SHIKATA LABORATORY.

Vorstand: Dr. Masuzô Shikata, Professor of Chemistry of Forest Products in the Department of Agriculture, Kyoto Imperial University.

Chapter I. A preface to Studies upon the Dropping Mercury Cathode and Polarograph.

Research concerning the reduction potentials of organic compounds are given in this series of papers.

1. The polarograph and its applications.

By **Masuzo Shikata.**

Journ. Soc. chem. Industr. Japan, **33,** 1492–1470 (1930).

Our research concerning the mercury dropping cathode and polarograph are herein described. The history and new applications of this method are also given.

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2. The Behaviors of Colloid Particles on the Deposition Potentials of Metallic Ions.

By **Masuzo Shikata** and **Nobushige Hosaki.**

Journ. Soc. chem. Industr. Japan, **32,** 1135–1139 (1929).

(1) The mercury dropping cathode and the polarograph give exact current voltage curves. Therefore, the saturation current due to metallic ions can be used for the micro-analysis of metallic ions.

(2) The author tried to find the saturation current caused by the discharge of colloidal particles.

(3) Electrolyses were carried out in alkali salts (such as Na- and Li- salt), in the presence of gelatine as well as agar. The current voltage curves with such colloidal substances were compared with those without such substances.

(4) The electrolysis with the colloid gives no marked new saturation current, but the depositions of the alkali metals are influenced by the presence of such colloidal substances.

(5) The presence of gelatine or agar makes the deposition of alkali metals positive.

(6) As to an electrolytic reduction of organic substance, the presence of gelatine or agar makes its reduction potential negative.

3. Considerations as to the Electrolytic Reductions of Organic Compounds and their Relation to Polarity.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. chem. Soc. Japan, **53**, 834 (1932).

From the polarographic studies on the electrolytic reduction of many organic compounds, the authors found the following relations which might be called the "electronegativity rule of reduction potentials".

The reduction potentials of the organic compounds inclined to be more easily reducible the more the electronegative group were substituted in the same compounds.

This general rule is to be seen in the examples given in Table I.

Table 1.

Compounds	Formula	*Electrolytic reduction potentials* (Calculated from 1 normal calomel electrode)
Aceton	$CH_3 \cdot CO \cdot CH_3$	−1.278 V
Acetylacetone	$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$	−1.204
Acetoin	$CH_3 \cdot CO \cdot CHOH \cdot CH_3$	−1.139
Acetophenone	$CH_3 \cdot CO \cdot C_6H_5$	−1.116
Benzophenone	$C_6H_5 \cdot CO \cdot C_6H_5$	−1.013
Benzoin	$C_6H_5 \cdot CO \cdot CHOH \cdot C_6H_5$	−0.953
Benzoylacetone	$C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$	−0.010
Dibenzoylmethane	$C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_5$	−0.819
Diacetyl	$CH_3 \cdot CO \cdot CO \cdot CH_3$	−0.402
Diphenyltriketone	$C_6H_5 \cdot CO \cdot CO \cdot CO \cdot C_6H_5$	−0.249
Benzil	$C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$	−0.203

Another example of this general rule is found in the case of the substitution of nitrobenzene.

dinitrobenzene > nitrophenol > nitrobenzene > nitraniline

Thus the substitution with the negative group makes the reduction potential more positive.

4. A Study of the Electrolytic Reduction Potentials of Organic Compounds.
Part I. The Reduction Potential of Isovaleraldehyde.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc, Japan, **2**, 610 (1926),
Memoirs College Agri., Kyoto Imp. Univ. No. 4 (1927).

Summary of the Results.

(1) Measurements of the reduction potentials of isovaleraldehyde with the polarograph, show the validity of the following formula for the first approximation.

$$\pi = -\frac{RT}{2F} \log \frac{k'}{[H^{\cdot}]^2 C_{R\cdot CHO}}$$

Calculating k′ in the case of isovaleraldehyde of $1.868.10^{-1}$ mol solution in 0.1 n HCl we found log k′=34.672.

Thus it was shown that the reduction proceeds reversibly in an acid and an alkaline solution. In a neutral solution a R. P. was always more positive than a theoretical value.

(2) If we compare the solutions of various concentrations of isovaleraldehyde with solutions of the same hydrogen ion concentration, they show abnormal shifts. By introducing the correction of an adsorption coefficient in the formula

$$\pi = -\frac{RT}{2F} \ln \frac{k'}{\frac{1}{C^m_{R\cdot CHO}[H^{\cdot}]_2}}$$

we find that

m=1.380 for a strongly acid solution
m=1.330 for an alkaline solution
m=0.272 for an ammonium chloride solution
m=0.287 for a neutral solution.

From these results, the possibility of a negative adsorption of isovaleraldehyde by a mercury cathode in NH_4Cl or a neutral solution has been proposed.

(3) Three reducible impurities in 2% Kahlbaum's isoamylalcohol solution were detected by the polaograms, two of which were found to be an aliphatic aldehyde and a furfural.

(4) A comparison of the sensitiveness of the polaographic method and Schiff's reagent, showed that the former is twenty times more sensitive than the latter.

(5) From the effect of isoamylalcohol upon the R. P. of isovaleraldehyde, it has been concluded that the reduction product of isovaleraldehyde is isoamylalcohol.

5. A Study of the Electrolytic Reduction Potentials of Organic Compounds.
Part II. The Reduction Potentials of Pyridine.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **3**, 746 (1927),
Memoirs College Agri., Kyoto Imp. Univ. No. 4 (1927).

Summary of the Results.

(1) The reduction potential of pyridine was measured with the dropping mercury cathode and the polarograph.

(2) In the reduction of pyridine two waves in the current voltage curve were found. It was proved that the first wave is due to the reduction of the pyridine ion, and the second wave to the reduction of the undissociated pyridine molecule.

(3) We examined the extent to which the theory of reversible reduction can be applied to such an irreversible reduction system as the pyridine—piperidine system.

By assuming the following formula as applicable, we calculated a socalled "theoretical value" and compared it with the observed value.

$$\pi = -\frac{RT}{6F} \ln \frac{k'}{[H^{\cdot}]^6 [\overline{Pyridine}]}$$

for the R. P. of the undissociated pyridine molecule.

and

$$\pi = -\frac{RT}{6F} \ln \frac{k''}{[H^{\cdot}]^6 [\overline{Pyridine^{+}}]}$$

for the R. P. of the pyridine ion.

Calculating from the R. P. I of $1.251.10^{-1}$ m in a 0.1 n HCl solution (R. P. I= −1.296 V):

$$\log k'' = 102.606 \text{ for pyridine ion}$$

Calculating also from $1.251.10^{-1}$ m pyridine in the mixture (0.001 n HCl + 0.1 n KCl) solution (R. P. II= −1.590 V):

$$\log k' = 116.407 \text{ (for pyridine molecule)}$$

By taking these values as standards, it was found that in an acid solution, the R. P. shows a parallel relation with the theoretical value, although the deviation is much greater than that of the reversible reduction; but in a neutral and an alkaline solution, the relation is not so simple.

(4) To show the behavior of pyridine at the electrode, the adsorption coefficient was introduced into the formula and calculated.

For a relatively high concentration of pyridine:

in acid solutions m=0.219 (for pyridine ion)
in neutral solutions m=0.089 („ „ „)
in alkaline solutions m=0.223 (for undissociated pyridine molecule)

(5) The electrolytic reduction potential is recommeneded as a general expression for reduction potentials in the reversible and irrevertible reduction.

6. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part III. Reduction Potentials of Nicotinic Acid.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **3**, 1173 (1927),
Memoirs College Agri., Kyoto Imp. Univ. No. 4 (1927).

Summary of the Results.

(1) The reduction potential of nicotinic acid was measured with the dropping mercury cathode and the polarograph.

(2) Two stages of the reduction process were observed.

