zero on either side, the surface of the mercury gets a high charge, positive or negative. In either case there is a strong attraction developed between the surface of mercury and the solvent molecules due to ion-dipole interaction. This occurs in most cases more or less sharply at certain potentials This leads to a sudden desorption of the surface active substance, which is attended usually by a large transfer of charge from one side to the other side of the interface. This causes the exhibition of capacity peaks which have been referred to as the desorption peaks. In the case of lisapol the desorption peaks on either side of the electrocapillary zero can be seen. With the other detergents also there would be at least two desorption peaks in each case; but the measurements have not been extended to the anodic potentials as there is a fear of complication due to electrolytic action at the mercury surface. It appears from the above that the characteristics of a surface active substance can be studied from the depression of the capacity as well as the magnitude and position of the desorption peaks.

3. *Behaviour of detergents at the dropping mercury electrode*

All the detergents studied in this paper show a tremendous depression in capacity in the neighbourhood of the electrocapillary zero. The position of maximum adsorption is slightly different in different cases. This might have been caused partly by the shift of the electrocapillary zero and partly by the differences in the nature of forces between the charged surface and the adsorbed molecules. In the case of aerosol O. T. the minimum due to adsorption is very flat extending from 0. 2 volts to about 1.1 volts Further extensive study with compounds of similar structure would establish the cause of this flat minimum. In all the cases studied the desorption peaks occur and are of considerable height except in the case of lisapol. The comparatively low peaks in this case is presumably due to the fact that we are dealing with an uncharged molecule, the desorption of which does not involve large transfers of electric charge across the interface. One generalization that is possible is that as the pH is lowered the magnitude of the peak diminishes in the case of anionic detergents and increases with cationic detergents. With lisapol which is a nonionic detergent the decrease of pH lowers the maximum. One of the important effects of low pH with anionic detergents is to produce a form which is uncharged and would therefore produce less of changes of capacity on desorption. The lowering of the peak may also be due to the increase in molecular weight caused by micelle formation making the molecules sluggish. It is of interest to note that pH has not got much influence on the depression capacity due to adsorption in any of the cases studied, with the exception of cetyl pyridinium bromide. It is of interest to note that the desorption peak comes up at a very high potential of about 1.7 volt in the case of cetylpyridinium bromide. This is presumably due to strong attraction between the positively charged cetylpyridinium bromide ions and the negatively charged mercury surface. This attractive force gets increased as the negative potential applied increases. Thus the cetylpyridinium ion becomes a serious competitor to water dipoles. At the highest potentials, however, the adsorption of water molecule takes the upper hand and a desorption peak is caused. In between the maximum depression of the capacity and the desorption peaks, a small maximum in the curve has been observed in all the cases except with cetylpyridinium bromide. The significance of this requires further investigation.

CONCLUSION

The study of a few of the detergents under conditions of different pH have yielded results of great interest It is indeed probable that an extensive study in this field may lead to the development of an effective tool for the evaluation of surface active agents. The technique has also the potentialities of being used for judging the elimination of surface active substances present in cane juice during its clarification.

SUMMARY

The effect of the detergents lisapol, cerefak, aerosol O. T., cetylpyridinium bromide and lauryl-p-toluidine-2-sodium sulphonate on the dropping mercury electrode capacity has been studied. There are many interesting features exhibited by the surface active agents

and the results are indicative of the possibility of the technique offering a valuable tool for assessing the surface active agents and to judge the removal of surface active substances from cane juice during clarification.

ACKNOWLEDGMENT.

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ELECTROCHEMICAL REACTIONS IN ALTERNATING FIELDS

EFFECT OF FREQUENCY ON CURRENT EFFICIENCY

by

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INTRODUCTION

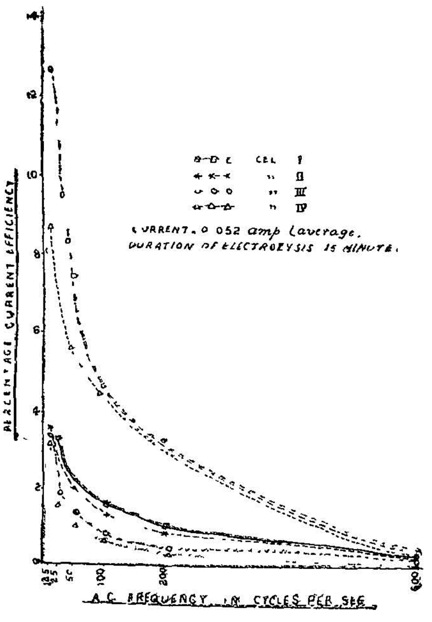
After the classical work of Shipley and Goodeve[1] on the electrochemical effects of the alternating current this mode of investigation was largely neglected. The only recent work on the quantitative measurement of current efficiency for electrolysis using alternating current is by A.N. Kapanna[2] and H.P. Agarwal[3]. In the system studied by the former there were complications due to the electrode surface being altered by the deposits produced by the current; the latter was able to overcome the above difficulty using platinum electrodes and ferric sulphate of 0.33 N strength as the electrolyte, but he confined his study to the use of a frequency of 50 cycles per second. The object of the present work is to see the effect of different frequencies varying from 12.5 to 600 cycles per second and also to investigate the effect of current density, temperature and duration of electrolysis on current efficiency. The electrolyte used was 0.5 M-ferric sulphate and the electrodes were of platinum. The results obtained have been interpreted on the basis of the theory of absolute reaction rates[4].

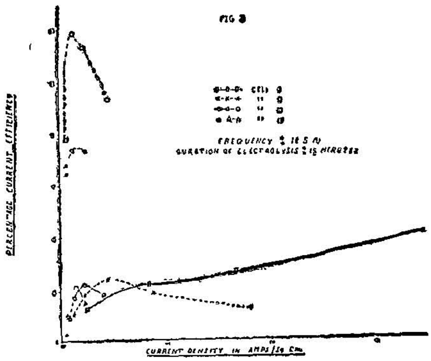
EXPERIMENTAL:

The experimental set-up and procedure was exactly the same as used by Agarwal[3] except for the source of alternating current. In the present experiment a B.S.R. Oscillator type L.O.50 A was used as the source of alternating field. Since, however, this did not give the required power, a multi-purpose power amplifier was designed and set up. The amplifier consisted of a three stage L-F amplifier designed for a very wide frequency response of 12.5-15000 cycles per second. It was anticipated that the output response would not vary much over the ranges required.

In all the experiments four electrolytic cells having different electrode dimensions were put in series so as to minimize the effects due to change in nature and magnitude of the quantity of electricity passed while interpreting the effects of dimensions of the electrode on current efficiency. Since the net reaction was found to be reduction, the current efficiency was calculated by taking into account the total amount of cathodic current passed and the actual amount of net reduction that took place. The amount of reduction was determined by titrating the resulting ferrous salt against standard 0.01 N permanganate. The electrolysis was conducted for a duration of 5 min., 10 min., and 15 min. The magnitude of the current was varied from 0 013 amp. (average) to 0.208 amp. (average). Three readings were taken in each case. The mean of these values was used for calculating the current efficiency. The experiments were conducted at room temperature. (22° to 25° C) and with boiling electrolyte. In the experiments carried out with boiling electrolyte, each of the electrolytic cells was fitted with a reflux condenser so as to keep the concentration of the electrolyte constant. The extensive data obtained comprised about 1500 readings, and current efficiencies were calculated for all the readings. In the interest of brevity, they are not included in the paper. The results for the variation of percentage current efficiency at room temperature and at boiling temperature for one particular current value and duration of time are plotted on one and the same graph against the variation of frequency. All these graphs gave similar results and so only one characteristic graph of this type is shown in fig. 1. For seeing the effect of current density on percentage of current efficiency both at room temperature and boiling temperature similar graphs were plotted for each duration of electrolysis at individual frequencies. These curves are also similar to one another and hence only one characteristic graph of this type is given in figure 2. For interpreting the effect of duration of electrolysis on current efficiency the ratio of current efficiency for 15 minutes duration of electrolysis to that of current efficiency for 5 minutes duration has been calculated and is given in table 1.

Fig 1





DISCUSSION

From the results plotted in fig. 1 it is apparent that the experiments carried out at different current densities with lower frequencies of alternating current yield much higher current efficiencies at room temperature as well as at boiling temperature than those obtained by using alternating current of higher frequencies. The current efficiency for the net reduction would increase tremendously if the reaction products formed at the electrode when the cathodic half wave is effective are removed more quickly by way of phase separation or diffusion, as there is very little possibility of the reaction being reversed during the anodic half wave of the current. If the duration for which the cathodic half wave is effective increases, then not only would more of the reduction products be formed, but they would also have sufficient time to diffuse away from the electrode so that the reaction would not be reversed when the anodic half wave comes into operation. This is actually what happens when 12. 5 cycles frequency is made incident.

In the case of electrolysis carried out at 12 5 cycles per second the time during which the cathodic half wave is effective is 48 times greater than that of the current passing at 600 cycles per second. When the frequency of 600 cycles is incident, the interval of time during which the cathodic half wave operates is so short that the reduction product formed can hardly diffuse away from the electrode and hence the reaction is almost completely reversed by the anodic half wave which follows the cathodic one. It is for this reason that at 600 cycles the current efficency is almost zero while in the case of 12.5 cycles it is of the order of 3% at low current densities. Even at very high current density values, the current efficiency at 600 cycles per second for the net reduction reaction is of the order of 0.5%, while in the case of 12 5 cycles it is of the order of 15%.

There is a general parallelism between current densities and current efficiencies, the latter increasing with increase in the former. This can be very well explained on the basis of the theory of 'absolute reaction rates' (4) as applied to electrode processes. According to this theory, the instantaneous rate of reduction process would increase exponentially with rise in the potential of the electrode. Therefore one may expect that at higher current densities which would normally mean higher peak potentials one would get larger accumulation of the products of reaction at the electrodes, which would bring about a larger extent of diffusion and hence increase the current efficiency with reference to the net reduction reaction. Further, with increase in the current density the overvoltage of the electrode surface for hydrogen and oxygen evolution would be greatly exceeded by the electrode potential and hence brisk evolution of gas would take place. This evolution would cause vigorous stirring at the electrode surface and the resulting convection process would facilitate the movement of the products of the reaction. This would again cause an increase in current efficiency, A careful examination of fig. 2 shows that the current efficiency may not be a single valued function of current density, particularly at high values of current densities. Corresponding to a particular currnent density the current efficiency values obtained for the four electrolytic cells (which have different electrode dimensions) were not of the same order, but varied slightly from one another, though all the experiments were carried out under similar conditions. This divergence in current efficiency values corresponding to a particular current density might be due to the fact that the distances between the electrodes of the four electrolytic cells were not the same, thereby causing differences in the I.R. drops. It is also possible that with progressive electrolysis the surface of the electrodes gets progressively modified by deposition of thin films of iron or iron oxide and causes a change in overvoltage for the liberation of oxygen and hydrogen gas. This again would affect the current efficiency. In the case of curves drawn at room temperature it is seen that the four curves which correspond to the four cells are not very similar as some of them either meet at a point or cross one another. But at boiling temperature the curves are almost similar and do not cross one another. It appears from this that the current efficiency is not a single valued function of current density at room temperature, but at the boiling point there appears to be a tendency for correlation between current density and current efficiency.

TABLE 1.

Effect of duration of electrolysis on current efficiency.

(Values given are for the ratio $\frac{\text{Current efficiency for 15 minutes duration of electrolysis}}{\text{Current efficiency for 5 minutes duration of electrolysis}}$)

Temperature	Frequency of the current in cycles per second	Cell I having electrode dimensions Length: 0.55 cm., Dia: 0 035 cm. Magnitude of the current in amp. (average)					Cell II having electrode dimensions: Length: 1.05 cm., Dia: 0 035 cm. Magnitude of the current in amp. (average)					Cell III having electrode dimensions. Length: 2 1 cm, Dia: 0.035 cm. Magnitude of the current in amp. (average)					Cell IV having electrode dimensions. Length: 4.15 cm., Dia. 0.035 cm. Magnitude of the current in amp. (average).				
		0.013	0.026	0.052	0.104	0.208	0.013	0.026	0 052	0.104	0.208	0.013	.026	.052	.104	.208	0.013	.026	.052	.104	.208
Boiling temperature	12.5	...	...	...	...	...	...	...	...	...	...	0.6	0.8	0.7	0.9	...	0.9	0.7	0.6	0.8	...
	25	...	...	...	...	...	...	...	...	...	...	0.7	0.8	0.7	0.7	0.8	0.7	0.5	0.6	0.6	0.8
	50	...	...	...	...	...	...	...	...	...	...	0.8	0.6	0.8	0.9	0.9	0.8	0.6	0.8	0.8	0.7
	100	0.8	1.2	0.5	0.9	0.8	0.8	1.2	0.6	0.9	0.8	0.7	0.6	0.6	0.9	0.9	0.6	0.8	0.9	0.8	0.6
	200	0.9	0.9	0.5	0.8	0.8	0.7	0.8	0.8	0.7	0.8	0.8	0.9	0.7	0.7	0.5	0.7	0.7	0.9	0.7	0.5
	600	...	...	...	...	...	...	...	...	...	...	0.6	0.4	0.4	1.8	0.6	0.6	0.7	0.8	0.6	0.4
Room temperature	12.5	0.5	1.0	0.9	0.9	...	0.9	1.1	0.9	0.9	...	0.8	1.0	0.8	0.9	...	1.1	0.8	0.9	0.9	...
	25	0.5	0.7	1.0	0.9	0.9	0.7	0.7	1.0	0.9	0.7	0.6	0.6	0.9	0.9	0.8	1.0	0.6	0.9	1.0	0.9
	50	0.4	0.9	0.9	1.3	0.7	0.3	0.7	1.0	1.4	0.9	0.3	1.0	0.7	1.3	0.9	0.3	0.7	0.8	1.3	1.0
	100	0.4	0.6	0.9	0.8	1.0	0.3	0.6	1.0	1.1	1.1	0.3	0.6	0.7	1.0	1.0	0.3	0.6	0.6	1.0	1.0
	200	0.3	0 6	0.7	0.9	1.0	0.3	0.8	0.8	0.8	1.0	0.3	0.5	0.5	0.9	1.0	0.3	0.3	0.6	0.8	1.0
	600	...	...	0.8	0.7	0.8	...	...	1.0	1.0	0.8	...	...	0.5	1.2	1.2	...	...	0.2	1.0	1.6

At room temperature the current efficiency appears to be less reproducible, and there is no regular change of current efficiency with change in the duration of electrolysis. At boiling temperature however, there is a definite tendency for the current efficiency to fall with increase in duration of electrolysis. The values obtained for the ratio, current efficiency for 15 minutes duration of electrolysis/current efficiency for 5 minutes duration of electrolysis in experiments done at room temperature as well as at boiling temperature are given in table 1. An examination of the table would confirm the above conclusions. When an alternating current is passed through a solution of pure oxidant (e.g. ferric sulphate), the cathodic half wave would have its full effect, whereas the anodic half wave would be less effective due to the diffusion away from the electrode of some of the ferrous ions formed As the electrolysis is conducted for longer intervals of time the net reduction reaction causes the formation of appreciable ferrous ions which would facilitate the oxidising action of the anodic half wave. This results in diminishing the net cathodic reaction and causes a fall in the current efficiency with time at boiling temperature. Some experiments were tried with cells having very small electrodes at boiling temperature and high current density. The results have not been included in this paper since it was found that the dimensions of the electrodes were changed as a little platinum went into solution. This fact of dissolution of platinum at high current density values at lower cycles of alternating current and boiling temperature requires further investigation.