(3) For the first stage of the reduction, the observed R.P. was compared with the theoretical value calculated by the following formula at 15°C.,

$$\pi = -\frac{0.05713}{2} \log \frac{k'}{[H^{\cdot}]^2 C_{C_5H_4NCOOH}}$$

in which by taking the R. P. of 0.01 mol nicotinic acid in (0.01 n HCl+0.1 n KCl) solution, i.e. −0.984 V as a standard, we have

$$\log k = 28.33$$

In an acid as well as in a neutral salt solution, the observed R. P. showed a satisfactory concordance with the calculated values. Thus the first stage has been concluded to be the reduction of the carbonyl group of nicotinic acid to aldehyde.

(4) The second stage of the reduction is considered to be the reduction of the pyridine ring of nicotinic acid, by comparing it with the R. P. of pyridine as set forth in our preceding paper.

(5) The reduction of nicotinic acid in an excess of alkali does not take place, owing perhaps to the desorption of negatively charged nicotinic acid ions at the polarised mercury cathode. R. P. in a sodium acetate or sodium bicarbonate solution was about 0.02 V more negative than the calculated value.

(6) The maximum current voltage curve was observed in a sodium bicarbonate solution, in which the potential of maximum current intensity was almost independent of the concentration of nicotinic acid.

(7) The reduction potential of benzoic acid was studied for the sake of comparison, with the result that in hydrochloric acid, no reduction but only the deposition of the hydrogen ion was seen, while in a potassium chloride solution the R. P. was over 0.240 V more negative than that of nicotinic acid. Thus the group effect of a carbonyl group is considered to be more effective than

a benzene ring.

(8) A final conclusion as to the reduction process has been withheld for the time, until the isolation of the reduction product, now under investigation, is completed.

7. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part IV. On the Reduction Potentials of Ketonic Radicals and their Relations to the Constitutions.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **4**, 91 (1928),
Memoirs College Agri. Kyoto Imp. Univ. No. 8 (1930).

Summary.

(1) The electrolytic reduction potentials of ketonic compounds such as diacetyl, acetoin, acetone, methylethylketone, acetophenone, benzophenone, benzil, and benzoin were measured with the dropping mercury cathode and the polarograph.

(2) In order to show the relation of the reduction potentials of these compounds to their concentrations and hydrogen ion concentrations, their so-called theoretical values were calculated by the Nernst formula of the reversible reduction type, and were compared with the observed values at 25°C.

$$\pi = -\frac{0.05911}{2} \log \frac{k'}{[H^{\cdot}]^2\,[\text{reducible compound}]}$$

(3) For diacetyl, when the R. P. (−0.345 V) (from 1 n calomel electrode) of the $1.13 \cdot 10^{-3}$ mol in (0.01 n HCl+0.1 n KCl) solution was taken as a standard, we found

$$\log k' = 4.681$$

The observed reduction potentials showed relatively small deviations from the calculated values in the acid solutions, but in the alkaline solutions the observed R. P. was more positive than the calculated R. P.

(4) In the case of acetone, $\log k' = 34.941$ and the R. P. (obs.) showed much larger negative deviations and could not be regarded as reversible.

For methylethylketone, $\log k' = 34.418$. That is, methylethylketone is more easily reducible than acetone, although their difference is not conspicuous.

(5) For acetoin, $\log k' = 30.453$, and the deviations from the calculated values were of about the same magnitudes as in the case of acetone.

(6) For acetophenone, $\log k' = 28.235$.

(7) In the cases of benzophenone, benzil and benzoin, a certain amount of ethyl alcohol was added to the electrolysing solution. As the ethylalcohol was found to make the reduction potential negative, we did not calculated $\log k'$.

We may say from the results of the experiments that the reduction potentials of aromatic ketones showed much smaller deviations than those of aliphatic ketones and that the reductions of the aromatic ketones have a reversible character, although the authors hold the view that there is no definite difference or discontinuity between reversible and irreversible reductions. In the alkaline solutions the R. P. of aromatic ketones showed larger deviations than in the acidic solutions. Moreover, the direction of the deviations were reversed, that is, the R.P. (obs.) of alkaline solutions was much positive than the calculated R. P.

Further, the polarograms of aromatic ketones showed typical saturation curves, while those of the aliphatic ketones were slowly increasing and did not show definite saturation curves. So we may say that a minute quantity of an aromatic ketone in a solution may more easily determinable by the polaographic method than an aliphatic ketone.

(8) The solubility of the following compounds in water at 25°C was determined by the polarographic method.

Benzophenone	$4.41 \cdot 10^{-4}$ g. mol. per liter.
Benzil	$8.86 \cdot 10^{-5}$ „ „ „ „
Benzoin	$1.51 \cdot 10^{-4}$ „ „ „ „

(9) The group effects of CH_3, C_6H_5, CO, OH on the reducibility of ketonic radical are noteworthy.

If we compare the reduction potentials of the solutions, containing about 10^{-4} mol. of reducible substances in (0.01 n HCl+0.1 n KCl) mixture, we get the following results:

	Diacetyl CH_3–CO–CO–CH_3	Acetoin CH_3–CO–CH(OH)–CH_3	Acetone CH_3–CO–CH_3	Aceto-phenone CH_3–CO–C_6H_5	Benzo-phenone C_6H_5–CO–C_6H_5	Benzoin C_6H_5–CO–CH(OH)–C_6H_5	Benzil C_6H_5–CO–CO–C_6H_5
Concentration ($\times 10^{-4}$ m.)	1.13	1.13	1.03	1.05$_4$	1.0	1.0	1.0
R. P.	−0.402	−1.139	−1.278	−1.116	−1.013(II)	−0.953(II)	−0.203
Diacetyl	0	−0.737	−0.876	−0.714	− 0.326	− 0.551	+0.199
Acetoin		0	−0.139	+0.023	+0.126	+0.186	+0.936
Acetone			0	+0.162	+0.265	+0.322	+1.075
Acetophenone				0	+ 0.103	+0.163	+0.913
Benzophenone					0	+0.060	+0.810
Benzoin						0	+0.750
Benzil							0

As is seen in the above table, the differences of the compounds R•CO•R and R•CO•CO•R are

Acetone and Diacetyl	−0.876 V
Benzophenone and Benzil	−0.810 V

Those of R•CO•R and R•CO•CH(OH)•R are

Acetone and Acetoin	−0.139 V
Benzophenone and Benzoin	−0.060 V

CO is more easily reducible in the C_6H_5 group than in the CH_3 group as is shown in the following:

Acetone and Acetophenone	−0.162 V
Acetophenone and Benzophenone	−0.103 V

The substitution of two CH_3 and C_6H_5 shifts the reduction potential about 0.2 Volts.

Diacetyl and Benzil	−0.199 V
Acetoin and Benzoin	−0.186 V
Acetone and Benzophenone	−0.265 V

From the above comparisons there seems to be a definite group effect and a group orientation effect on the reduction potential of a ketonic group not only in a qualitative, but also in a quantitative sense, although not to a satisfactory degree.

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8. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part V. On the Reduction Potentials of Ketonic Radicals and their Relation to the Chemical Constitutions. (*Continued.*)

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **4**, 771 (1928),
Memoirs College Agri., Kyoto Imp. Univ. No. 8 (1930).

Summary.

(1) The reduction potentials of acetylacetone, acetonylacetone, benzoylacetone, dibenzoylmethane and diphenyltriketone were measured with the dropping mercury cathode and the polarograph.

(2) In order to show the relation of the reduction potentials of these compounds to their concentrations and hydrogen ion concentrations, the so-called theoretical values of R. P. were calculated by the Nernst formula of the reversible reduction type assuming that two atoms of hydrogen were taking part in the reduction. They were compared with the observed values at 25°C

$$\pi = -\frac{0.05911}{2} \log \frac{k'}{[H^{\cdot}]^2\,[\text{Reducible compound}]}$$

(3) Results of a part of the experiments were given in Fig. 5 (in the original paper) showing P_H reduction potential curves.