There seems to be every possibility that the electrochemical reactions which are brought about by using alternating current may be closely connected with the development of 'redoxokinetic potential' as studied by Doss and Agarwal[5].

SUMMARY

Current efficiency is a function of frequency and the former increases with decrease of the latter at different current densities and temperatures. In the experiments carried out with boiling electrolyte it has been observed that the current efficiency decreases with increase in the duration of electrolysis even at the same current density. There is a general parallelism between current densities and current efficiencies—the latter increasing with the increase in the former, although it is worth noting that current efficiency is not a single valued function of the current density. Experiments at boiling temperature have yielded much higher current efficiencies than at room temperature.

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* USE OF ROTATING ELECTRODES IN ELECTROLYTIC REACTIONS

by
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Rotating electrodes have been in use for a long time in the estimation of different metals present in a solution by depositing them separately at known potentials[7]. The state of steady potential attained readily by a rotating electrode is taken advantage of for this purpose.

In the field of electroplating too, the utility of rotating electrode has not been unknown, but its use has not found very wide application in commercial electroplating probably because of the mechanical difficulties presented by the varied and peculiar shapes of the objects to be electroplated.

Although a full discussion of the theoretical principles underlying the phenomena of rotating electrodes may not be possible at this stage, it would be profitable to examine critically the changes occurring at an electrode when it is stationary and when it is rotated, so that the knowledge might be applied with advantage to many of the electrolytic preparations of chemicals, inorganic and organic.

The effect of rotation of the cathode has often been considered to be purely mechanical, but as a result of work published in the last two decades, the idea is gaining ground that the effect is not so simple as that, but that the predominant role of rotation is its effect on the thickness of the film which lies next to the surface of the electrode. The assumption has been made that the electrode surface has immediately next to it a film of electrolyte which is the seat of the transformations initiated by the passage of the current. It follows that the rotaion of the electrode will reduce the thickness of this film and cause it to come into contact more and more with new portions of the electrolyte[9]. The composition of this film may thus change markedly as the electrolysis proceeds, and these fluctuations would therefore affect, qualitatively and quantitatively, the reactions taking place. This would account satisfactorily for the observations made in the plating of metals by many workers that the grain structure and quality of the metal deposited on a rotating cathode are affected by the speed of the rotation.[1,4,14] Accepting the idea of the "cathode film", it would be easy to understand how the impoverishment of this film in metal ions would affect the characteristics of the deposited metal. The rate of depletion is a function of the speed of rotation which determines the diffusion and also of a number of other factors such as current density, transference numbers of the ions present, temperature, viscosity, etc. The low concentration of metal ions in the film will favour the discharge of the other ions present, in particular, hydrogen. The discharge of hydrogen may lead to the evolution of gas causing mechanical agitation of the electrolyte or a combination with the metal to form hydrides or solid solutions or even a simple occlusion in the metal. With the discharge of hydrogen, the electrolyte next to the cathode will become definitely alkaline, and this may lead to the formation of basic salts among the reaction products formed within the space of the cathode film[18]. These again will affect, either adversely or favourably, the quality of the electrodeposit. Thus in electroplating with zinc or cadmium at low current densities, it is observed that spongy deposits of metal are formed in neutral, and more readily in alkaline solutions, and this is explained as being in all probability due to the formation of basic salts in the bath. If this inter-

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pretation be accepted then it would carry with it fresh evidence in support of the idea that the effect of the high speed rotating electrode differs fundamentally from those of the other methods of mechanical agitation or circulation commonly resorted to, in as much as it affects the composition itself of the cathode film, and alters it so that the sequence of discharge of the various ions present in the solution and also their proportionate amounts may be changed radically.

Some of the early researches in this field led to the conclusion that the cathode when stationary, was covered with a liquid film, a fraction of a milli metre in thickness, and that upon rotating the electrode, the thickness of this film was reduced considerably, depending upon the speed of rotation[10]. The raising of temperature seemed also to affect the thickness of the film in the same way, but this influence was supposed to be exercised by decreasing the viscosities of the solutions resulting in a higher rate of bombardment of the electrode surface by the metal ions or by the depolariser molecules[8].

Studies of the pH of this film at a cathode with varying current densities have shown that while this decreases with increasing current density, the fall at a stationary cathode is only gradual, whereas at a rotating cathode there is a sharp drop in the pH of the cathode film[14]. It has also been found possible to regulate the lowering of this pH of the cathode film by the speed of rotation of the cathode. The conclusion has thus been sought to be justified that a cathode film was essential for the successful operation of a metal deposition or other reaction, and that this film could be maintained within the favourable limits by a definite speed and a definite current density of the cathode, corresponding to the desired thickness and pH of the film.

While the bulk of the electrolyte serves as a general reservoir for ions and as a conducting medium, the discharge of ions tends to reduce the concentration of ions only in the thin film adjacent to the electrodes, this region determining the nature and course of the reaction. At a cathode, as a result of this, the single electrode potential tends to become more negative and this marks the beginning of cathodic polarisation. With increasing current densities, more ions in the cathode film are discharged, causing a reduction of ions and the consequent diffusion of ions from the bulk of the solution which tries to counterbalance to some extent this process of depletion of ions in the cathode film.

It will be obvious from the above that while agitation of the electrolyte by means of mechanical stirring or circulation will generally reduce the concentration polarisation, it could not be compared in its effect with that of the rotation of the electrode itself. The latter reduces the polarisation to a minimum by applying the maximum shear at the metal-liquid interface[10]. The 'limiting' or 'maximum' current would then seem to depend on the means by which this polarisation is overcome. Factors which are known to determine the limiting current, such as concentration, temperature, rate of stirring of solution, etc., are much less effective than the rotation of the electrode itself[8].

The conditions mentioned above would hold true also for the anode, with the exception that the single potential of the anode would become more positive as a result of the increase of current density and the consequential depletion of ions at the anode film. In commercial practice, polarisation of all sorts may be regarded as 'ohmic' resistances forming part of the circuit, and are to be avoided as far as possible. Apart from causing an increase in the consumption of energy, high polarisation leads to undesired electrode processes setting in.

The effect of motion of an electrode surface relative to the electrolyte on the reaction occurring during electrolysis, has received considerable attention during the last two decades, particularly the effect of the relative cathode-catholyte motion during the electro-deposition of metals, and several theories have been proposed to account for the effect of such motion on equilibrium electrode potentials in non-electrolytic cells [12 15 16 17].

An attempt has been made to derive a reasonably satisfactory relationship between the thickness of the electrode film or the so-called diffusion layer which has been estimated to be in the region of 0.05 cm., [10 16 13] and the speed of rotation of the electrode, and this has led to certain interesting conclusions [2 3]. From studies on the effect of rotation of anode on the current efficiency of the cerous-ceric transfo·mation, a reversible reaction free from side reactions, it has been found that the rotation caused an increase in current efficiency. Furthermore, the mathematical form of the relation of current efficiency to rotation-speed has been shown to be analogous to that of the heat-transfer coefficient of a liquid film at a solid-liquid interface to the speed of the fluid past the solid surface.[19]

As a result of plotting in curves the results of a series of experiments on the oxidation of cerous sulphate solutions of different concentrations at a rotating cylindrical smooth platinum anode, with rotational speeds varying from 0 to 5100 r. p. m., it was found that a satisfactory representation of the data could be obtained in the form of the equation, $\alpha = \alpha_0 + bv^n$
where

α = observed current efficiency
α_0 = current efficiency at a stationary cathode
v = linear velocity of the surface of the anode (m./second),
b and n = constants.

It is apparent that in such a case, log $(\alpha-\alpha_0)$ should be a linear function of logv This has been tested by plotting log $(\alpha-\alpha_0)$ vs. logv (peripheral speed of anode in m/second), and the equation has been found to conform moderately well with the data through a considerable range of conditions, except at the over-all efficiency approaching unity, i. e.. 100 per cent, when it breaks down.

By simple graphic means, the slopes of the linear portions of the curves yield an approximate value of 0.66 for 'n' in the equation, $\alpha-\alpha_0 = bv^n$. It is significant and noteworthy that this relationship of $\alpha-\alpha_0$ being proportional to the 0.66th or 2/3rds power of the rotational speed, is of the same type and order of magnitude as that between the heat-transfer coefficient for a fluid film at a solid-fluid interface and the velocity of the fluid over the surface (Badger and McCabe, Elements of Chemical Engineering, 2nd edition. Chapter IV, McGraw Hill Co., N. Y. City, 1936). Since the heat transfer coefficient is diffusion-controlled, the conclusion has been drawn that the electrolytic reaction at a rotating electrode is governed in a similar manner [19].

Observations of the type described above have been made very thoroughly for cases of metal deposition and for some inorganic oxidations. There are no reasons, however, to suppose that they would not hold equally well for other electrode processes such as electro-organic oxidations and reductions. Unlike the majority of inorganic systems, however, those involving organic molecules are in general irreversible in the thermodyramic sense. In such a system the electrode potential attained would be usually independent of the concentrations of the oxidised or reduced forms, but would vary with other factors, such as current density, composition of the electrolyte, nature of the electrode surface, etc. Notwithstanding the fact that the potential varies with conditions, the electrode potential in the field of reduction in particular, does show a certain reproducibility if conditions are standardised carefully. This has been taken advantage of in the dropping mercury electrode or the polarograph. The use of the rotating cathode corresponds more or less to conditions prevailing at a dropping mercury electrode, standard conditions of potential being attained easily at these.

In most electro-organic processes, the slowest step is one of diffusion of the depolariser to, or that of the reaction product from, the electrode. Apart from overvoltage, electrode potential has also to be considered to be of considerable significance, in as much as it must reach a certain minimum value before action can proceed. Overvoltage would only set an upper limit to the potential, since at this point hydrogen (or oxygen) is evolved. It would be seen, therefore, that in the case of an inefficient reduction, the potential is removed but little from its maximum value, since inefficiency implies concomitant gas evolution. An efficient reduction occurs when the depolariser inhibits effectively gas evolution by reducing the electrode potential. Aromatic nitrocompounds belong to this category as they cause generally a large reduction in cathode potential.

Just as electrolysis at an appreciable rate will reduce the concentration of the ions carrying the current around the electrode, so will the reaction of an organic molecule at an electrode lead to a deficiency which is normally made good by diffusion of more material from the bulk of the solution. Lowering of the concentration of the organic depolariser around the electrode facilitates the competing electrode processes which, for anodes, is oxidation or oxygen evolution and for cathodes, is reduction or hydrogen evolution, thus leading to a lowering of current efficiency. In most cathodic reductions, the rate of reduction is controlled largely by the rate of diffusion, and this will not be affected materially, therefore, by an increase in current density. It will, on the other hand, increase the evolution of gas which would mean reduced current efficiency. The most effective way to increase current efficiency, therefore, is to increase diffusion and this can be accomplished best for reasons explained above, by the use of rotating electrodes whereby the most effective agitation and penetration of the depolariser molecules into the so-called "diffusion layer" at the electrode takes place. There are many cases of electro-organic reduction, e.g., that of azobenzene to hydrazobenzene, where the rate of reduction has been observed to rise with increasing speed of rotation of the cathode, until a stage is reached beyond which no further change occurs[5]. At this point diffusion must be considered to have ceased to be the controlling factor for the process of reduction.

Experiments conducted on the reduction of a large variety of organic compounds, e. g., nitrobenzene, acids like crotonic, sorbic, and cinnamic, acetone and dihydropyran, representing different types of reduction processes, have all shown the current efficiency to be markedly increased by the high speed rotation of a suitably constructed cathode.[21] The latter enables the use of much higher current densities without any appreciable drop in efficiency. In those cases where there is a tendency for two products being formed by reduction at different electrode potentials, one of them as a result of reduction at a higher and the other at a lower potential, the use of high current densities leads to formation of more of the higher potential product, especially at a stationary cathode, because of the rapid increase in electrode potentials. With a rotating cathode, however, under similar conditions of increased current density, this does not happen, because the rapid rotation prevents the cathode potential from reaching such high values. A good illustration of this is found in the electrolytic reduction of nitrobenzene in acid medium to para-aminophenol, when aniline is invariably a by-product.[20] Para-aminophenol is the principal product formed at a rotating cathode, even at very high current densities, but at a stationary cathode, under identical conditions, more aniline and less aminophenol is formed, because of the higher potential. The over-all efficiency also is greater at the rotating cathode[22].

A similar interesting case has been observed in the reduction of acetone to pinacol in which isopropyl alcohol, occurring invariably as a by-product, is formed in greater amounts at a stationary than at a rotating cathode, especially under conditions of high current densities. The same behaviour has been found to be true of the other types of reductions mentioned above[21]. The case of reduction of salicylic acid to salicylaldehyde studied recently has shown that at a rotating cathode the yield was above 40 per cent, whereas at a stationary cathode with a stirrer for the electrolyte, the yield never exceeded 10 per cent[23].

In view of the interesting results obtained at a rotating cathode, it was considered advisable to study the application of this technique to a number of anodic reactions also. Rotating anodes have now been employed with advantage in the oxidation of glucose to gluconic acid, the electrolysis of sodium chloride to sodium chlorate, the oxidation of metallic copper to cuprous oxide in an alkaline sodium chloride bath and in the preparation of ammonium persulphate from ammonium sulphate.

In all these cases rapid current electrolyses have been tried without the efficiency of the process suffering in any way or the nature of the electrode reaction being changed.

A little consideration will show that the formation of desired products with high current efficiencies under conditions of high current density and of the consequential high current concentrations, should be of great importance in industrial practice, in as much as it would shorten considerably the duration of the reactions and make the use of cell units of high capacity possible. The saving in floor space and in time is calculated not only to effect savings in initial investment, but also in thermal and electrical energy, specially when the electrolyte has to be maintained at a high temperature and in circulation. There is, however, another side of the picture to be considered. As a result of the higher voltage required for the rapid current electrolysis, the consumption of electrical energy for a given quantity of material may be greatly increased. The full significance of the use of rotating electrodes on an industrial scale will therefore become apparent only as more of these processes are studied in detail on pilot plant scales.

The successful adoption of the technique in some of the reactions mentioned above are well on the way, and the investigation of a number of others will be undertaken in future.

The energy efficiency of an electrolytic process is of prime importance in technical work from the standpoint of economy, and is of greater significance than the current efficiency. Efforts have therefore to be directed to raise the energy efficiency as high as possible. One method of realising this object is to decrease the resistance of the electrolyte and thereby lower the working voltage. This should be done very effectively by the rotating electrode, by overcoming polarisation which may be regarded as adding to the 'ohmic' resistance. Polarisation has been attributed to a "counter electromotive force caused either by exhaustion of the substances used in the electrolytic reaction faster than they can be replaced, or by the accumulation of the products of this reaction faster than they can be removed[6]". It is hoped that a remedy for this would be found to lie to a large extent in carrying out the reactions at rotating electrodes, whereby the polarisation voltage at moderate current densities would be reduced as low as possible.

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* ELECTROLYTIC RECOVERY OF LEAD AND ANTIMONY FROM BATTERY WASTES

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Metals reclaimed from such materials as scrap, sweepings, drosses, etc are usually termed "secondary" metals to distinguish them from 'primary' metals, derived directly from ores. Secondary lead and antimony account for nearly 50 and 40 per cent respectively of the total production of these metals in the U. S. A.[1] The problems facing the storage battery industry in India are essentially those of getting the raw materials. The cost of production of storage batteries has increased to nearly four times the pre-war level and the Planning Commission's report on the Five year Plan (1951-56) has rightly emphasized the urgent need for the reclamation of lead and antimony from battery wastes in India. The report also suggests that an organisation may be set up for collecting these scraps as is done in U. K. About nineteen factories in India are at present engaged in the production of storage batteries with an installed annual capacity of 540,000 units, the actual production being 250,000 units in 1951[2]. The amounts of raw materials required for the manufacture of a sufficient number of storage batteries to make India independent of imports have been estimated to be as follows:-

(For 340,000 units)

Lead	...	2500 tons.
Antimony	...	175 tons.
Lead Oxides	...	2700 tons.
Rubber	...	1600 tons.
Wooden separators	...	17 million units.[3]

Only 20 per cent of these raw materials can be met from indigenous sources. The entire quantity of lead is imported from Australia and Burma, and the position with regard to antimony is in no way better, since the stibinite (Sb_2S_3) deposits which occur mostly in Chitral have fallen to Pakistan. Incidentally, it may be noted that the annual consumption of antimony for the quinquennium ending 1956, has been estimated to be between 300 to 400 tons.[4] Secondary lead and antimony are therefore of vital importance now to our country.

So far, only pyrometallurgical methods appear to have been employed for the production of secondary lead and antimony.[5] Battery scrap, consisting of lead plates, lugs, oxides, and sulphate is smelted in a suitable furnace with suitable fluxes. The products are obtained in three distinct layers, viz., (1) molten metal, (2) slag and (3) matte. The metal produced cannot be employed as such for the manufacture of new grids, since in the first place it is contaminated with the oxides of aluminium, magnesium, zinc and iron, etc. (derived from furnace walls), and in the second place, it has lost most of the antimony by oxidation. This is subjected to a process of softening (Harris softening), which consists in repeatedly treating the molten metal with sodium hydroxide and sodium nitrate whereby antimony, tin, arsenic etc., are preferentially oxidised and removed as scum. Some of the disadvantages in the thermal treatment of battery wastes may be outlined as follows: (1) a high temperature is required for the efficient smelting of the charge, (2) the disposal of matte and slag is a difficult problem, (3) about 25 per cent or more of the antimony is lost by volatilization.[6] Hence the softened metal has to be replenished with antimony if it has to be re-employed for making new grids. Furthermore, the Harris softened metal cannot be used for

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making new grids due to the presence of impurities and the German practice has been to use such reclaimed metal mainly for the production of oxides.[7]

Uniformity of quality, efficient control over the process and the absence of such problems as the disposal of slag, matte etc., are some of the characteristics of electro-hydro-metallurgical processes, as contrasted with the pyrometallurgical ones. An electrolytic process is now being worked out in these laboratories for the efficient reclamation of lead and antimony from battery wastes. These battery wastes. consisting of grids, connectors, oxides, sulphates, etc., are melted at a low temperature (300°C) (lead forms an eutectic with 12 per cent of antimony, the composition having a melting point of 250°C). The alloy thus obtained by low temperature-melting is however not suitable to be re-employed for making new grids being contaminated with oxides. It needs further purification. The whole operation consists of three parts namely, (1) electrolytic separation and recovery of pure lead from the alloy (2) treatment of the anode mud produced during electrolysis, for the reclamation of antimony, and (3) treatment of the pastes.

The first part of the problem viz., production of electrolytic lead has been successfully completed. An attempt to separate lead from antimony by electrolysis of the alloy from a fluosilicate bath was not successful, since the complete separation of the two metals could not be effected satisfactorily. This has been accomplished by conducting the electrolysis in a fluoborate bath, the cathodic deposits being found to contain no antimony, and the bath solution to be free from antimony.

A wooden tank lined with bituminous paint with a capacity of 5.5 litres constituted the cell. The electrolyte consisted of a mixture of lead fluoborate, free fluoboric acid and boric acid. The anode was an alloy of lead and antimony while the cathode was 8:18 stainless steel. Experimental conditions for obtaining high-purity lead with maximum current efficiency have been worked out.

ADDITION AGENT: The current efficiency was found to decrease with the duration of electrolysis. Thus while it was 95 per cent for 6 hours, it was reduced to 75 per cent in 16 hours. There was also "treeing" observed all along the edges of the cathodes. These defects have been remedied by suitable addition agents and also by stirring or by circulation of the electrolyte.

DIAPHRAGM: The antimony of the alloy is left as a black powder, the so-called "anode mud"—part of which adheres loosely to the anode, and part falls into the bath, polluting it. The 'anode mud' falling to the bottom is not only likely to cause short-circuits but also to set up a chemical action between its components and the free acid of the electrolyte.[8] The cell voltage too increases with time. To obviate these difficulties a canvas diaphragm has been introduced so that the mud falling from the anode might be held in the bag and prevented from polluting the bath. The mud is also made more adherent by increasing the amount of addition agents, and a combination of the two has worked very efficiently.

INTER-ELECTRODE DISTANCES: Starting from a distance of 3" (centre to centre), experiments were made varying electrode distances to 2.75", 2.5", 1.75" and 1.5". 'Treeing' was completely prevented, and there was found to be no danger of short-circuits even with 1.5".

CURRENT DENSITIES: Higher current densities cannot be employed especially if the antimony content is high. A current density of 36 amps/sq. ft. has been tried. In this case there was much 'treeing' in spite of energetic stirring. In general, current efficiencies decreased, as expected, with increasing current densities. Thus, at 21 amps. per sq. ft., the current efficiency was only 93 per cent, whereas at 15 amps per sq. ft. the current efficiency was nearly 100%.

ANODE COMPOSITION: Two anode composition have so far been tried, viz., 5.1% and 9.8% of antimony. Cell voltage varied with anode composition, viz., 0.5 V for 9.8% of antimony and 0.87 V for 5.1% of antimony. Thus there was an increase of nearly 36% in the cell voltage, which means an increase of 36% in the energy consumption. The optimum current density was 15 amps. per sq. ft. Under these conditions the energy consumption of lead produced was 0.08 KWH per lb.

TEMPERATURE AND pH: Since the bath was sufficiently acidic the question of control of pH did not arise. Similarly although temperature may have some effect, since high effiiciencies have been obtained without the necessity of raising the temperature, a study of the effects of temperature on the electrolysis was not considered necessary.

MATERIALS OF CONSTRUCTION: A wooden tank made of untreated teak wood begins to warp after sometime. Hence the modern trend is towards the use of R. C. tanks with bituminous lining. An R. C. tank with bituminous lining has been constructed and is capable of producing 3 lbs. of lead per day (24 hour basis).

TREATMENT OF ANODE MUD: The anode mud obtained by electrolysis of the lead-antimony alloy has been analysed. It is found to contain between 85 and 90 per cent of antimony. The extraction of the mud by leaching with various reagents in solution, and the recovery of antimony from the solutions so obtained by electrolysis are in progress.

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ELECTROCHEMICAL PRODUCTION OF CHLORATES

by
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The need for increasing the production of high grade potassium chlorate suitable for defence purposes has been pointed out in the Report of the Planning Commission. Besides, potassium chlorate can be used with nitro hydrocarbons as an explosive in the mining industry. Its use in the match industry and in fire works is well-known. Sodium chlorate has recently come into prominent use as a weed-killer and as the starting material for making perchlorate which is used as a rocket-fuel. Chlorates are also employed in printing, textile fabrics, dyes, paper manufacture, bleaching and as disinfectants in medicine.

It has now become the established practice to make sodium chlorate first and then convert it into any salt required. This has the advantages that a high concentration of chlorate can be built up starting with a cheap raw material like common salt and the operational difficulties associated with the crystallizing of potassium chlorate in the electrolytic bath are avoided. In the early days chlorates were produced chemically by the chlorination of alkali hydroxide and later by the chlorination of lime-slurry to produce calcium chlorate, which was then treated with a potassium salt to get potassium chlorate. The chlorine evolved during electrolysis of magnesium chloride. for the production of magnesium required in the Kroll's process of titanium manufacture is also used in making potassium chlorate. However for the primary manufacture of chlorates, the electrochemical process has come to stay, mainly because of technical developments in industrial electrolysis[1].

The chief innovations in the electrolytic production of chlorates are:-

(i) cathodic reduction has been substantially minimized, if not entirely obviated, by the addition of chromate to the electrolyte.

(ii) High current efficiencies of the order of 85-90% have been attained by controlling the acidity of the electrolyte and maintaining its pH between 6 5 and 7.0[2]. In neutral or alkaline medium, the maximum possible current efficiency has been found to be only 66.7%

(iii) The substitution of treated graphite for platinum or platinum-iridium as anode material has made the process considerably cheaper. Cathodes are of iron or mild steel.

However there is wide divergence of opinion regarding the temperature[3] at which electrolysis is to be done, the exact method of controlling the acidity of the bath[1] and the optimum current density and current concentration to be employed.

The formation of chlorate by the electrolysis of brine is the result of a series of complex electrochemical and chemical reactions, which have to be carefully regulated. They can be represented by the following equations:

$$6NaCl + 6HO_2 + 6\,F. \rightarrow 6NaOH + 3H_2 + 3Cl_2$$
$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$
$$2Cl_2 + 2H_2O \rightleftharpoons 2HOCl + 2HCl$$
$$NaOCl + 2HOCl \rightleftharpoons 2NaClO_3 + 2HCl$$
$$4NaOH + 4HCl \rightarrow 4NaCl + 4H_2O$$
$$\overline{NaCl + 3H_2O + 6\,F. \rightarrow NaClO_3 + 3H_2.}$$

Now according to the final equation, six Faradays are required per mole of sodium chlorate and the over-all reaction should be 100% efficient. But there are several secondary reactions possible, which are less efficient or altogether deleterious, like the reduction of hypochlorite at the cathode and the discharge of hypochlorite ion at the anode, producing chlorate at a current efficiency of only 66.7%. As mentioned above the former can be largely avoided by using chromate in the solution The reaction.

$NaClO + 2HClO \rightarrow NaClO_3 + 2HCl$ is favoured in acid solutions and at warm temperatures.

The acidity has to be carefully controlled and there should not be either excess or insufficiency of acid. both of which will entail loss of efficiency caused by secondary reactions involving the escape of chlorine or the discharge of hypochlorite ions.

While a high temperature is generally considered[4] to be conducive to high current efficiencies, the increased graphite consumption[5] has to be considered in terms of the cost and trouble of frequent replacements.

Current densities industrially employed vary over a wide range[1], 10 to 50 amps. per sq. ft. for the cathode and 10 to 150 amps. per sq. ft. for the anode. There is a variety of industrial cell designs[1,6] with the electrodes occupying a small fraction to almost the whole of the space in the electrolyser. Low current concentrations are reported to be most advantageous[4,3].