(4) For acetylacetone, taking the reduction potential (−1.097 V) of a

$1.033 \cdot 10^{-2}$ molar solution in the mixture [0.01 n HCl, 0.1 n KCl] as a basis for calculation we found

$$\log k' = -31.09$$

For acetonylacetone

$$\log k' = 32.94$$

(−1.152 V for $1.0 \cdot 10^{-3}$ molar solution in the mixture [0.01 n HCl, 0.1 n KCl])

For benzoylacetone

$$\log k' = 22.70$$

(−0.901 V for $1.0 \cdot 10^{-3}$ molar solution in the mixture [0.01 n HCl, 0.1 n KCl])

For dibenzoylmethane

$$\log k' = 22.90$$

(−0.887 V for $1.0 \cdot 10^{-3}$ molar solution of 50% alcoholic medium [0.01 n HCl, 0.1 n KCl])

For diphenyltriketone,

$$\log k' = 2.46$$

(−0.311 V for $1.0 \cdot 10^{-3}$ molar 10% alcoholic solution of 0.1 n NH_4Cl)

(5) 1, 3-diketone, such as acetylacetone, benzoylacetone, dibenzoylmethane showed two distinct reduction potentials, due to the enol forms and keto forms of these compounds. Further their enol forms were always more reducible than their keto forms.

(6) The negatizing effect of ethyl alcohol upon the reduction potential of benzoylacetone was tested with the result that their R. P. changes parallel with the alcoholic concentration.

(7) The solubility of benzoylacetone to water was calculated to be 2.36×10^{-3} mol per liter at 25°C.

(8) The group and orientation effects on the reduction potentials of ketonic compounds were found to be as follows.

1, 2-diketones were more reducible than 1, 3-diketones, for example:

Diacetyl and acetylacetone	0.802 V
Benzil and dibenzoylmethane	0.616 V

1, 3-diketone was more reducible than 1, 4-diketone, although the difference was much less conspicuous than in the former cases.

Acetylacetone and acetonylacetone	0.055 V

The substitution of the methyl group for the phenyl group made the R. P. more positive as was mentioned in Part IV of our papers.

Benzoylacetone and acetylacetone	0.264 V
Dibenzoylmethane and acetylacetone	0.385 V

With regard to 1, 2-diketone and 1, 2, 3-triketone, the former contrary to our expectation, was more reducible than the latter.

Benzil was more reducible than diphenyltriketone. This is noteworthy as diketones were in other cases as was reported in our previous paper far more reducible than monoketones.

9. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part VI. On the Reduction Potentials of Nitrophenols.

By **Masuzo Shikata** and **Mamoru Watanabe.**

Journ. Agri. chem. Soc. Japan, **4**, 925 (1928).

Summary.

(1) The electrolytic reduction potentials of ortho-, meta-, and para-nitrophenol were measured with the dropping mercury cathode and the polarograph.

(2) Analogous to the case of nitrobenzene [Shikata: Trans. Faraday Soc., No. 61, XXI, 42 (1925)] the first stage of reduction was thought to be the system nitrophenol-nitrosophenol.

(3) Two waves of reductions were found in a slightly alkaline solution, in which the easily reducible wave was proved to be due to the reduction of the undissociated nitrophenol and the second wave to be that of the ionised nitrophenol. It should be noticed that the negatively charged nitrophenol ion was more difficultly reducible than the undissociated molecule, and this was quite contrary to the case of pyridine, that is, the pyridine ion (cathion) was more easily reducible than the undissociated pyridine molecule at the dropping mercury cathode.

(4) The reduction potentials of these compounds in the solutions of various hydrogen ion concentrations were compared with the calculated values from the following formula at 25°C, using the 1 n calomel electrode as the standard electrode.

$$\pi = -\frac{0.05911}{2} \log \frac{k'}{[H^{\cdot}]^2 [\text{Reducible compound}]}$$

(5) For *o*-nitrophenol, taking the reduction potential (0.072 V) of a 10^{-3} molar solution in 0.1 n HCl containing 3% ethanol as the standard,

we found that $\log k' = 2.57$

and that for ionised *o*-nitrophenol,

$$\log k'' = -0.02.$$

For *m*-nitrophenol, by taking the reduction potential (0.043 V) of the 10^{-2} molar solution in 0.1 n HCl as the standard, we found that

$$\log k' = -2.55$$

and that for ionised *m*-nitrophenol,

$$\log k'' = -3.46.$$

For *p*-nitrophenol, i.e. 0.090 V under the same conditions as the former standard, we found that

$$\log k' = -0.95$$

for the reduction of free molecule and that

$$\log k'' = 5.51$$

for that of *p*-nitrophenol ion.

(6) Coincidence of the observed values with the calculated values was fairly good in the case of the slightly acid solutions, but the observed values of all nitrophenols were much more positive than the calculated values in alkaline solutions.

(7) The following series may be given for the reducibilities of isomeric nitrophenols and nitrobenzene.

o-nitrophenol > *m*-nitrophenol > nitrobenzene > *p*-nitrophenol.

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10. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part VII. On the Reduction Potentials of Oxygen, Iron Salts, Hemoglobin, Methemoglobin and Hematin.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **5**, 352 (1929).

(1) The electrolytic reduction potentials of oxygen, iron salts, hemoglobin, methemoglobin and hematin were measured with the dropping mercury cathode and the polarograph.

(2) The electrolytic reduction potential of oxygen which was dissolved in a 0.1 n neutral salt aqueous solution under one atmospheric pressure was +0.064 V at the 1 n calomel electrode, and when air was dissolved in the same solution, the electrolytic reduction potential of oxygen was −0.033 V.

(3) The electrolytic reduction potential of Fe^{+++} to Fe^{++} was remarkably positive, and the reduction potential shifted by $\frac{RT}{F}$ when ten times diluted with hydrion concentration. Therefore, it was assumed from this fact that Fe^{+++} behaves as a hydrogen acceptor.

(4) The reduction of ferric citrate took place in three stages. The first reduction stage was regarded as the reduction of Fe^{+++} to Fe^{++}, the second stage, that of ferric citrates anions and the third stage, that of Fe^{+++} to Fe.

(5) The reduction of hematin took place in two stages due to the reduction of its neutral molecules as well as the hematin ions. The electrolytic reduction of hematin may be regarded as a ferri-ferro system, owing to the fact one equivalent of hydrogen is required for its reduction.

(6) The reduction potential P_H curve of methemoglobin showed that it has an amphoteric nature.

(7) Hemoglobin and a defibrinated cow blood showed the reduction waves on their polaograms.

11. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part VIII. On the Reduction Potentials of Camphor and Fenchone.

By **Masuzo Shikata** and **Mamoru Watanabe.**

Journ. Agri. chem. Soc. Japan, **5**, 904 (1929).

(1) The electrolytic reduction potentials of camphor and fenchone were measured according to the polarographic method.

(2) Their current voltage curves showed two reduction waves the second of which seemed to be caused by the main reduction.

(3) The reduction potentials of the second waves did not show normal shifts during changes of the concentrations of the reducible compounds or of the P_H solutions.

(4) The saturation currents of the second waves were much smaller than the other reducible compounds and hardly appeared at a concentration below 10^{-4} molar.

12. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part IX. On the Enol-Keto Tautomerism.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **7**, 524 (1931).

(1) The electrolytic reduction potentials of benzoylacetic ester, acetacetic ester, benzoylacetone and acetylacetone were measured according to the polarographic method.

(2) The reduction potentials of their keto forms were more positive than their enolic forms.

(3) Neither the concentrations of the keto forms nor of the enolic forms calculated from the polarograms agreed with the results obtained by the use of chemical methods under the same conditions.

(4) The enolic form partly dissociated in a strong alkaline solution; and the dissociated enolic form had a more negative reduction potential than that of the undissociated enolic form.

(5) The reducibility of the compounds described above obeyed the negativity rule of electrolytic reduction.

13. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part X. The Reduction Potential of Bilirubin.

By **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **6**, 533 (1931).

(1) The electrolytic reduction potential of bilirubin was measured using the polarographic method.

(2) Bilirubin took two hydrogen atoms by the electrochemical reduction. That is, the primary reduction production product of bilirubin was an intermediate compound which was reduced to mesobilirubin.

(3) The solubility of bilirubin measured by the polarographic method was about 9 mg per 1 l in a P_H=7.0 buffer solution at 25°C.

(4) It was shown in this experiment that at least two oxidized compounds were formed when the solution of bilirubin made contact with the atmosphere.

14. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XI. The Reduction Potential of Allylalcohol and the Behaviour of a Catalyst upon an Electrolytic Reduction.