Generally on an industrial scale, the brine (25-30% sodium chloride) after purification to remove calcium, magnesium and sulphate is treated with 20°Be hydrochloric acid and sodium chromate (2 gms/l.) and circulated through a series of electrolytic cells arranged in a cascade so that the solution flows by gravity from cell to cell. The electrode assembly consists of alternating cathodes of mild steel and anodes of graphite, with an inter-electrode distance of 0. 25 to 1 inch. The use of hollow graphite anodes permitting internal coo ing and of stainless steel cathodes has been patented. The chlorination of the cell-liquor before recycling is another patented process[8]. When a concentration of 500 gms. of chlorate per litre is built up, the cell-liquor is heated to 90°C to destroy any unreacted hypochlorite and concentrated in double effect evaporators to get sodium chlorate, or treated while hot with potassium chloride solution to obtain potassium chlorate on cooling. The product is centrifuged, dried and packed.

Investigation of the various factors controlling current efficiency in the preparation of chlorate by the electrolysis of sodium chloride solution has been taken up in these laboratories. As six Faradays of electricity can at best give one gram-molecule of chlorate and as only low current concentrations (15 amps./l) are generally employed, the process is inordinately time-consuming. Attempts have therefore been made to develop the technique of using a rotating anode. This technique has enabled the application of much higher current concentrations (60 amps/l) thereby increasing the cell capacity and accelerating the production of chlorate without affecting the current efficiency (nearly 90%). Though the possibility that this may necessitate an increased energy-consumption is realized, it may be worthwhile ascertaining whether the increased cost of production may not be off-set by savings in investment on smaller units of electrolysers, labour charges, floor-space etc. Work is in progress in order to assess the ultimate advantages of the new technique.

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ELECTROLYTIC PREPARATION OF GLUCONATE

by

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Calcium is one of the bilogically important mineral elements. It appears to be involved in the transformation of chemical into mechanical energy in muscle, and calcium ions are necessary for the normal coagulation of blood. Calcium gluconate is widely used in medicine for the treatment of pathological conditions caused by calcium deficiency. Improvement of the processs for its manufacture is therefore of importance.

The oxidation of aldose sugars to the corresponding carboxylic acids in the presence of various buffers was first studied in 1870.[1] Early work was largely confined to the study of oxidation by bromine or chlorine in the presence of different buffers. Other chemical methods which were developed later involved the use of oxidising agents like alkaline cupric hydroxide, mercuric oxide, potassium ferricyanide, nitric acid potassium permanganate etc. But these chemical methods are not wholly satisfactory for the commercial manufacture of the salts of sugar acids due to the difficulty of controlling the oxidation and separating the desired product. The fermentation method does not give a quantitative yield and requires careful control to prevent side reactions.

Loeb[2] was the first to study the electrolytic oxidation of glucose in sulphuric acid between lead electrodes. He obtained a variety of oxidation products ranging from gluconic acid to oxalic acid and carbon dioxide. Isbell and Frush[3] developed an electrolytic process for the oxidation of glucose and other aldoses with alkali bromide as electrolyte, wherein the bromide, which was the charge carrier, was continuously regenerated during electrolysis. Fink & Summers[4] studied the mechanism in greater detail and arrived at optimum conditions for the production of the salts of various aldonic acids

Besides ease of operation and control of the process, and the ready separation of the desired product which characterize electrolytic processes in general, the electrolytic oxidation of glucose has decided advantages over the chemical and biological processes in that a very small amount of the oxidising agent is used and can be continuously regenerated during the oxidation. The exhaustive study made by Fink & Summers[4] enabled the production of pure calcium gluconate on a commercial scale from an alkali bromide cell using graphite electrodes with an efficiency of 91 per cent.

Balasundaram and Hirani[5] attempted the electrolytic production of calcium gluconate from the cheaper starting material, cane sugar. But they encountered serious difficulties in large scale practice. The fructose which is unaffected during electrolysis accumulated in the cell and made the separation of gluconate difficult. The product obtained even after two crystallisations was contaminated with the unreacted ketose. The accumulation of fructose in the electrolytic medium made the reuse of the mother liquor impossible with the result that large quantities of gluconate and the entire quantity of bromide used were lost.

Kappanna and Joshi[6] studied the alternating current electrolysis of glucose in potassium bromide with suspended calcium carbonate and reported a maximum efficiency of 55% with a frequency of 3 between platinum electrodes. Lal and Mukherjee[7] studied the process developed by Fink & Summers and reported the optimum concentration of glucose as 10-12 per cent for maximum efficiency and yield and minimum anode corrosion. The addition of an equivalent amount of chloride in place of bromide, though it increased the efficiency, caused much anode corrosion and the yield was low.

An enzymic method for the production of calcium gluconate was patented in 1948[8] in which the mycelial mat of Aspergillus niger. obtained as a waste product in the fermentation process for citric acid manufacture was made use of.

With the object of improving the existing efficiency of oxidation and shortening the duration of electrolysis, the use of a higher current density than that employed by Fink and Summers was attempted by carrying out oxidation at a rotating graphite anode. The results obtained at the rotating anode are interesting: better yields are obtained, and high current densities of the order of 28 amps/dm^2 can be used without affecting the current efficiency or increasing the bromine loss to objectionable limits. This technique may be important in commercial practice, as it shortens the period of electrolysis considerably and makes the cell-unit more compact, thus enabling large savings in floor space and initial investment. Pilot plant studies are in progress.

Calcium gluconate is obtained as a white crystalline or granular powder. Its solubility in water is 3.3 in the cold and 20 at boiling point. It readily forms supersaturated solutions, in which form it is used for injections. As even a minute particle of dust or any extraneous matter will precipitate the solid, stabilisers are added to prevent precipitation during administration or storage. It is insoluble in alcohol. The gluconate is ideally suited for calcium therapy, because it is soluble, practically tasteless and non-irritating to tissues. It is used as an antidote for fluorine and oxalic acid poisoning. Gluconic acid always contains a proportion of lactone; the property of lactones of slowly regenerating acid when dissolved in water, which can be controlled within certain limits by varying the temperature and concentration makes the gluconate suitable for the manufacture of fruit jelly and baking powders. It is also used in the preparation of homogeneous pastes such as dentifrices and polishing agents.[10]

PRODUCTION: The normal annual demand for calcium gluconate in India is about 90,000 lbs., most of which is imported. The indigenous production is estimated to be 500 lbs.

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HEAVY WATER

by

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On the basis of the number of isotopes of hydrogen and oxygen which are known to exist, it has been estimated that 30 different water molecules are possible, but in general usage, heavy water refers to deuterium oxide (D_2O). The existence of the heavier isotopes of hydrogen was first discovered by H.C Urey and co-workers in 1932 They found that the water obtained from an industrial cell which had been in use for a long time for the production of oxygen and hydrogen had a higher density than water. This was later confirmed by G.N. Lewis and Macdonald, who, starting with 20 litres of water containing alkali from an old electrolytic cell, obtained by repeated electrolysis a sample of 0.5 cc. of water with a density of 1.073 in which about 70% of the hydrogen was heavy.

Heavy water is a normal constituent of all natural waters and occurs to the extent of 1 part in 5000. Among the various methods of prepartion, the electrolytic method of separating the lighter isotope of hydrogen has been found to be the most efficient. Preparation of heavy water is a time-consuming process and high currents are passed continuously to effect concentration. The method generally adopted for large scale production is to concentrate water by continuous electrolysis in stages to obtain a residue with the required concentration of heavy water. During the later stages, the gases may contain deuterium which is recovered by combustion. A plant operating continuously with 100 amp. was producing 90 gms. of deuterium oxide (99.9%) starting with 90l. of water already enriched to 0.5% D_2O, the first sample being obtained after 290 hrs. of continuous working. This will give an idea of the time and electrical energy required for the production of heavy water which is therefore very costly-recent quotations—are $ 83 per lb. of per pure deuterium oxide. Norway is one of the world's chief producers of heavy water.

Heavy water looks and handles like ordinary water and cannot be distinguished from it by the naked eye. The density of pure D_2O is 1.10596. It melts at 3.813°C and boils at 101.431°C. Its latent heat of fusion, vaporisation and heat capacity are all higher than those of ordinary water. Its refractive $index_{20}$ is 1.32828(less than that of ordinary water which has an index of $refraction_{20}$ of 1.33300). These differences in physical properties are used in estimating the concentration of heavy water in a given sample. Like water, it solvates ions and enters into water of crystallization. The solubilities of salts are distinctly lower than in ordinary water. By the interaction of heavy water with magnesium nitride, ammonias (in which the hydrogen atoms are predominantly D_2) are produced, which have higher melting points, boiling points and latent heats.

The usefulness of heavy water lies in its nuclear properties. The nucleus of heavy hydrogen contains a proton and a neutron compared to a single proton in the case of ordinary hydrogen. The deutron (the nucleus of heavy hydrogen) is a source of neutrons for nuclear chain reactions for power production and manufacture of fissionable material. Deuterium is also used as a moderator to slow down the higher velocity particles which are emitted in nuclear reactors. It is useful as a projectile in nuclear reactions and is often needed in cyclotrons and other accelerators. Because of the secrecy restrictions imposed by the Atomic Energy Commission, detailed information on these points are not available in literature. Deuterium is one of the best non-radioactive isotopes for use as a tracer element.

Lewis predicted that heavy water will not support life. Experiments have proved that seeds do not sprout in it. Mice become increasingly thirsty when they drink heavy water. It is lethal to higher organisms. Some primitive sea animals die when placed in it. It is said that while a concentrated solution acts as a poison, very dilute solutions have a tonic effect, stimulating vegetation. Later experiments on the physiological effects of heavy water show that the filaments of "Spirogyra" in water of specific gravity 1.00006 are characterized by lack of movement, absence of abscission or cell dysfunction, and greater longevity.

For a long time, chemists had no suspicion that the atmosphere contained any constituent other than those recognised by Lavoisier in the 18th century. There was a similar time lag in the development of knowledge concerning the finer composition of water which is now known to contain at least 2 different types of both hydrogen and oxygen atoms. A new organic chemistry in which each compound containing C (which also has got two isotopes C^{12} and C^{13}) and hydrogen is duplicated by the synthesis of a "heavy" partner will doubtless become an accomplished fact in course of time.

PRINCIPLES AND APPLICATIONS OF POLAROGRAPHIC ANALYSIS

by
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In 1920, J. Heyrovsky of Czechoslavakia introduced for the first time a dropping mercury electrode in electrolysis. He used it as one of the electrodes in an electrolytic cell to determine the concentration of electro-oxidizable or electro-reducible constitutents in a solution. Till 1937, most of the fundamental and applied work on polarography was done by the inventor and his collaborators like Ilkovic, Shikata and others. Later on, this analysis began to be increasingly used in many countries, and a continuous flow of papers on polarographic theory and practice followed.

The phenomenal rate at which contributions to polarographic literature have increased testifies to the popularity of the method among scientific investigators. It has come to stay in the analytical laboratory. It comes in handy where, otherwise, tedious chemical pro cedures have to be undertaken to estimate traces of impurities in substances.

The primary circuit for polarographic analysis consists of an electrolytic cell with a dropping mercury electrode and a mercury pool serving as the other electrode. a potentiometer to vary the applied voltage and a galvanometer to record the current. On applying a gradually increasing potential to the solution containing the electroactive substance in the cell, no perceptible increase in current may be observed till the decomposition potential is reached. Further increase in potential produces a sudden rise in current which subsequently attains a limiting value.

The electroactive substance is oxidised or reduced at the dropping mercury electrode in proportion to its concentration in the solution. The process occurs at this electrode which is polarisable because of its small area compared to the very large area of the other electrode. The step in current, called the diffusion current, is the direct result of the above reaction. Even when no voltage is applied, a small current always flows in the system. It is called the 'residual current' and its value should be subtracted from the total limiting current to obtain the true diffusion current.

The current-voltage curve obtained on plotting the values read from an experiment gives a wave whose height is measured. This represents the diffusion current which is proportional to the concentration of the electro-oxidized or electro-reduced substance. The half wave potential is characteristic of the particular substance under test. It is independent of the change in concentration. This property serves for identification purposes.

To conduct an analysis, it is necessary to choose a suitable procedure according to the nature of the substance under examination. Usually substances in the concentration range $10^{-3} - 10^{-5}$ M give polarograms of reasonable height. Polarographic characteristics are **normally** obtained only if the process is diffusion-controlled. Hence any other interference should be avoided. A supporting electrolyte of concentration greater than 50 times that of the electroactive substance is chosen to eliminate electrical migration. Sometimes a sudden abnormal increase in current called 'polarographic maxima' may be noticed and, to avoid errors due to this, a colloidal substance like gelatin (about 0.005%) is also added. The final solution must contain in addition to the substance under test, a supporting electrolyte of very high concentration and a maxima suppressor.

Since oxygen dissolved in the solution will get reduced at the dropping mercury electrode, it is obviously necessary to eliminate it by passing an inert gas like nitrogen or hydrogen for about 5-10 minutes just before starting the experiment. A thermostatic control to keep the temperature at 25°C±0. 2°C is necessary.

Equipment based on the fundamental circuit can be assembled from components available in a laboratory. Alternatively, compact automatic or visual recording instruments are offered by reputed manufacturers. With the visual type, the observed values of current and voltage have to be plotted to get the polarogram whereas it is directly obtained with automatic instruments

The diffusion current and the half wave potential are determined from the polarograms. By comparison with standardization charts, or applying the Ilkovic equation.

$$i_d = 605\, n\, D^{\frac{1}{2}} C\, m^{\frac{2}{3}} t^{\frac{1}{6}},$$

the concentration of the substance under examination can be calculated.