By **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **7**, 666 (1931),
Memoirs College Agri., Kyoto Imp. Univ. No. 17 (1931).

Summary.

(1) The reduction potential of allylalcohol was determined by using the dropping mercury cathode and the polarograph.

(2) The electrolytic hydrogenation of the ethylene radical of allylalcohol did not take place within 2 V. From comparison of the reduction of allylalcohol, ketones and some easily reducible unsaturated organic acids, it was discovered that the reducibility of organic compounds is influenced by their electronegativity.

(3) The effectiveness of colloidal platinum black as a catalyser during the electrolytic reduction of allylalcohol was slight.

(4) The increase of the hydrogen ions concentration of neutral electrolyte solution by the addition of platinum colloid was assumed to be due to selective absorption or the basal exchange of ions by colloid.

(5) The deposition of $H^{\cdot}$ became more positive in the presence of platinum colloid resulting from the activation of $H^{\cdot}$ caused by it.

(6) The effect of colloidal platinum black on the deposition of metallic ions of a dilute solution is explained by Prof. Shikata's theory.

(7) Colloidal platinum black acts as a depolaryser in the electrolytic decomposition of water.

The author expresses his cordial thanks to Prof. Shikata for his kind advice and encouragement.

15. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XII. Reduction Potentials of Dinitrobenzenes.

By **Masuzo Shikata** and **Nobushige Hozaki.**

Journ. Agri. chem. Soc. Japan, **7**, 674 (1931),
Memoirs College Agri., Kyoto Imp. Univ. No. 17 (1931).

Summary.

(1) The electrolytic reduction potentials of dinitrobenzenes were studied by the polarographic method.

(2) The electrolytic reduction of dinitrobenzenes took place in two stages; and according to the conclusion that two hydrogen atoms took part in each stage of the reduction, the reduction process may be assumed to be a type of the nitro-nitroso system. Therefore we may say that two nitro groups of dinitrobenzene had a different reduction potential.

(3) The reducibility of dinitrobenzene in ortho, meta and para was arranged in the order of ortho, para and meta in 0.1 n HCl solution and para, ortho and meta in 0.1 n NaOH.

(4) The reduction potentials of dinitrobenzenes were more positive than those of nitrobenzene and nitrophenol and this fact agrees with our "negativity rule" of reducible compounds.

(5) *p*-Dinitrobenzene had the third reduction potentials in the solution of pH=10 or above it. These phenomena were never seen in the cases of ortho and meta isomers.

(6) The solubilities of dinitrobenzenes by the polarographic measurement were as follows:

o-dinitrobenzene: 0.1308 g/L at 25°C
m-dinitrobenzene: 0.8075 g/L „ „
p-dinitrobenzene: 0.1195 g/L „ „

16. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XIII Reduction Potential of Azobenzene.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, 8, 954 (1932),
Memoirs College Agri., Kyoto Imp. Univ. No. 17 (1931).

Summary.

(1) The electrolytic reduction potentials of azobenzene were measured according to the polarographic method, with the dropping mercury, stationary mercury and platinum cathode.

(2) From the R. P. measured by the dropping mercury cathode, the electrolytic reduction of azobenzene may be regarded as a reversible azo-hydrazo system in the range of 1.1 to 5.0 by pH.

(3) R. P. measured by the stationary mercury cathode with a cathodic surface area of 0.785 mm^2 gave the same value as that of the dropping cathode.

(4) The polarograms obtained with the stationary mercury cathode always has a maximum and this maximum is due to the accumulation of the reduction product on the cathode.

(5) R. P. measured by the platinum cathode with a surface area of 0.785 mm^2 were about 150-200 mV more negative than in the other two cases.

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17. A Study ot the Electrolytic Reduction Potentials of Organic Compounds. Part XIV. Reduction Potentials of Dinitrophenols.

By **Masuzo Shikata** and **Nobushige Hozaki.**

Journ. Agri. chem. Soc. Japan, 8, 1121 (1932),
Memoirs College Agri. Kyoto Imp. Uni. No. 17 (1931).

Summary.

(1) The electrolytic reduction potentials of α, β- and γ-dinitrophenols were measured by the polarographic method.

(2) The reduction of dinitrophenols took place in two stages as was the case of the dinitrobenzenes due to their two nitro groups.

(3) The reducibilities of dinitrophenols are arranged thus: $\gamma > \beta > \alpha$ in the first stage and $\beta > \alpha > \gamma$ in the second stage.

(4) The reduction potentials of dinitrophenols, dinitrobenzenes, nitrobenzene and nitrophenols were compared and their mutual relation was found to obey our negativity rule.

(5) The solubilities of dinitrophenols estimated by the polarographic method at 25°C are as follows:

2, 4 (or α)-dinitrophenol: 0.0865 g/L
2, 6 (or β)-dinitrophenol: 0.2853 g/L
2, 5 (or γ)-dinitrophenol: 0.1123 g/L

18. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XV. Reduction Potentials of Nitranilines.

By **Masuzo Shikata** and **Eiichi Taguchi.**

Journ. Agri. chem. Soc. Japan, **8**, 1225 (1932),
Memoirs College Agri. Kyoto Imp. Uni. No. 29 (1934).

Summary.

(1) The electrolytic reduction potentials of *o*-, *m*- and *p*-nitranilines were measured by the polarographic method with the dropping mercury cathode.

(2) Nitranilines are weak bases. Therefore, it was possible to detect the R.P.s of ionic and molecular forms under certain conditions. The R.P. of ionic form was more positive than that of molecular form. This is a characteristic relation of weak basic reducible compounds.

(3) The R.P.s of nitranilines in ionic form were more positive than that of nitrobenzene, but the R.P.s of nitranilines in molecular form were more negative than nitrobenzene with the exception of meta. This is explained with our negativity rule of electrolytic reduction.

(4) Of the three nitranilines, the R.P. of meta was more positive than those of ortho and para, and the R.P.s of the latter two nearly the same. This may be interpreted as the induced alternating polarity of the benzene ring.

(5) The reducibility of various nitro compounds was arranged.

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19. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XVI. Reduction Potential of *p*-aminoazobenze.

By **Masuzo Shikata** and **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **9**, 207 (1934).

Summary.

The results of the study of the electrolytic reduction potential of *p*-amino-azobenzene with the polarograph and the dropping mercury cathode at 25°C were as follows:

(1) The reduction potential of *p*-aminoazobenzene was more positive in a lower concentration than that in a higher concentration in every PH solution.

(2) Owing to the weak basic property of *p*-aminoazobenzene, there were two reduction potentials which were due to the dissociated and undissociated forms in some proper acidic solutions. In a high acidic solution, *p*-aminoazobenzene changed to a quinoid form which was demonstrated by spectrographic study. The reduction potential of the quinoid form was more positive than that of the azoid form, and further, that of the dissociated form was more positive than that of the undissociated form.

(3) The reduction potential of *p*-aminoazobenzene which substituted for the NH_2 group in azobenzene was more negative than that of the latter. This was to be expected from our negativity rule of electrolytic reduction.

(4) The solubility of *p*-aminoazobenzene in water 25°C was found to be $2.815 \cdot 10^{-4}$ g. mol per litre by the polarographic measurement.

20. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XVII. The Reduction Potential of Dimethylaminoazobenzene.

By **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **9**, 227 (1933).

Summary.

The results of the study on the electrolytic reduction potential of dimethylaminoazobenzene with the polarograph and the dropping cathode were as follows:

(1) The reduction potential of dimethylaminoazobenzene was more negative in a high concentration than that in a low concentration, except in the case of a solution of which PH was lower than 2.2.

(2) In an acidic solution, the reduction of dimethylaminoazobenzene showed the reduction potentials of quinoid, dissociated and undissociated azoid forms the same as in the case of *p*-aminoazobenzene.

(3) The maximum currents of the polarograms of dimethylaminoazobenzene in acidic solutions were increased by further concentrating ethanol. From these facts, we assume that dimethylaminoazobenzene becomes easily adsorbable on the mercury cathode in acidic solutions.

(4) The mutual relation among the reduction potentials of azobenzene, *p*-aminoazobenzene and dimethylaminoazobenzene was found to follow our negativity rule of electrolytic reduction, that is, the reduction potential of azobenzene was most positive and that of dimethylaminoazobenzene most negative among them.

21. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XVIII. A Restudy of the Electrolytic Reduction of Camphor.

By **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **10,** 330 (1934).

The polarographic study of camphor was previously performed by Prof. M. Shikata and M. Watanabe. The authors found that the polarograms of camphor had generally two reduction waves.

Their reduction potentials were independent of the hydrogen-ion concentration of electrolyzing solutions and their saturation currents were much smaller than various other compounds in the same condition.

The author again studied the electrolytic reduction of camphor to explain the mechanism of the appearance of abnormal reduction waves.

He found that three waves appeared on the polarogram obtained from 0.1 n HCl containing 10^{-2} m camphor.

He discussed the phenomena after a consideration of the electrocapillar curve and concluded as follows:

(1) The first wave is not due to true reduction but to the replacement of Cl′ by camphor molecule on the electrode surface.

(2) The second wave is the true reduction wave, the potential of which is shifted by the change of pH as anticipated by Nernst's formula.

(3) The third wave is due to the destruction of a molecular camphor layer on the electrode surface.

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22. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XIX. On the Limiting Current Voltage Curves.

By **Masuzo Shikata** and **Isamu Tachi.**

The Journal of the Electrochemical Association of Japan, **2,** 201 (1934).

Abstract.

With the dropping mercury cathode and the polarograph, the electrolytic reduction potentials of many organic compounds have been already measured. Their current voltage curves (polarograms) showed limiting currents with certain concentrations of reducible compounds, say, 10^{-4} mol/*l.*

A comparison of their limiting currents in the same conditions showed that the limiting currents of nitro compounds were larger than those of ketonic or azo compounds, and that among nitro compounds the limiting currents of

dinitro compounds were larger than those of mononitro compounds, and also that there were little differences among the limiting currents of mono and diketones.

Under the assumption that the limiting currents are due to the reduction of organic compounds diffused only from the bulk to the cathode surface, the diffusion constants of reducible compounds were calculated. As an application of limiting current to micro-analysis, the determination of the solubilities of organic compounds were illustrated.

22. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XX. The reduction Potential of Quinine.

By **Masuzo Shikata** and **Eiichi Taguchi.**

The Journal of the Electrochemical Association of Japan, **2,** 233 (1934).

Abstract.

According to the polarographic study of quinine in solutions with various pH values, it was found that the reduction of quinine took place generally in three stages. In the first reduction stage, two hydrogen atoms were required for the reduction of a molecule of quinine in the solutions of which pH values are 8.0 to 10.8, and the shifts of the reduction potentials agreed with the following Nernst formula in that pH range.

$$\pi = -\frac{RT}{2F} \ln \frac{k'}{[H^+]^2[\text{quinine}]}$$

The third reduction wave showed a maximum current in certain solutions. The proper conditions for the determination of the concentration of quinine are given in the present paper.

24. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XXI. On the Ascending Part of the Currents Voltage Curve of Electrolysis, " Adsorption Current ".

By **Masuzo Shikata** and **Isamu Tachi.**

The Journal of the Electrochemical Association of Japan, **2,** 275 (1934).

Abstract.

The ascending part of a polarogram, so-called " adsorption current," has an inclination, which shows the velocity of a depolarization action or the velocity

of the electrolytic reduction. If an adsorption current is traced by the co-ordinates with π and log i, a curve is obtained which generally consists of two straight line parts. The slopes of these lines vary with the types of reducible compounds. These facts are due to the differences of the velocity of the electrolytic reduction of reducible compounds. In this paper, the results of studies on the slopes of the adsorption currents of some azo-compounds, nitro-compounds and ketones are reported.

25. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XXII. A Consideration of the Mechanism of the Electrolytic Reduction.

By **Isamu Tachi.**

Journ. Agri. chem. Soc. Japan, **11,** 734 (1935).

I have observed the behaviour of a small drop of a difficult soluble organic compound such as nitrobenzene, camphor oil and carbonetetrachloride on a small surface mercury cathode by the photographic method.

It was found that the drop of each organic compound gradually became flat on the cathode surface by polarization, and then it had a tendency to regain its original state by further polarization. This phenomenon agreed with the electrocapillary phenomenon of polarized mercury.

The contact angles of organic compounds to mercury as well as the changes of the angles with polarization differed from one another owing to their characters as well as to the nature of electrolyte solutions. Camphor oil became more flat than nitrobenzene and carbonetetrachloride. Nitrobenzene became more flat in an alkaline medium than in an acidic medium.

In connection with these facts, the mechanism of the reduction of nitrobenzene and of camphor were discussed.

26. A Study of the Electrolytic Reduction Potentials of Organic Compounds. Part XXIII. Reduction Potential of Quinoline.

By **Isamu Tachi** and **Hiroshi Kabai.**

The Journal of the Electrochemical Association of Japan, **3,** 250 (1935).

Abstract.

Three waves appear on the polarogram of quinoline when electrolysed in a weak acidic solution. The first wave is due to the reduction of dissociated

molecules and the second, that of a non-dissociated form. The third wave may be considered as the deposition of hydrion and in this case the overpotential is considerably lowered.

From a comparison of the polarograms of quinoline and of quinine, we may conclude that the reduction of quinine is due to that of quinoline nucleus.

27. A Study of Copper Complex Salts with the Polarograph. Part I.

By **Masuzo Shikata.**

Memoirs College agri. Kyoto Imp. Uni., No. 4, 59–74 (1927).

(1) The deposition potentials of copper complexes were measured with the dropping mercury cathode and the polarograph.

(2) The electrolyses were carried out in System $CuCl_2$—LiCl, System $CuCl_2$—KCl, System $CuCl_2$—NH_4Cl, System $CuSO_4$—Na_2SO_4—NaCl, System $CuSO_4$—$Al_2(SO_4)_3$, System $CuSO_4$—$(NH_4)_2SO_4$, System $CuSO_4$—K_2SO_4, and in a cupric ammino-oxides solution.

(3) The equilibrium constant K was calculated, by assuming the formation of $CuCl_3'$ in System $CuCl_2$—LiCl.

$$K=\frac{[Cu^{\cdot\cdot}]\,[Cl']^3}{[CuCl_3']}$$

For the same concentration of copper, K was found to be 3.98×10^{-9} (mean) for the different concentrations of LiCl between 0.05 and 1 n.

(4) For System $CuSO_4$—$MeSO_4$, the effect of a change of concentrations of a sulphate was less conspicuous than in the chloride complex.

(5) The formations of maximum and minimum current intensities were observed. These phenomena were explained as the change of an adsorption of a copper complex at the electrode.

(6) The height of a saturation curve, and its relation to the concentration of a neutral salt were discussed.

28. A Study of Copper Complex Salts with the Polarograph. Part II.

By **Masuzo Shikata** and **Yuji Kita.**

Progress of Physical Chemistry (Butsuri Kwagaku no Shimpo) **2,** 75–90 (1929).

(1) The deposition potentials of copper complexs were measured with the dropping mercury cathode and the polarograph.

(2) The electrolyses were carried out in System $Cu(NO_3)_2$—KNO_3, System

$Cu(NO_3)_2$—NH_4NO_3, System $Cu(NO_3)_2$—$LiNO_3$, System $Cu(NO_3)_2$—$NaNO_3$, System $Cu(NO_3)_2$—$NaNO_3$, System $Cu(NO_3)$—$NaNO_3$—NaOH, System $Cu(NO_3)_2$—H_2O.

(3) As was reported in Part I of this paper, in system $CuCl_2$—LiCl, the formation of $CuCl_3'$ was clearly proved by the shift of the deposition potentials of copper ion. In the cases of copper nitrate complex, the relation was more complicated than in the former case. This phenomenon must be due to the hydrolysis of the nitrate complex; but it was not possible to get a clear conception by the polarographic method.

Chapter II. Preface to a Study of the Tundra Peat of Karafuto.

The size of the so-called Karafuto Tundra bog in Japan is over 250,000 hectares. We began our research on the peat of the Tundra bog in 1925.

Our scheme for the utilization of this large tract of land is as follows:

(1) The chemical researches on the Tundra peat and Tundra bog.