The polarographic method is very helpful in determining minute traces of impurities In some cases, simultaneous determination of substances is possible. Very little amounts of test solution are required to conduct the experiment. The method is especially useful in the study of the mechanisms of reduction and oxidation in organic chemistry.

Polarography is extensively applied in inorganic, organic and biological chemistry. In metallurgy, it is chiefly employed to estimate impurities in metals and alloys-e g. lead, cadmium, copper etc., in zinc and its alloys; copper, nickel and cobalt in steel. The development of organic polarography was slow in the beginning but in recent times great strides have been made in applying this to the study and elucidation of many organic reactions. It is very useful for estimating traces of organic substances in others e. g., aldehydes, ketones, aromatic nitro compounds etc., Polarography is also applied in the study of isomeric transformations and determination of structure as well as in organic preparations. Agricultural chemicals like BHC and DDT offer a very important field for polarographic estimations. Biochemical applications include protein analysis, determination of the activity of penicillin solutions, diagnostic tests for cancer etc.

The modern tendency is towards applying polarography as a pilot technique for establishing optimum electrolyte and cathode potential conditions for electrolysis. Instead of the dropping mercury electrode, solid micro electrodes like platinum wire (either stationary or rotating) are coming into increasing use, especially in large scale organic preparations. Yet another field of application has been the kinetics of reactions to determine the extent of completion of the processes.

REFERENCES :

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NOTES AND NEWS

COMMITTEES AND CONFERENCES:

The Electroplating Sectional Committee of the Indian Standards Institution held its first meeting underthe Chairmanship of Dr. T. Banerjee of the National Metallurgical Laboratory at the Central Electrochemical Research Institute on the 25th and 26th March 1954 The meeting was attended by Shri J.P. Mehrotra of the I. S. I. (Convenor), Shri S. C. Bose of the Directorate-General of Ordnance Factories, Shri A. K. Bose of the India Industries Ltd., Calcutta, Sri H. C. Sampath of Mitra & Co , Bombay and Shri Santiago of the Hindustan Aircraft Ltd., Bangalore. Shri S. Ramachandran of this Institute was present as an observer.

SYMPOSIUM

A symposium on 'Electrochemical Processes and their applications to Indian Industry' was held in the Central Electrochemical Research Institute on the 27th and 28th March 1954. Research workers from various laboratories and representatives of industry and various Government Departments attended as delegates and participated enthusiastically in the proceedings. Dr. B. B. Dey, Director of the Central Electrochemical Research Institute and Dr. Rm. Alagappa Chettiar, Chairman of the Advisory Board welcomed the distinguished guests and delegates. Sir S. V. Ramamurthi, I. C. S. (Retd.) who inaugurated the symposium emphasized the importance of electricity as an instrument of social and economic progress. The Institute gave a dinner in honour of the delegates on the 27th evening at the Bhavanagar Stadium and this was followed by a dance recital given by the pupils of the Tamil Isai Palli, Devakottai, which was greatly appreciated. The symposium concluded on the 28th afternoon with a thanksgiving speech by Dr. A. Jogarao, Convenor of the symposium.

ADDRESSES AND LECTURES

Sri G. C. Mitter, Master, Assay Department and Silver Refinery Project, Calcutta and President of the Indian Institute of Metals visited the Institute on the 9th January 1954 and addressed the members of the staff.

Sri K. D. Malaviya, Deputy Minister for the Natural Resources and Scientific Research, visited the Institute on the 25th January 1954 and addressed the members of the staff. A group photograph of the Institute staff with the Minister was taken on the occasion.

Sir A. Lakshmanaswami Mudaliar, Vice-Chancellor of the University of Madras visited the Institute on the 11th February 1954 and addressed the members of th staff.

Dr. K. S. Krishnan, Director, National Physical Laboratory, New Delhi, visited the Institute on 18.3.54 and addressed the members of the staff.

STAFF

We welcome the following members who have joined this Instituteduring the last quarter:

1.	Shri Siddhartha Ghosh.	Senior Scientific Assistant.
2.	Shri R. Srinivasan.	Junior Scientific Assistant.
3.	Shri B. S. R, Sastri.	do
4.	Shri K. R. Shenoy.	do
5.	Shri T. D. Prasada Rao.	Senior Laboratory Assistant.
6.	Shri PL. Annamalai.	do
7.	Shri R. Ramakrishnan.	Accountant.
8.	Shri K.T. Veeraraghavan.	Photographer.
9.	Shri A. Sebastian.	Mechanic.
10.	Shri S. Ramaseshan.	III Division Clerk.
11.	Shri S. Venkatasubramanian.	Record-Sorter.

Shri K. S. Gopalakrishnan, Administrative Officer, left this Institute on the 31st March 1954 to rejoin his parent office at Delhi. Within the short period of his stay with us, Shri K. S. Gopalakrishnan endeared himself to all the members of the staff by the unvarying friendliness with which he treated everybody. Though not a scientist by profession, his outlook even on administrative matters was a scientific one. His consummate sense of artistry was mainly responsible for the success of the various official and social functions organized in this Institute. His departure from our midst has occasioned the keenest regret and we are only voicing the feeling of one and all in the Institute in wishing him long years of happiness in the future.

Shri.T.A. Sundaram, Accountant, left this Institute on reversion to his parent office He was an able and popular member of the staff whom we are sorry to lose.

SOCIAL AND PERSONAL

The first annual day of the Institute was celebrated by the staff club on the 26th January 1954. Shri T. M. Narayanaswami Pillai, M. L. C., Retired Chairman of the Madras Public Service Commission was the chief guest and Dr. B B. Dey was in the chair. The function began with speechesby Dr. Dey, Shri T.M. Narayanaswami Pillai and Dr. Alagappa Chettiar, and after the distribution of prizes to winners in the various sports events there was an enjoyable programme of variety entertain- ment got up mostly by members of the Institute Staff. The celebrations conclu ded with an open-air dinner to which several distinguished guests had been invited.

An excursion to Alagar Koil, a well-known temple at the foot of a hill 10 miles from Madurai, and to Madurai City was arranged by the staff club on the 3rd March 1954. Members of the party thoroughly enjoyed the day's programme.

VISITORS

	Name	*Date of visit*
1.	Shri G. C. Mitter, Assay Department & Silver Refinery Project.	9-1-1954
2.	Shri K. D. Malaviya, Deputy Minister for Natural Resources & Scientific Research.	25-1-1954
3.	Sir A. Lakshmanaswami Mudaliar, Vice-Chancellor, University of Madras.	9-2-1954
4.	Dr, P. V. Cherian, Chairman, Madras Legislative Council.	2-3-1954
5.	Mrs. Mona Hensman, M. P., Madras.	12-3-1954
6.	Dr. K. S. Krishnan, Director, National Physical Laboratory, New Delhi.	18-3-1954
7.	Sir S. V. Ramamurthy, I. C. S. (Retd.)	26-3-1954
8.	Prof. M. S. Thacker, Indian Institute of Science, Bangalore.	28-3-1954
9.	Shri Humayun Kabir, Secretary to the Ministry of Education, Government of India.	16-4-1954

BOOK REVIEWS

Structure of Metals, Crystallographic Methods, Principles, and Data by Charles S. Barret (Mc Graw Hill Publishing Co. Ltd., London, 1953) pp. xvi+661

The author's purpose of writing a volume "to serve both as a text and as a reference book", seems to have been achieved in the book under review. Starting with the fundamentals of crystallography, stereographic projection and X-rays, the author goes on to give a description of experimental techniques and the various instruments and apparatus, followed by a discussion of the applications of X-ray diffraction in physical metallurgy. One chapter has been devoted to electron diffraction, its applications and usefulness in metallurgy.

The theoretical basis of the properties of various types of metals and alloys has been adequately dealt with from the stand-point of crystal structure. The numerous references to original literature and the accounts of current research in the field make the volume an extremely useful reference book.

The lucid style in which the book is written, the numerous sketches and diagrams included in it and the avoidance of extensive mathematical treatment of the topics are bound to make it interesting and useful to a wide circle of workers in metallurgical and allied fields. Inclusion of such chapters as 'Determination of crystal structure by Fourier Series' and 'Crystal Geometry' and various data on the crystal structure of metals in the appendixes will be welcomed by the more advanced readers.

N. N. S.

Chemical Constitution by Ketelaar, J. A. A., (Elsevier Publishing Co., Amsterdam etc., 1953) pp. vi +398.

Professor Ketelaar's book in Dutch has been translated into English by Dr. L. C. Jackson. In a small compass of about four hundred pages, the author has given a systematic treatment of recent developments in the theory of the chemical bond. This book is valuable as a complement to the usual textbooks of inorganic and organic chemistry. The author has given a fresh approach to the subject by trying to correlate the physical and chemical properties of substances with their molecular structure; in this he has succeeded to a certain extent.

The book in the main falls into four broad divisions dealing with four types of bonding—ionic, atomic, metallic, and Van Der Waals. The first two sections have received greater attention. Under ionic bond are discussed, among other things, ionic radius, crystal structure and lattice energy;complex systems have been discussed in great detail; and other topics included are electrolytic dissociation, acid-base strength, solubility etc. The section on atomic bond includes a discussion of the hydrogen atom, the hydrogen molecule ion, and the hydrogen molecule, resonance, theory of colours etc. The metallic bond receives a brief treatment and the section on mechanical properties makes interesting reading. The last part deals with Van Der Waals forces in relation to physical and chemical properties.

Professor Ketelaar has freely used the ideas and formulae of wave mechanics in many places; and there may be a few who might feel that the book appears to be too mathematical But it is no longer possible for students of physical chemistry to evade mathematics. References to recent literature are fairly extensive, and this book will be of great use to Honours students teachers, and research workers.

S. R.

Electroanalytical Chemistry by James. J. Lingane (Inter Science Publishers Inc., New York, 1953). pp. ix+430

The book is meant to be a comprehensive treatise on practically the whole field of electroanalytical chemistry, leaving out only polarography, because it has been discussed in several recent monographs. Of the eighteen chapters in the book, the first ten chapters are devoted to the fundamental principles and concepts of electrochemistry which form the basis of analytical methods. The first chapter introducing the subject matter of the book is followed by one on the measurement of e. m. f. of galvanic cells. The interpretation of the e. m. f of galvanic cells in the third chapter is refreshingly clear, and the sign-conventions employed in representing electrode and cell reactions are lucidly set out. The fourth chapter is on pH and its measurement The next four chapters deal with potentiometric titrations as applied to acid-base, precipitation and oxidation-reduction reactions and automatic mechanisms. Specific examples of redox titrations are discussed and the technique of automatic titrations is explained. The ninth chapter on conductometric analysis brings out its advantages for the estimations of very weak acids like boric acid, phenol, hydroquinone etc., of ammonium ions and for estimations involving very dilute solutions and mixtures of strong and weak acids. Reference is made to high frequency methods also. In the tenth chapter on electrolysis, the relative merits of constant current, constant applied voltage and controlled potential methods in electro-analysis are discussed and the principles of the controlled potential technique are described.

The actual technique of controlled potential analysis and instruments for the automatic control of potential called 'potentiostats' are described in chapters XI and XII. In this connection, the use of depolarizers is critically examined and the criteria for their choice are indicated. The latest developments in potentiostats and information regarding manufacturers of these instruments and their accessories are given.

The next two chapters give detailed accounts of electro-gravimetric estimations and separations by the controlled potential technique. Internal electrolysis or spontaneous electrogravimetric analysis is the subject of chapter XV. In this method the cell is designed to function spontaneously, without an external source of e. m. f., by suitable choice of an anode so that it displaces the metal ion already in solution. However because of the low driving voltage, the method is tediously long and restricted to separations of small quantities of metals.

Electrographic analysis by which a pattern of surface structures of alloys can be got by anodic dissolution on absorbent paper soaked in a suitable reagent giving a coloured product is dealt with in a short chapter. The method. as at present developed is only qualitative or at best semi-quantitative.

The last two chapters are devoted to coulometric analysis which has been described as 'the newest of all electrometric methods' and is applicable to oxidizable or reducible substances. In one method, electrolysis is conducted with the potential of the working electrode controlled till the current falls to zero and the quantity of substance reacted is computed from the reading of a coulometer in series with the cell. In coulometric titrations, electrolysis is done with constant current till the end is shown by a chemical indicator or by electrometric measurement. This method is particularly suited to the estimation of micro quantities of substances with great precision, using reagents generated during electrolysis.

It is a matter for appreciation that proper emphasis has been laid on fundamental concepts. The omission of a chapter on polarography from an otherwise comprehensive treatise on electro-analytical chemistry may perhaps be regretted. Information given about the manufacturers of special gadgets and instruments mentioned in the text is a welcome feature of the book. The book is bound to be a valuable help both to students specializing in electrochemistry and to research workers. The printing and get-up leave nothing to be desired

N. S.

Progress In Organic Chemistry, Vol II
• editer by J. W. Cook
(Butterworths Scientific Publications, London 1953). pp. viii+212

This volume in the "Progress series" has been published in a comparatively short time after the issue of Volume I. As usual the volume deals with certain topics in organic chemistry of current interest and importance, and the contributions are all from recognised authorities on the subjects included here. The book presents various topics in a 'concise rather than in a comprehensive manner'.

The volume opens with a review of some of the recent developments in theoretical organic chemistry, in particular the applications of quantum mechanics. This new method of approach has offered ample scope for the study of the structure and reactivity of organic compounds and no person is more suited to write on this topic than Prof. M. J. S. Dewar. The chapter certainly should be of great appeal to all students of organic chemistry

Then follows a survey of the progress made in the study of organic fluorine compounds which have recently attained a large degree of importance both in the academic and industrial fields. A very instructive account is given of the methods of manufacture, properties and applications of the various organic fluorine compounds.

The remaining four chapters are devoted to the chemistry of natural products; the triterpenoids, cortisone and its partial synthesis; the relationship of natural to carcinogenic aromatic compounds; and finally an account of recent developments in the chemistry of pyridine and its derivatives.