(2) The chemical researches on the mother plants of the Tundra peat forming flora.

(3) Researches on the utilization of Tundra peat as a new raw material. In this line we have succeeded in making pressed peat board called "Tundrite," and active charcoal from this Tundra peat.

Several papers were published concerning Tundrite and other artificial lumbers.

For the preparation of pressed board (Tundrite) from Tundra peat, the electric current, especially alternating current, is employed. This process is quite different from the ordinary electrosmotic process. We have proposed regarding the effect of the electric current, a new working hypothesis which we call "the theory of electric boundary layer disturbance".

1. Tundra, as a New Natural Resource.

By **Masuzo Shikata.**

Nippon Gakujutsu Kyokai Hōkoku **6**, 617 (1931).

There are in Karafuto over 250,000 hectares of bog, which is ordinarily called Karafuto-Tundra, and which may be classified as a high bog. In this

report, the author gives the botanical description of bog-forming plants and the results of chemical analyses of the tundra peat. Several suggestions for its industrial utilization are proposed. The manufacture of an artificial lumber was carried out on a small scale in the author's laboratory.

2. Tundra Peat and Tundra Bog of Karafuto, Japan.

By **Masuzo Shikata.**

Nippon Gakujutsu Kyokai Hōkoku **8,** 31 (1934).

The author summarised his studies on tundra peat and tundra bog in Karafuto, the change of chemical compositions, hydrogen ion concentrations, and heat of combustion for various depths of tundra peat bog.

It was emphasized that research by various branches of science (chemistry, botany, geology, agriculture and forestry) were to be hoped for.

3. Studies on Artificial Lumbers. Part I. On Thermal Conductivity of Artificial Lumbers.

By **Masuzo Shikata, Yuji Kita** and **Sei-ichi Naganuma.**

The Journal of the Japanese Forestry Society, **13,** 558 (1931).

The thermal conductivity of tundrite (pressed peat board) pressed cork board, celotex and wood pulp tex was measured by the comparison method.

4. Studies on Artificial Lumbers. Part II. On the Tensile Strength of Artificial Lumbers.

By **Masuzo Shikata, Kinjire Sato** and **Osamu Ito.**

The Journal of the Japanese Forestry Society, **14,** 972 (1932).

The tensile strength of artificial lumber was measured with the cement testing machine.

The test pieces were cut in the European continental briquette form.

Such a method gave satisfactory results.

5. Studies on Artificial Lumbers. Part III. On the Bending Strength and Abrasion Test of Artificial Lumbers.

By **Masuzo Shikata, Kinjiro Sato** and **Osamu Ito.**

The Journal of the Japanese Forestry Society, **14,** 975 (1932).

The bending and abrasion tests were carried out by the ordinary method used for natural lumbers. No artificial lumbers were so resistant to abrasion as the natural lumbers.

6. Studies on Artificial Lumbers. Part IV. The Surface Finishing of Artificial Lumbers.

By **Masuzo Shikata** and **Kinjiro Sato.**

The Journal of the Japanese Forestry Society, **15,** 1090 (1933).

The authors studied the surface finishing of Tundrite (pressed peat board manufactured in our laboratory). The surface coating film must be elastic, because of the elastic properties of such pressed board. An undercoating of rubber latex, with ordinary shellac varnish finishing gave satisfactory results.

7. Studies on Hard Pressed Board.

By **Masuzo Shikata** and **Saisuke Fujii.**

Journ. agri. chem. Soc. Japan, **11,** 604 (1935).

The electric boundary layer disturbance, which gave good results in the manufacture of Tundrite (pressed peat board) was tested for manufacturing hard press boards from raw material. The raw materials used were bagasse, wheat straw, barley straw and sawdust. The hard pressed board from bagasse and straw showed higher tensile strength and bending strength than ordinary texes (for example celotex). They have tolerably high nail holding power, so that they can be used as packing cases.

8. Active Charcoal from Tundra Peat. Part I. Studies on the Raw Material of Active Charcoal.

By **Masuzo Shikata** and **Sei-ichi Naganuma.**

Journ. agri. chem. Soc. Japaa, **11,** 988 (1935).

Active charcoals were prepared from oak sawdust, rice hull, bagasse and Tundra peat of Karafuto under nearly the same conditions.

The Tundra peat proved to be excellent material for active charcoal. Activation with superheated steam showed better results than that with chemicals.

9. Chemical Studies on Bog-Moss. Part I. Chemical Composition of *Sphagnum Fimbriatum, Wils.* (Hime-Mizugoke).

By **Masuzo Shikata** and **Mamoru Watanabe.**

Memoirs College Agri. Kyoto Imp. Univ., 22 (Chemical Series No. 12 (1932).

Introduction.

There are over 250,000 hectares of so-called Karafuto "Tundra" in Japanese Karafuto Island.

One of the present authors (Shikata) has been studying since 1924 the chemistry and the chemical utilization of tundra peat. Chemical researches on the Karafuto tundra peat will be given at a later date. In carrying out the investigations on the chemical utilization of tundra peat, the present authors observed that lignin as well as cellulose contained in the tundra peat were very different from those of soft and hard woods. This fact might partly be ascribed to the weathering of the original mother tundra plants. However, in making a chemical study of the fresh tundra plants, the present authors were inclined to doubt that there might be some difference in the cellulose and lignin of woods and of *Sphagnum*. The present authors have undertaken chemical studies on the composition of bog-moss. As was the case in tundra and dry bog-peat in Europe, the bog-moss plays a great rôle in the so-called Karafuto tundra. In table I, several examples are given from the results of botanical analyses of the upper layers of Karafuto-Tundra peat in the Horonai River District.

The importance of bog-moss in the formation of tundra-peat can be understood clearly.

Table 1. Composition of the peat of Karafuto tundra.

Number of samples	Composition	Wt. of fresh sample (g)	Wt. of air dried sample (g)	% of air dried sample (%)	% of water lost by air drying (%)
1	*Sphagnum*	185	34	71	82
	Other substances	29	14	29	52
2	*Sphagnum*	139	24	21	83
	Weathered product	90	17	65	81
	Other substances	290	73	64	75
3	*Sphagnum*	452	67	53	85
	Weathered product	55	11	10	80
	Other substances	216	49	37	77

Experiments.

Sample:—The bog-moss *Sphagnum fimbriatum* (Himemizugoke)—used in the present experiments were taken from the fresh peat of the upper layer of the tundra of the Horonai River District, Shisuka Province, Karafuto. The other plants accompanying the bog-moss were *Polytrichums*, *Oxycoccus microcarpus Turcz.* (Himeturu-kokemomo), *Eriophorum Scheuchzerii*, *Hoppe.* (Sagisuge).

Sampling:—The moss involved various impurities such as roots, leaves and stalks of the above mentioned plants. After the sandy matter was washed out, the moss was air dried in the direct sunshine for a few days. We prepared two kinds of samples: one—nominated A in Table 2—was separated from the other plant impurities as far as possible and the other—nominated B in Table 2—was not separated. Both samples were powdered by a mill; and the fraction, between 35-mesh and 65-mesh, was taken. The materials coarse than 35-mesh were then reground and sifted as before.

Analytical method:—Estimation of water, cold and hot water soluble matter, alcohol-benzen (1 : 1) extract, and alkali (1 per cent caustic soda solution) soluble matter was carried out as usual. Lignin was determined by using 72 per cent sulphuric acid. Cellulose was estimated by the usual chlorinatlon method as well as by a modified one. In the modified form, after usual chlorination, we heated the chlorinated samples with 1 per cent caustic soda solution in boiling water bath instead of sodium sulphite solution. We used the modified method because, as is seen in Table 2, the amount of the residue of alkali extract—regarded as the cellulose content—was always less than that of the cellulose determined by the usual chlorination method.

In the determination of alpha-cellulose, the material used was cellulose prepared by means of the modified method. This cellulose became so hard when it was dried, that it could not be crushed by means of a mortar, so we poured on it 5 c.c. of 17 per cent caustic soda solution and kept it 2 days at room temperature. Then it was crushed and 28 c.c. of the same caustic soda solution was added. After 30 minutes alpha-cellulose was separated by a centrifugal machine. The usual remaining treatment follows.

Pentosan was determined by the phloroglucin method. Galactan was calculated from the music acid obtained by oxidation. Mannan was estimated by osazone formed with phenylhydrazine after hydrolysis with hydrochloric acid. Crude protein was determined by the ordinary Kejhldahl method. The results of these determinations are given in Table 2.

Discussion of the results:—The water content in moss as well as in peat is very difficult to determine, because the moss had constituents which were destroyed by the temperature of 105°C. The colour of the sample changed to light brown within 10 to 30 minutes when placed in the thermostat. The weight of the sample decreased with the lapse of time and it was difficult to obtain the constant weight, therefore the percentage of water in moss is supposed to include some amount of matters destroyed at 105°C.

Table 2. Chemical composition of bog moss.

Samples / Contents	A (pure)		B (contaminat)	
	air dry (%)	abs. dry (%)	air dry (%)	abs. dry (%)
Water	19.60	0	17.48	0
Cold water extract	6.84	8.51	6.43	7.77
Hot water extract	11.85	14.74	11.80	14.31
Alkali (1% NaOH soln.) extract	29.02	36.11	30.10	36.48
Benzene-alcohol (1 : 1) extract	1.47	1.83	1.67	2.20
Lignin	11.67	14.51	18.10	21.91
Cellulose { by the usual chlorination	48.53	60.49	44.97	54.48
Cellulose { by the modified method (a)	20.84	25.91	21.12	25.55
Residue of alkali extract*	30.40	37.42	35.44	42.94
α-cellulose { in the cellulose (a)	34.05	42.37	35.05	42.49
α-cellulose { in the raw material	8.83	11.00	8.97	10.88
Ash	3.21	3.99	3.28	3.98
Pentosan	11.89	14.78	11.98	14.54
Galactan	1.63	2.07	2.51	3.47
Mannan	trace	trace	trace	trace
Crude protein	0.88	1.10	4.22	5.12

* Remarks: The amount of cellulose determined by the usual chlorination method was considerably larger than the residue of alkali extract.

Moreover, the quantity of hot water soluble and alkali soluble matter was very large. The fact, as previously described, that the amount of the residue of alkali extract is less than that of cellulose separated by the usual chlorination method shows that there are substances which were not attacked by chlorine and sodium sulphite solution but soluble in 1 per cent alkali solution. At present we are not in a position to say to what substances such a phenomenon was ascribable. The chlorination method, in the case of moss, followed by washing with sodium sulphite solution to dissolve lignin chloride, would not be suitable for estimating cellulose. A great difference was observed, in the amount of cellulose, between the usual and the modified chlorination methods.

The colour of the cooked liquor of chlorinated cellulose, after repeating the chlorination three or four times, is colourless in the case of wood analyses, but in the case of the moss analyses it was light brown. When we treated the chlorinated cellulose, after repeated chlorination with sodium sulphite solution, the colour of the waste liquor was deeper than that of the chlorinated cellulose treated with caustic soda solution. Moreover, after repeating the procedure six times the colour of the waste liquor still remained. When caustic soda solution was employed the material became more and more gelatinous with every treatment. For example, when we treated four times with caustic soda solution, the hydration of the cellulose part went so far that it was very diffiult to filter

with the Jena glass filter and it became pastry. However, this difficulty in filtration was easily overcome by the application of a centrifugal machine. When the cellulose part thus treated was dried it became as hard as ivory. When woods and bast fibres were chlorinated, even in caustic soda solution was employed for dissolving the lignin chloride, they did not attain such a state. These are differences between cellulose isolated from moss and that of woods and bast fibres.

As previously described, when the moss was kept in the thermostat to estimate the amount of water, its colour changed to light brown. The change was even more conspicuous in the case of the moss cellulose separated by means of the usual chlorination method was kept in the thermostat, when the surface of the sample was partly carbonized and blackened. But in the case of the cellulose separated by the modified method, the carbonization did not occur although the colour changed from white to dark gray.

Using this material, alpha-celluose was determined. The alpha-cellulose obtained was not white, but had a somewhat gray shade. But colour change was not observable when it was kept in the thermostat. Therefore, we might regard this material as considerably purified alpha-cellulose of which the content in the moss was very little (about 9 per cent), as seen in Table 2.

As previously described there are many difficulties in the determination of cellulose in the moss. We cannot say at present what method is most reliable in the determination of cellulose. The chief characteristics of cellulose contained in the bog-moss will be described in a later part of the present series.

Lignin separated from moss by the present method resembled that of wood (fir—*A. sachalinensis, Mast.*) in appearance, but solubility in 4 per cent caustic soda solution was very different. Although moss lignin dissolved very easily, wood lignin was hardly soluble at the temperature of boiling water.

The higher percentage of ash depends partly upon the fact that the soil matter which has been adsorbed by the plant was not washed out completely.

Summary.

1. We determined the chemical composition of bog-moss which was produced on Karafuto Island, Japan.

2. The analytical method was briefly described, and the results of the analyses were discussed.

3. The bog-moss changed its colour on being heated in the thermostat at a temperature of 105°C.

4. The cellulose which was isolated by the usual chlorination method was partly carbonized in the same thermostat.

5. The amount of the cellulose separated by usual chlorination method was far more than the residue of the alkali extract.

6. Therefore in the determination of cellulose it is more advisable to apply the modified chlorination method, using 1 per cent caustic soda solution.

7. There was a great difference in the amounts and the character of

celluloses which were isolated by the above two methods.

8. We pointed out some different properties which were exhibited by moss and wood cellulose.

9. Lignin was also differentiated from that of wood.

10. The amount of alpha-cellulose was remarkably small. It was only 9 per cent against the air dried sample.

Chapter III. Preface to "A Study of the Electric Boundary Layer Disturbance".

As was said in Chapter III, "The theory of the electric boundary layer disturbance" was proposed by the present authors. In the following series of papers, we have tried to demonstrate this working hypothesis by experiments.

Especially the energy absorption of the low frequency electric wave was measured.

1. Kataphoresis and its applications.

By **Masuzo Shikata.**

Report of the Institute of Chemical Research, **1,** 38–49 (1929).

The theories of kataphoresis and its applications were described.

2. Alternating Current Effects on the Colloidal Systems.

By **Masuzo Shikata** and **Shichiro Fukuwatari.**

Journ. Soc. chem. Industr. Japan, **35,** 42 (1932).

In a polarographic research we have found that the discharge of the particle of the lyophile colloid such as gelatine or agar, takes place simultaneously with the deposition of the metallic ions (*Journ. Soc. chem. Industr. Japan.* **32,** 1135). We also found that an alternating current not only makes the drain of water from the tundra and its desiccation easy, but that it also gives a plasticity in the manufacture of the artificial board from tundra. Such effects of the alternating current we have called "electric disturbances." We have attempted to observe experimentally these effects of an A.C. on several colloidal systems.

The influences of an alternating field on the following properties and phenomena of the colloidal solution were studied:

Exp. 1. on the stability of the sol,
Exp. 2. on the phenomenon of periodic precipitation,
Exp. 3. on the adsorptive power of active charcoal,
Exp. 4. on the viscosity of a gelatine solution,
Exp. 5. on the hydration of gelatine and its velocity,
Exp. 6. on the evaporation and the desiccation of gelatine gel.

In the experiment, the solution to be treated was put between two concentric glass cylinders, and a high tension alternating field (10,000 volts, 60 cycles/sec.) was applied between the cylinders and the effective current was kept as small as possible.

Among these experiments, there was no appreciable effect with regard to 1 and 3, but with regard to 2, 4, 5, and 6, the following A.C. effects resulted:

Exp. 2.—The formation of a Liesegang ring in a gelatine medium by ammonia and magnesium chloride was tried. As the medium of the diffusion-waves (Wo. Ostwald, *Koll. Zeitschr.* **36,** 208 (1925)) was influenced by the A.C., the reaction products were precipitated in a different manner from the thermic effects (K. Popp, *Koll. Zeitschr.* **36,** 380 (1925));

Exp. 4.—The gelatine solution (5% and 10%) treated electrically in advance, had a higher viscosity than that which was not so treated;

Exp. 5.—In the hydration of Nelson's photographic gelatine with pure water or ethyl alcoholic aqueous solutions (1.5%, 5%, 8%), the total volume contraction was observed in a capillary tube, and it was found that the progress of volume contraction was retarded by the alternating current;

Exp. 6.—The 40% gelatine solutions were evaporated gradually at 30°C under a constant reduced pressure in order to trace the decrease of their weights at proper intervals.