Books like this should appeal to all organic chemists wishing to have an intimate and up-to-date knowledge of recent progress made in the various fields of organic chemistry.

H. V.. K. U.

Organic Protective Coatings, edited by William Von Fischer and Edward G. Bobalek
(Reinhold Publishing Corporation, New York 1953). pp. viii+387

This book is a welcome contribution in the field of modern protective coatings. There are 16 chapters dealing with the development of various types of coatings such as corrosive and luminescent pigments, aminoplast resins, hotspray lacquers, emulsion and latex paints, synthetic resin coatings for the protection of metal surfaces, new applications of organic coatings to electric insulation, and the use of silicone resins in heat-resistant paints. Several chapters present the theories of physics and chemistry as applied to coatings technology. The problems of formulation, specification, and application of organic coatings are well presented and the reader gets a clear picture of the subject. Many examples are included which illustrate the manner of approach to everyday problems connected with paint formulation and the practical economic factors involved in selecting the proper coating for any specific application. This book is bound to be of very great value as a standard reference book for all industrial and research chemists and chemical engineers and also for manufacturers and users of paints, varnishes and lacquers.

V. A.

Industrial wastes: Their disposal and Treatment, editer by Willem Rudolfs ACS-Monograph No. 118 (Reinhold Publishing Corporation, New York, 1953). pp. VI+497.

This book in seventeen chapters provides an exhaustive and up-to-date treatment of industrial waste materials from the practical point of view. Extensive references to literature in the field are given. The volume has been written by a group of experts in the waste disposal problems of various industries such as acid and explosives, steel pickling, coal and oil, leather, pulp and paper etc. Each chapter contains brief descriptions of the waste producing processes, sources of wastes, recovery and remedial measures, quantities and characteristics of the wastes, methods of treatment etc. The physical, chemical, metallurgical and biological aspects of each problem are very clearly presented. Engineering details and the fundamental principles involved in industrial waste treatment are discussed at sufficient length to enable their application to the treatment of individual wastes for which no specific methods have been established. This book will prove to be of immense value to all chemists and engineers in industry confronted with waste-treatment problems as well as to research workers in the field.

V. A.

ABSTRACTS

Polarographic wave: Lewis, J. A., *Industrial Chemist*, **29**, 58 (1953).

Measurement of wave height, graphical construction for damped and undamped polarograms, behaviour of various maxima suppressors and rudiments of subtractive or derivative polarography are discussed. The method of standardizing curves is preferred to that of standard addition which is inapplicable to an irreversible wave with a nonlinear relationship between height and concentration.

Extension of sensitivity of polarographic analysis with rotating amalgam electrodes: Cooke, W. D., *Anal. Chem.*, **25**, 215 (1953).

A rotating amalgam electrode yielded larger diffusion currents and smaller charging currents, and was stable for long periods of time. Purity of supporting electrolyte and removal of oxygen in the solution before conducting the experiment were important. Polarograms for Co''' in 0·02 *M* NH_4Cl, 0.02 *M* NH_4 Ac, and 0·01 *M* H Ac, and Cd in 0 02 *M* NH_4 OH and 0·02 *M* NH_4Cl were taken. Cd waves were drawn out because of amalgam formation. An anomalous peak was found in the acid medium. A special cell is described.

An improved Randles Type Cathode Ray Polarograph. Reynolds, O. F., and Davies, H, M., *Analyst*, **78**, 314 (1953).

The principle of the linear sweep cathode ray polarograph is sketched and some details are given of the modifications and improvements made. Interpretation of cathode ray polarographic curves is discussed and a reduced form of Randles equation applicable to this instrument given.

Potentiometric polarography - controlled current scanning: Adams, R N., Reilly, C. N., and Furman N. H., *Anal. Chem.* **25**, 1160 (1953).

Method for getting polarograms using solid electrodes is described. The conventional technique is reversed, manually controlled current scanning and observation of the resulting voltage with a continuous indicating pH meter being applied. IR drop connections are eliminated and linear concentration-diffusion current condition obtained. On applying this method to determination of Fe''' in synthetic mixtures containing Fe_2O_3, results within 1% of the true value were obtained.

Measuring resistance of polarographic cell circuits: Pesce, M. R., Kuesbach S. L., and Ladisch R. K., *Anal. Chem.* **25**, 979 (1953)

An oscilloscope and Wheatstone bridge arrangement were used to determine IR drop of polarographic cells. The cell was made part of the bridge, and a sine wave signal of 600-1500 cycles per sec. was fed into the system. The bridge was then balanced by using the oscilloscope to determine the null point. Cell resistance measurements were found to be correct to $\pm$ 20 ohms.

Reaction occurring in CO_2 - H_2O mixtures in a high-frequency electric arc: Wilde, K. A., Zwolinski B. J. and Parlin, R. B., (Univ. of Utah, Salt Lake City), *Science*, **118**, 43 (1953).

CO_2 and H_2O mixtures gave no reaction products except CO from the decomposition of CO_2 to the extent of about 9%. Most of the parameters affecting the process were investigated, including current (75-200 ma.) pressure (50-250 mm. of Hg), flow rate (5-35 cc/sec) and H_2O/CO_2 ratio. Formaldehyde was absent, either there was an insufficient supply of H_2 atoms, or any product formed was decomposed thermally in the region of the arc plasma itself or at the electrodes.

The anodic oxidation of ferrous sulphate in flow discharge electrolysis: Hickling, A., and Linacre J. K., *J. Chem. Soc.* 711, (1954)

Oxidation of the ferrous salt takes place with marked evolution of H_2 from the soln. and it is reported that the oxidation largely arises from the dissociation of water molecules owing to bombardment of the soln. by positive gaseous ions. The oxidation yield (G, in equivalents/Faraday) depends upon the concentration of ferrous sulphate, the nature of the electrolyte, the temperature, and the presence of O_2. It is represented by the equation.

$$G = 1 + n[(Fe^{++}) + A]/[(Fe^{++}) + A + B]$$

where n is the number of equivalents of oxidising agent formed/ Faraday by the dissociation of water, and A and B are constants, which can be evaluated for any given set of conditions.

The development of the electrochemical industry in India: Rama Char, T. L., (Indian, Inst Sci., Bangalore) *J. Electrochem. Soc.* **100**, 7C (1953); *C. A.* **47**, 12063, (1953) A review.

Theory of electrochemical chlorate formation. De Valera, V., *Trans. Faraday Soc.* **49**, 1338 (1953).

A mathematical treatment of the factors affecting chlorate formation during chloride electrolysis is given and expressions for the C. E. in terms of cell-design and other factors are deduced.

Determination of current efficiency of Diaphragm Alkali Chlorine cells by gas analysis: Kircher, M S., Engel, H. R., Ritter B. H. and Bartlett A. H., *Trans. Electrochem. Soc.* **100**, 448 (1953).

A method of calculating the current efficiency of alkali chlorine cells by analysis of the anode gas and the method of collecting a cumulative sample are given. The analysis is based on the fact that there is direct correlation between the CO_2 content of the anode gas and the C. E.

Electrolysis of Alkali Chlorides: Colin, P. H., and Barr L. F. K., (to Stora Kopparbergs Bergslags Aktieholag) *Swed. 140574, June* 2, 1953; *C. A.*, **47**, 11053*b* (1953).

Alkali chlorides are electrolysed by the amalgam method with graphite electrodes, which have been treated with Cl or HCl at 700-1500°.

Electrochemical chlorine-caustic soda production in the Gulf Coast Area: Chrencik, F. (Diamond Alkali Co., Pasadena, Texas), *J. Electrochem. Soc.*, **100**, 182*C*, (1953); *C. A.* **47**, 12063 (1953). *A review.*

Chlorates by electrolysis of alkaline chlorides: the effect of some factors: Salas, S. O. E. (Univ. Concepcion, Chile.) *Bol. Soc. Chilena Quim.* 4, 43 (1952); *C. A.* **47**, 9823 (1953).

The effect of the following factors on current efficiency were studied: (a) changes in pH from 5·5 to 7·0; (b) c.d.'s at anode and cathode; (c) temp. (20-90°); (d) NaCl concn. (50–308 g./l.); (e) addn. agents (0.5 to 5 g./l. of $Na_2Cr_2O_7$); (f) anode materials (magnetite). The current efficiencies were improved by increasing the pH to 6.7 - 6.9, increasing the anodic c.d. and a high NaCl concn. $Na_2Cr_2O_7$ (2-3 g.) should be used for best current efficiency. The current efficiencies were lowered slightly on increasing the cathode c.d. (1.9 to 36 amp/sq. dm.), on increasing temp., or increasing current per unit vol. of soln. With magnetite the current efficiencies were lower and the potential drop was greater, but they increased with temp. The potential drop became less as the temp. increased. The tests were made on 750 cc of soln. contg. NaCl 300, and $Na_2Cr_2O_7$ 1 g./l. at 45°, pH 6.8, 2.85 amp/sq.dm. at the anode, with 7 amp-hrs and a current concn. of 1.33 amp./l.

Electrolytic preparation of hypochlorite: Goument V. O., *Brit.* 6,82,365, *Nov.* 5. 1952: *C. A.* **47**, 3732*a* (1953).

An apparatus is described consisting of three chambers. Salt is placed at the bottom of the middle chamber and the electrodes are placed in the inner chamber which communicates at the bottom with the middle chamber. Both hypochlorite soln. and escaping H are transferred through pipes with control valves to the outer chamber (storage compartment). By means of a needle valve the escape of H is so regulated that a const. level of liquid is built up in the inner chamber and water supplied through a non-return valve when H pressure decreases the level of the electrolyte below a normal operation level.

Continuous production of bromine by electrolysis: Yoshio Ida, *Japan* 7008, 1951 Nov 12; *C. A.* **47**, 4769*a* (1953).

Brine contg. 0.065 g. Br/l is fed at the rate of 15 l/hr. and CCl_4 is fed at the rate of 600 ml/hr. into an electrolyte cell having a rotating activated carbon anode (4 r. p. m.) with fixed axis. and the soln. is electrolysed with a d.c. of 0.3 amp., 3.75 V and 0.15 amp/sq.dm. to give 73% Br, recovery. The C.E. for Br. yield is 73%.

Sulphuric acid recovery: (*a*) Wicker, D B. (to American Viscose Corp) *U. S.* 2,631,973, Mar. 17, 1953; *C. A.*, **47**, 4719*d*, (1953).

Sulphate is recovered as H_2SO_4 soln. substantially free of ions other than those of water and H_2SO_4 from an aq. salt soln. contg. 0.1 - 10% H_2SO_4 and 0.5 - 25% of an alkali metal sulphate by (i) introducing a Pb electrode and PbO_2 electrode into the salt soln. to form a deposit of $PbSO_4$ on the electrodes and (ii) impressing a d.c. on the electrodes at a potential of 2 V. with the positive side of d.c. source connected to PbO_2 electrode and negative to Pb, while the electrodes are suspended in water or aq. H_2SO_4 soln. to liberate the sulphate ions from the electrodes as H_2SO_4. A typical waste effluent from the viscose-rayon plant contg. about 0.5% H_2SO_4, about 1% Na_2SO_4 and 0.03% $ZnSO_4$ can be satisfactorily processed to recover H_2SO_4 in a conc. upto 10%. The current consumption in the process is about 125 amp/hr/lb H_2SO_4 at a potential of approx. 3 3 V, equiv. to approx. 400 w.hr./lb. H_2SO_4

(b) U. S. 2,631,974, (Conwell J. W. to same assignee). In the first step the deposit of $PbSO_4$ is formed on Pb & PbO_2 electrodes by passing a d c. from an external source through the salt soln. with the Pb connected to +ve and PbO_2 to—ve. In the second step the reverse d.c. is continued till H_2SO_4 concn. of the electrolyte is higher than its concn. in the electrolyte of the first step. The fixation of $PbSO_4$ is preferably stopped before a pH of 7 is exceeded.

Electrochemical preparation of sodium hydrosulphite: Patel, C. C. and Rao, M R. A. (Indian Inst. Sci. Bangalore) *Proc. Natl. Inst. Sci. India* **19**, 211, 215, 231 (1953); *C. A.* **47**, 12061, (1953)

The direct electrochem. method can efficiently produce hydrosulphite with a Hg. cathode (Fe, Pb, Ni and Zn cathodes give lower yields and have side effects), a catholyte with 20 - 30% $NaHSO_3$ and a high concn of NaCl and an anolyte of concd. NaCl soln. which yields Cl as a by-product. Optimum anode and cathode efficiencies are somewhat above 90%. Passing of SO_2 in the catholyte helps formation of bisulphite and maintains a low pH Temp. should be at the most 5°, c.d. 2-3 amp/sq.dm. at the cathode. $Na_2S_2O_4 . 2H_2O$ crystals have to be removed from time to time.

Hydroxylamine hydrochloride by electrolysis Yamada, S., et al, *Japan* 2664 (May 26, 1951): *C. A* **47**, 12064 (1953).

A Pb container, the inside of which is coated with Pb-Hg, is used as a cathode; a PbO_2 anode is placed inside the container sepd. by a diaphragm from the cathode. The catholyte is 20% HCl and the anolyte 20-30% H_2SO_4. Electrolytic reduction takes place at a cathodic c.d of 6 amp/sq.dm. and an anodic c.d. of 15-25 amp./sq.dm. with the catholyte at 10-20° and the anolyte at 30°. 50% HNO_3 is added dropwise into the catholyte.

Mechanism of the anodic formation of lead chromate: Wagner, C., *J. Electrochem. Soc.* 101, 60 (1954)

This paper deals with the interplay of diffusion and conversion processes governing the anodic formation of lead chromate during the electrolysis of a soln. of sodium chromate and sodium chlorate between lead electrodes. At sufficiently high c.d. the boundary layer contains excess lead ions and flows downward in virtue of its higher density. Lead chromate is formed, in part at a distance of 0.01 to 0.1 cm. from the anode by counterdiffusion of lead ions and chromate ions, and in part at the lower edge of the anode by mixing of boundary layer and bulk soln.

Electrolytic production of high-purity manganese dioxide: Chakrabarti, H. K and Banerjee, T. (Natl. Met. Lab., Jamshedpur) *J. Sci. Ind. Research (India)* **12B**, 211 (1953); *C.A.* **47**, 9823, (1953)

Factors influencing the production of high purity electrolytic Mn dioxide were studied using a 3-compartment cell with stainless steel cathodes and a Pb-Sb anode. The conditions which were conducive to max. efficiency were found to be: c.d. of 0.54 - 0.80 amp/sq.dm., temp. of 70° - 80°, concn. of Mn sulphate 200 g/l., and concn. of H_2SO_4 less than 50 g./l. The product was about 90% Mn dioxide, with minute traces of Pb and lower oxides of Mn, and about 10% moisture. A mechanism has been proposed to explain the oxidation process.

High grade MnO_2 from low grade domestic ores: Schrier E., and Hoffman H. W., *Chem Eng.* (1954), 152

Raw ore is crushed, ground to 20 mesh, calcined to convert manganese to divalent form, leached with H_2SO_4 to dissolve the metals in the ore, the soln. of the sulphates decanted from insoluble matter, and the heavy metals precipitated by treatment with BaS. All the precipitate is settled in a thickener and the clear soln. decanted. Fe and other impurities are removed by aeration. Subsequent filtration gives a suitable cell solution MnO_2 is deposited on anodes of graphite. The deposits are separated, washed dried and packed. Cell voltage was 2.2 to 2.6 V, anodic c.d. 7-9 amp/sq. ft. cathodic c.d. 11.6-15 amp/sq.ft. temp. 90-94°C, energy consumption 1 KWH/lb MnO_2. Complete flow sheet is also given.

Electrolysis with rotating vertical electrodes: Inventa A G. fur Forschung und Patentverwertung Swiss 281,429, July 1, 1952 (*cl.* 36*h*; *C. A* **47**, 9828 (1953)

An appts. and process using a rotating vertical disc electrode and liquid metal are described. The liquid metal is introduced into the central part of the rotating disc and moves towards the peripheral part of the disc. Economy in current consumption and lower initial cost are the outstanding features. Examples describe application to the electrolysis of NaCl, Na_2SO_4 and $ZnSO_4$. Hg is the metal used.

4. The reduction of some nitrocompounds at a stirred mercury surface.
Bergmann, I., & James, J. C., (Late), (Chemistry Department, University of Glasgow), *Trans. Faraday Soc.* **50**, 61 (1954) Part I.

The reduction states of some nitro compounds at a stirred mercury surface were studied and the results found to agree with those obtained by polarographic methods in both aqueous and non-aqueous media. The rearrangement of the intermediate β-phenylhydroxylamine in aqueous buffers and its pK values have been studieed by reductive preparation and by spectrophotometric examination in order to clarify its role in the polarographic reduction of nitrobenzene.

Anodic Synthesis: Part X.. Synthesis of Nervonic acid: Bounds, D. G., Linstead, R. P., and Weedon, B C L. *J. Chem Soc.* 448-51 *Jan.* 1954.

Both nervonic acid from brain cerebrosides of cattle and man and selacholeic acid from shark liver oil have been formulated as cis-tetracos-15-enoic acid on the basis of their reactions and degradation. These two apparently identical natural products have been synthesised by the anodic chain extension of oleic and elaidic acids respectively without stereomutation about the double bond.

3 Electrolytic reduction of benzoic, phenylacetic, and cinnamic acids and their esters at a platinized platinum cathode.

Ono. S., Hayashi, T, and Nakaya, J., (Department of chemistry, Naniva univ. Osaka) *Trans. Electrochem. Soc.*, **101**, 104-09, (1954).

The reduction of these aromatic acids and their esters at a platinized platinum cathode was studied and was found to be different from that at a lead cathode or a mercury cathode. With platinized platinum as cathode, cyclohexyl derivatives were obtained and the carboxyl group reduced. Electrolysis at a platinized platinum cathode under pressure was also studied and the results confirmed the catalytic nature of the process.

4. Electrolytic reduction of Quinones.

(a) Electrolytic reduction of benzoquinone under pressure, Ono. S., (Nanuia Univ., Japan). *J. Chem. Soc. Japan; Pure Chem. Sect.* **73**, 852-5 1953 *C. A.* **47**, 1953.

p-Benzoquionone was electrolytically reduced to cyclochexanol with a platinized platinum cathode in 2N sulphuric acid under a hydrogen pressure of 1 to 25 atmospheres. Cyclo-hexanol was obtained from p-benzoquinone: hydroquinone and phenol formation increased with increasing pressure. With a lead cathode under a hydrogen pressure of 1 to 30 atmospheres, benzoquinone was reduced to hydroquinone and a resinous mass which gave diphenyl on distillation with zinc dust. The yield of resin increased at the expense of hydroquinone with increase in pressure of hydrogen.

5. Recent trends in Electro-organic Industry in Japan Ito, A., (Sankyo Drug Manuf. Co. Tokyo), *Jour, Soc. Org. Synthet. Chem, Japan* **11**, 252-3 (1953).

(a) **Synthesis of calciam gluconate.** Calcium gluconate is being manufactured in Japan by oxidising glucose by indirect electrolysis with bromine as charge carrier. 21.6 kg of glucose 1.56 kg. of bromine and 1.32 kg of powdered calcium carbonate are left overnight in 80 litres of water to form calcium bromide and then electrolysed in two 40 litre cells with graphite electrodes at 30°C. for 10 hrs. Voltage is 5-6 and amperage per cell 290-300. The electrolyte is stirred continuously by blowing in air and 5.28 kg. of $CaCO_3$ is added in small quantities at a time to neutralise the liquid. On cooling the liquid in water for three days, the calcium gluconate crystallises out quantitatively It is recrystallised at least twice before being used for medicinal purposes. The mother liquor can be utilised over again for at least ten successive operations. Average yield is 90%. Current density not mentioned. Current conoentration about 5 amps per litre.

Reduction of cyano pyrimidine:

2-methyl 4-amino 5-cyanopyrimidine (I) prepared by condensing. $Me.H_2N.C:NH$ with $C:CHOC_2H_5$ (CN, CN) was reduced to 2-methyl 4-amino 5-aminomethyl pyrimidine as follows: Two large diaphragm cells with cooling arrangement were used. The anode chamber contained 10-15% HCl and the catholyte contained 10% I. and 10% HCl and 0.01% $PdCl_2$. Graphite rod was used as anode. Platinum was a better anode but costlier and a reticulated silver plate served as cathode. After rapid electrolysis at 20°C (lasting not more than 10 hours at the most) Pd black was removed and the liquid concentrated under vacuo and cooled with ice to give the hydrochloride as needles (m.p.upto 262°C) pure enough for the synthesis of vitamin B_1.

8. Electrolytic preparation of benzoic acid sulphonamide: Erlenbach, M. & Sieglitz, A. *Brit Pat.* 691,187, *May* 6, (1953).

In the electrolytic manufacture of benzoic acid sulphonamide, the need for platinum electrodes can be eliminated, by proper preparation of a sheet lead anode as follows:- The clean lead plate is pickled in 20% acetic acid solution and anodically charged in 2*N* NaOH at room temperature using an initial c.d. of 1 amp/dm^2. At the second spontaneous voltage increase the plate is removed and washed. This anode is used in conjunction with a sponge lead cathode to electrolyse 10 gms. of 0-toluene sulphonamide suspended in 150 ml. of 10% Na_2CO_3 at 50°C and 2-3 volts at a c.d. of 2.7 amps/dm^2. Yield is 4.54 gms of product melting at 223°C.

Potato Starch for household use by electrolytic preparation. Aktien gesellschaft A. Heving (Havz Kuz: in ventor) *Ger. Pat* 811, 460, *March* 10, 1952; *C. A.* 47. 12056 1953.

The disadvantages of the usual chlorine and sulphur dioxide treatment of potato starch to make it suitable for household purposes can be avoided by generating the reagents electrolytically. An apparatus has been described which connects to the effluent from the final wash. In a typical operation a 25% starch suspension is mixed with a 2. 5% mixture of equal parts of sodium chloride and sodium sulphate and treated at 40°C for 10 to 15 min. with a current of 2. 8 amps. All these quantities are variable to give the most efficient operation.

Production and uses of hyperpure lead: I-Production in Italy: (A Tonolli & Co.): Piontelli, R. and Fagnani, L.,: *Chemica and Industria*, **34**, 629. (1952).

The advantages of the sulphamate bath for the electro-refining of lead are discussed. An average current efficiency of 93% has been obtained from a sulphamate bath employing current densities between 80 and 120 amps/sq. m., depending on the anode grade. Cell voltage varies from 0. 3. to 0. 5 at 25°C. Energy consumption per ton of lead is 140 KWH Purity of the lead is 99.995%. The decomposition of sulphamate into ammonium bisulphate with the simultaneous formation of lead sulphate does not involve more than .02 kgm of acid loss per ton of lead.

High purity Aluminium· Brenner, P., *Metal Progress*, **65**, 115 (1954).

Since the war, superpure aluminium (99 . 99%) has been produced on a considerable scale in some European countries by the three-layer electrolytic process. The price of such aluminium can be lowered since secondary aluminium contaminated with copper is used rather than virgin aluminium. High-purity aluminium being too soft for many purposes, a series of aluminium alloys have been devoloped on a high-purity aluminium base, particularly by the addition of magnesium. These alloys, designated as "Reflectal", lend themselves to mechanical, chemical or electrochemical polishing and are used for reflectors, hotel and hospital utensils, ornamental trim on automobiles and buses, as well as for useful household objects of all types. A large part of the high-purity alloys is used in the form of semi-finished products by the jewellery industry, where the finished articles are anodised and coloured. The gold-finished articles are very cheap and can barely be distinguished in colour and lustre from genuine gold. The wear resistance and stability of this alloy insure great durability.

The electrolysis of fused aluminates: *Bonnier, E., (Univ. Grenoble, France), Ann. Phy.* **8**, 259 (1953); *C. A* **47**, 10376 (1953).

The electrolysis of the following fused systems was studied: (i) Na aluminate with cryclite or NaF ; (ii) Ca aluminate with cryolite, Ca halide or AlF_3; (iii) Ba aluminate with cryolite, Ba, Mg, or Li halide; (iv) Mg aluminate with cryolite, Mg halide, Na, Li, or Mg fluoride. Eutectic temps. were established for portions of the binary systems, cryolite and Na or Mg aluminate. The electrolysis of (i) yielded Na or Al depending upon the compn. and cathode material, (ii) yielded alloys of Al containing Ca down to 0 5% (iii) yielded no definite compns. except for an alloy of Al, Ba, and Li, (iv) yielded Al - Mg alloys high in Mg.

Flux for casting of aluminium and its alloys: *Davis, J. A. and Eastwood, L.* (to Pennsylvania Salt Manufacturing Co.) *U. S.* 2,654,670, *Oct* 6, 1953; *C, A* **48**, 538 (1954).

When a flux containing a mixt of an alkali metal fluoborate and an alkali metal fluotitanate. in which at least one of the alkali metals is Na. is used in melting Al and its alloys, dross is not formed in objectionable amounts and grain -structure, pinhole porosity, Si modification and tensile strength are improved. The flux is prepared by fusing or sintering 25-75% Na-fluoborate with 25-75% Na-fluotitanate About 1% of the mixt-(by wt.) is added to the metal being melted, preferably by submerging it near the bottom of the melting pot. A 50:50 mixt. of fluoborate and fluotitanate 30, Na fluo-titanate 30, $CaF_2$6, and NaCl 34% is satisfactory.

Electrolytic production of copper powder: Rahman, A., and Khundkar, M. H., Dacca Univ. Pakistan) *Pakistan J. Sci. Research* 4, 51 (1952); *C. A.* **47**, 10376 (1953).

Conditions were studied for the eletrolytic production of Cu powder from the acid sulphate bath. A range of c.d. from 6 to 8 amp./sq.dm. was found most satisfactory. Effects of different concns. of Na_2SO_4 and H_2SO_4 in the bath were observed by reference to the rate of formation and the nature of the powder. At a cathode c.d. of 7 amp./sq.dm. and a Cu concn. of 12 g/l., optimum concn. of H_2SO_4 was 10 - 20 g./l. and of Na_2SO_4 was 50-75 g/l.

Metallic Titanium. Glaser, J. and Hampel, C A., *U. S.* 2,618,549., Nov. 18, 1952; *C. A.* **47**, 2115 (1953).

Crystals of Ti are produced by vigorous mixing of $TiCl_4$ with Na-amalgam containing less then 0.5% sodium at 190°-220°F. Ti is filtered off and the filtered residue of Ti containing Hg and NaCl heated in vacuum (0.0001 mm. Hg) at 400-700°F to remove Hg followed by heating at 1800°-2000°F to separate NaCl. Large ductile crystals of Ti, which could be cold-rolled to nearly 50% reduction in thickness were obtained. Crystals were stable in acid, water and air. Presence of NaCl apparently facilitates crystal growth.

Titanium: Starck, H C, *Ger.* 812, 117, Aug, 27, 1951; *C.A.***47**, 5856*g*(1953).

The vacuum reactor containing Ca, Mg or Na and maintained at 0.1 mm. Hg is washed with small quantities of gaseous $TiCl_4$ at room temp. to remove the remaining air. Temp. is then raised to 700 C and theoretical quantity of $TiCl_4$ introduced to react with the Ca, Mg or Na producing Ti metal. Costly inert gases are thus avoided.

Titanium: (Radtkc, S.F) *The Chemist*, **30**, 387 (1953).

A survey of the history, occurrence, production, important properties, present uses, potential aplications in chemical industry, present cost, fabrication and the future of the metal has been made.

The Metallurgy of Zirconium: Hayes, E. T., and Stephen W. W., *Metal Progress* **63**, 97 (1953).

The history of the metal, occurrence of its ores and the three methods of extracting the metal viz., the Kroll process, the electrolytic process and the thermal decomposition process are described. Sketch of the electrolytic extraction apparatus is given. The process of melting the metal and data on its physical and chemical properties, corrosion, machining and uses of the pure metal and its alloys and the various impurities and their amounts in iodide-zirconium are given,

Metal colouring by deposition of a thin film: Kikchi M. and Kaneko, N., *J. Electrochem. Soc. Japan* **21**, 17 (1953); *C. A.* **47**, 6796 *G*, (1953)

When a solution composed of Cu tartrate(0.1 to 0 2 *M*) and NaOH (1-2*M*) is electrolysed with a C anode and Cu (brass, Au, or Pt) cathode at 25° the cathode plate is coloured by a thin film coating on the surface of the plate.

Throwing power and covering power in Electroplating solutions: Pinner, R., *Electroplating and metal spraying*, **7**, 9, 49, 59 (1954).

The terms throwing power and covering power are explained. Factors affecting throwing power and covering power are discussed. Methods to determine throwing and covering powers are given. The effect of operating conditions like type of solution, conductivity and electrode distance, metal concentration, current density, pH, temperature, agitation, addition agents and structure of the surface, on throwing power and covering power are discussed.

Electro-deposition of aluminium from hydride-type plating baths: Brenner, A., and Couch, D. E. (to the united Sates of America) *U. S.* 2,651, 608, *Sept.* 8, 1953; *C. A.* **48**, 61 (1954).

Bright, smooth, ductile electrodeposits are obtained by the use of 0.5-1.0 *M* LiH and 2-3 *M* Al Cl_3 in Et_2O soln. A cathode c.d. of 2 amp./sq.dm. and a plate-reverse current ratio of 20:1 are used with Al anodes. Bis (2 chloroethyl) ether (4.8% by vol.) is used to harden the deposits. Other hydrides, concns., and additives gave poorer results.

Preparation of Aluminium surfaces for plating: Zelley, W, G., (to Aluminium Co. of America) *U. S* 2650, 886 *Sep.* 1953; *C. A*. **48**, 475 (1954).

The customary dil. zincate bath is improved by the addition of sol. nitrates, or nitrites, tartarates and $FeCl_3$. Typical prepn. steps include buffing, cleaning with a solvent, cleaning with alkali and rinsing with water, and dipping in hot H_2SO_4 and rinsing with water, and dipping in cold HNO_3 and rinsing with water, and dipping in zincate bath for 0.25-1 minute at room temperature and rinsing in water. Alternative bath compositions are (1) Zn 05, NaOH5 0, $NaNO_3$1, (2) ZnO 5, Na 50 $NaNO_3$ 1, NaK $C_4H_4O_6$, 50 and (3) ZnO 5, NaOH 50, $NaNO_3$ 1, NaK $C_4H_4O_6$ 50, $FeCl_3$. $6H_2O$ 1 g/1. cleansing with solvent and alkali and treatment with H_2SO_4 and HNO_3 may be eliminated if a double zincate treatment is applied. The first Zn coat is stripped in HNO_3 and the article is given a sedond dip in the improved dil. alk. zincate bath. A uniformly thin, adherent smooth Zn deposit is obtained.

Plating on Aluminium—The Phosphoric acid Anodising treatment: Buncer, B. E.,, *Metal Finishing* **52**, 70, 76 (1954).

This paper describes the method of direct plating of aluminium after anodising. It gives the various details of phosphoric acid anodising which has to be carried out before plating Al with Ni, Cu, or Ag. Optimum conditions for anodising are described. The details of plating procedures after anodising are also given. Equipment required is listed.

Milk white nickel plating:
Kozo Morii etal, (to Nitto Chemical Industries Co.,) *Japan, 4102 (1951) July ~0. C. A* **47** *2068h*, (*1953*).

An electrolyte containing 140 g $NiSO_4$, 15 g. $NiCl_2$, 75 g. $Al_2(SO_4)_3$ and 15 g. H_3BO_3 per litre is used for Ni plating on Fe plate at a c.d. of 0.6 to 1.4 amp/per.sq. mm. and at 30-40°.

Improving the properties of Ni Plating baths: Komusaari, H, *Metalloberflache*, **4**, *B162 (1952) Nickel bulletin*, **26**, *8*. (*1954*).

The throwing power was observed to increase astonishingly by the addition of 5 g. per litre of the sulphite, but affected the brightness badly. Reduction of the amount to 30-100 mg per litre of SO_2 in the form of sulphite produced no deleterious effects on the brightness but improved the throwing power, reduced the hydrogen porosity, and lowered the stress in the deposit. But it obstructed the precipitation of detrimental iron. A bath composition using saccharin as brightener is also given.

Determination of boric acid in Nickel plating baths and acid zinc plating baths by means of cation exchangers: Gabrielson, G. *Plating* **41**, *47* (*1954*).

5 or 10 ml Ni or Zn soution are percolated through a layer (of 10 and 150 mm diamr. and height respectively) of sulphonic acid type (Amberlite IR 120) in the hydrogen form at 4-5 ml/min. The following reactions take place:

$$NiCl_2 + 2R\ SO_3H \rightarrow 2\ HCl + (R\ SO_3)_2Ni$$
$$NiSO_4 + 2R\ SO_3H \rightarrow H_2SO_4 + (RSO_3)_2Ni$$
$$ZnSO_4 + 2R\ SO_3H \rightarrow H_2SO_4 + (R\ SO_3)_2Zn.$$

The resin bed is washed, with distilled water and the liquid titrated against *N* NaOH upto near neutralisation followed by NaOH to a blue colour using bromothymol blue. 7-8 g. mannitol are added and the titration continued to the end point. The method has a maximum relative error of 0.5%.

Plastics for plating-room: Foulke. D. G., *Proc. Am. Electroplaters' Soc.*, **39**, 127, (1952); *C. A.* **47**, 9827 (1953).

For lining tanks and ducts, polyester-fiberglass and pollyvinyl chloride have been used. It is difficult to fabricate polyethylene, Teflon and Kel-F although they offer a high resistance, Anode bags can be made with Dynel and nylon,

Preparation of metals for bonding rubber: Majchert-Planeta, N. and Kalinowska, J. *Przemyst. Chem.* **31**, 81, (1952); *C. A.* **47**, 9825*d* (1953).

Studies with Al and steel showed that thorough cleaning of the metal surfaces offered the best conditions for brazing. The optimum plating conditions were as follows:Bath containing $K_3Cu(CN)_4$ 49.03, Na CN 5, $Zn(CN)_2$ 7.5, Na_2CO_3 14.4, $(NH_4)_2SO_4$ 4.65, and Na_2SO_4 22.76 g./l at a c.d. of 0.3 amp./sq.dm., 3-4 V. for 20 min. at room temp. The bonding of rubber to such a brazed surface was very tenacious.

Electrophoretic coating of rubber: Planeta N. and Wiekiera, M., Przemyst *Chem.* **31**, 473 (1952); *C. A.* **47**, 10886 *f* (1953).

Rubber coating of metals by electrophoresis is reviewed and a description of the results of laboratory experiments is given. It is reported that a diaphragmless cell having Zn anodes and cathodes and a 20% rubber solution containing S, carbon black and an accelerator gives the best results.

Electrophoretic mobility of fresh hevea, latex: Bowler, W. W., *Ind. Eng. Chem.*, **45**, 1790 (1953); *C. A.* **47**, 12860*g* (1953)

Fresh latex behaves like proteins in the variation of its electrophoretic mobility with pH. The isoelectric point changes from clone to clone and to a little extent among the trees in the same clone. Higher dry-rubber content latex has greater mobility Seasonal variations in the trees do not affect the mobility. Repeated washings of latex particles with (1) 3% aq. NH_4OH and (2) aq. soln. contg. 2% oleic. acid and 3% excess of NH_3 changed the mobility-pH relations altogether.

Transparent electroconductive coatings: Lytle, W. O. and Junge A. E. (to Pittsburgh Plate Glass Co.) *U. S. 2, 651, 585,* Sept. 8, 1953 ; *C. A.* **48**, *971c* (1954).

These coatings are deposited on transparent articles like glass. An aq. mixt. of a metal salt like Sn. halide is introduced into an air stream and the stream is made to contact glass heated to >400°F but < freezing point of the glass, the water content of the atm. being controlled. The metal salt solution generally contains 1000 cc. anhyd. $SnCl_4$, 2000 cc. anhyd. MeOH, 60 g. NH_4HF_2 and 3000 cc. butyl carbitol acetate.

Electrically insulated conductor: Dorst S., (to Sprague Electric Co.) *U. S.* 2, 650, 975, *Sept* 1, 1953; *C. A.* **48**, 18641 (1954).

Cu, Cu alloys, or nichrome wires are used as anode in a bath comprising of a water dispersion of refractory insulating material (china clay) containing inorg. electrolytes (Na silicate). Both electrophoresis and electrolysis take place. The former causing deposition of the refractory material on the anode and the latter producing colloidal hydrated gel which serves as binder. After coating, the wire is heated to 250° to 1000°C.

Electroconductive glass articles: Lytle, W. O. (*to Pittsburgh Plate Glass Co*) *U. S.* 2, 648, 754, *Aug.* 11, 1953; *C. A.*, **47**, 10382*g* (1953).

Transparent glass surfaces are given transparent electro-conductive metal oxides coatings. Articles or sheet glass may be thus coated. Applications: Electrically heated windshields or windows of airplanes, automobiles, and railway coaches; heating elements for domestic purposes or in the laboratory.

Alkaline storage battery: Gary W. W. Jr., U, *S.* 2, 642, 469 (1953)

An alkaline type battery with a high discharge rate, a minimum weight and low cost comprises the following:- The negative and positive plates have porous backing membranes of filter paper, cotton or plastic. A coating of nickel hydroxide hydrogel, prepared by adding an aqueous solution of sodium or potassium hydroxide to a dilute boiling aqueous solution of a nickel salt in the presence of non-reactive conductors like nickel or graphite flakes, is applied to one surface of the positive plate. For the negative plates, a mixture of cadmium and iron oxides in a finely divided condition is applied to porous membranes. Nickel foil conductor grids are placed between each pair of membranes.

Primary battery. *Winckler, G. A. F.*, and Reinhardt *O. K., U. S* 2, 641, 623 (1953).

Improvements in primary cells employing zinc as anode, carbon as cathode, alkali as electrolyte and atmospheric oxygen as depolariser have been effected by employing a cathode formed of activatedcarbon with a plastic binder containing 15% by weight of ethyl cellulose as inner surface and partly coated with an airimpermeable material. The anode is a U-shaped strip of zinc molded into a cap which is supported within the carbon cup and closes the cell. The electrolyte is 25% sodium hydroxide solution.

Electric primary cell· Higgins, W. E. and Wilkinson, R. G , *U. S.* 2, 641 622 (1953).

To prevent the discharge of dry cells of leclanche type while not in use with a view to increase the shelf life the following procedures are adopted: (1) a small piece of magnesium alloy is embedded in the electrolytic paste of a leclanche cell and connected to the zinc casing. (2) a small piece of aluminium is connected to a zinc anode when a strongly alkaline electrolyte is employed (3) a small piece of magnesium is used when the anode is magnesium alloy containing small percentages of aluminium or zinc and (4) a small piece of magnesium alloy containing lithium, calcium or sodium is used when the anode is of other magnesium alloys or pure magnesium.

Separator for storage batteries: Booth ,F., (to Odham & Sons Ltd.) *U. S.* 2, 647, 157, *July 28, 1953; C. A.* **47**, *9190e (1953).*

Open-weave glass fiber coated with polyvinyl chloride. *U S.* 2, 647. 158. An alkali digest of light wood (balsa, quipo, or obiche) is shaken up with SiO_2 gel. To this suspension is added a wetting agent and phenol-HCHO resin (suspension 150, dispersing agent 3, and resin 3 parts). The resulting mixture is filtered and the solid mass, after drying under pressure at 90 95°, is subjected to heat treatment for polymerisation of the resin.

Porous battery separators: Baty J. A., *(to Cresset Research Corp.) U. S*, 2, 658, 987, Sept. 29, 1953; ; *C. A.* **48**, *473 (1954).*

This material is acid resistant and is formed by intimate mixing of silica-gel in an org. plastic binder like polystyrene which is water-insol., acid resistant and heat softenable. Polystyrene-in-water latex is mixed with a plasticizer, a wood-flour filler aud Na silicate soln. the proportions being critical. A glass fiber mat is coated with this mixture which is then hardened by immersion in aq. $(NH_4)_2 SO_4$ soln., washed and dried.

Separator for dry storage batteries: Fuller L. and Szper J. A., *U. S.* 2,655, 552, *Oct.* 13, 1953; *C. A.* **48**, 61c (1954).

Gum karaya is dissolved in distilled water and kieselguhr is stirred in so that a homogeneous mixture is obtained to which 60% non-vulcanised latex is added by mixing (0.5 lb. gum karaya, 25 gal. distd. H_2O, 90 lb. kieselguhr, and 17 lb. latex). The resulting paste is used for impregnating regenerated cellulose sheets 0.003 - 0.01 in. thick which are compressed to the required thickness.

Battery plate separator: Phillips, T. E; *(to Owens-Corning Fiberglass Corp).* U S. 2, 653, 985, Sept. 29, 1953; C. A. *48*, 1179a, (1954).

A method for the preparation of a combined separator and retainer for Pb storage battery plates. A 40-mil porous fiberglass mat bonded at their individual junctions by B-Stage phenol-HCHO resin is passed through rollers together with a similar 10-mil mat coated with an aq. emulsion of butadiene-styrene copolymer and diatomaceous earth. The mat combination is heated for coalescence "Treeing" is reduced by this material which is microporous on one side.

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