The residual water content of these samples treated with an A.C. beforehand, were less than that of the samples treated with a direct current, or not treated at all electrically.

We can conclude that the alternating current produces a certain effect upon a lyophile colloid such as a gelatine solution, and perhaps, also upon the state of the colloidal association of water with the dispersed particles. It is interesting to attribute it to the fact that some colloidal solutions may disperse electromagnetic waves anomalously in the range of low frequencies.

3. Electric Boundary Layer Disturbances and Their Application to the Manufacture of Artificial Lumbsr.

By **Masuzo Shikata, Kinjiro Sato** and **Yuji Kita.**

Report of the Institute for Chemical Research, **2,** 13–20 (1931).

The ordinary electrosmotic process for drying peat is very low in its electric

power efficiency. This low power efficiency may be chiefly ascribed to conduction by the ions. In order to elevate the power efficiency, the authors proposed that if a colloidal system be brought into an electric field, the ions and water on the boundary layer of the colloid particles would be disturbed. In ordinary electrosmosis, water molecules are conveyed by electrical means, while according to the authors' method, which they have named "the electric boundary layer disturbance", electric energy is used, so far as possible, to produce the disturbance; and simultaneously the disturbed water molecules are removed by a mechanical means, such as high pressure.

The authors succeeded in making artificial lumber from Tundra-peat by the application of this new method.

4. A Study of Electric Boundary Layer Disturbances. Part II.

By **Masuzo Shikata, Kinjiro Sato, Yuji Kita, Ichiro Kochiyama, Kiyoshi Tanaka** and **Shichiro Fukuwatari.**

Report of the Institute for Chemical Research, **2**, 63–71 (1931).

The authors tried to lay the experimental ground for their working hypothesis, "the electric boundary layer disturbance".

The change of flow as well as the change in the limiting water content under low temperature drying were observed in the case of the electrically disturbed peat.

5. A Study of Electric Boundary Layer Disturbances. Part III.

By **Masuzo Shikata, Shichiro Fukuwatari** and **Shizuo Ueda.**

Report of the Institute for Chemical Research, **3**, 8 (1933).

The velocity of water flowing through a very thin wood disk, such as spruce and oak, is much influenced by an alternating electric field. This phenomenon might be explained by the "boundary layer disturbance" hypothesis.

In order to prove this hypothesis, the energy absorption of low frequency range (40 to 3000 per second) electric wave by the tundra peat power in liquid paraffin was measured.

The absolutely dried tundra peat in paraffin showed a constant energy absorption for the various frequencies. However, the peat containing water showed a higher energy absorption in the higher frequency range. This change

of energy absorption might be ascribed to the different relaxation time of absorbed water.

6. A Study of Electric Boundary Layer Disturbances. Part IV.

By **Masuzo Shikata** and **Koichiro Kitao.**

Journ. agri. chem. Soc. Japan, **10,** 554 (1934).

Professor Michaelis has shown that a potential difference is always observed between both sides of a collodion membrane when KCl solutions of different concentration are separated by this membrane.

He ascribed this phenomenon to the difference of mobilities of the $K^{\cdot}$ ion and the Cl' ion through this membrane.

The authors have observed that if this membrane is once under the influence of an alterating electric field, for example 10 to 30 seconds in a 220 volts A.C. field of 60 cycles, the potential difference almost disappears, and after 5 to 10 minutes returns to its initial value.

This phenomenon might be explained as the "boundary layer disturbance" hypothesis.

7. A Study of Electric Boundary Layer Disturbances. Part V. Phenomena of Particles Containing Moisture in the Electric Field.

By **Masuzo Shikata** and **Shichiro Fukuwatari.**

Reports of the Institute of Chemical Research, **5,** 80 (1935).

Some phenomena represented by organic or inorganic particles suspended in benzene under an alternating, direct, and impulsive electric field (100-1000 volt/cm) were observed microspically:

(1) In the direct electric field, the particles behaved as charge carriers, and were charged positively at the anode or negatively at the cathode; but in the case of fibrous particles on the negative charge was bounded and reserved.

As charge carriers, inorganic crystal particles containing crystal water were more active than fibrous particles, but they were equally proportional to their water content.

(2) In an alternating electric field, the charge-carrying movement practically disappeared, and the phenomena due to polarization were more markedly observed. Thus the water content for determining the dielectric constants and the field gradients at the points of the particles become an important factor.

So we might be able to determine the alternating field effects on the dispersed system from the water content and the dielectric constants of the particles.

(3) These field effects were also measured by the variation of the condenser constants. These measurements showed that the impulsive waves were more effective, and that the other field affected the constants (i.e., the capacity, the conductivity, and the dielectric loss angle), thus suggesting the phenomena previously observed.

8. On the Dielectric Behaviour of Colloidal Systems. Part I. On the Adsorbed Water Phase in Fibrous Materials.

By **Takeshi Nishi** and **Shichiro Fukuwatari.**

Rikwagaku-Kenkyûsho-ihô, **11**, 1201 (1932).

The dielectric constants of a system, which the fibrous particles containing moisture dispersed in organic liquids, were measured at a low frequency range (40-3000 cycles), and the relation between these anomalous dispersion curves and the moisture content of the dispersed system was studied. As a result, at a certain per-cent (about 6% for 40 cycles, and 8% for 2500 cycles) the moisture had only a slight effect upon the value of the dielectric constants, but above this per-cent it produced a remarkable effect upon them. From these facts the adsorbed water phase was classified into three classes, viz., "the fixed water phase", "the adhesive movable water phase", and "the free water phase".

9. On the Dielectric Behaviour of Colloidal Systems. Part II. The Electric Field Effect on the Dispersed System of Fibrous Material.

By **Takeshi Nishi** and **Shichiro Fukuwatari.**

Rikwagaku-Kenkyûsho, **13**, 329 (1924).

Electric field effects on systems in which fibrous powder containing moisture was dispersed in air and benzene, were observed under 10 KV/cm, by measuring the variation of the capacity, the series resistance (Rs) and the dielectric loss (tan δ), and thus two kinds of variation of Rs were found. One was parallel with the thermal effect and the other was not only opposite to the thermal effect, but remained so for a long time, a hundred hours or so. This effect was interpreted as an electrical effect on the dispersed system, caused by an orientation of fibrous particles in the field and perhaps partly due to the removal of the "adhesive movable water phase" adsorbed in the fibrous particles.

10. On the Dielectric Behaviour of the Colloidal Systems. Part III. The Electric Effect of a Fibrous Particle.

By **Takeshi Nishi** and **Shizuo Ueda.**

Rikwagaku-Kenkyûsho-ihô, **14**, 514 (1935).

Recently, the state of water absorbed by a colloid has been discussed. This is a very important subject from the view point of biology. In these experiments, we measured by an a.c. bridge the changes of various properties of dielectrics, due to the charging of the above mentioned system, and we studied the mechanism of its effect.

Experiments were as follows:

(1) The influence of temperature on the charging and residual effect.
(2) The relation between the change of dielectric loss by charging and temperature change.
(3) The influence of the viscosity of a solvent on the charging and residual effect.
(4) The change of dielectric loss due to charging frequency.
(5) The influence of dielectric loss and residual effect due to impulse voltage.
(6) The change of the equivalent series electrostatic capacity, and of the charging effect of a.c. voltage, or impulse voltage, in the case of various water contents.

From the experimental results, we calculated the tan δ, dielectric constant mathematically, according to Deby's dipole theory. This calculation, based on the dipoles of water absorbed by the fibrous particle and starch, accorded well with the charactesistic tendency of the experimental data. That is, the dipole molecules (in our case, the water molecule absorbed by colloid particle) have a tendency to turn to the direction of the electric field against the thermal agitation. The electric energy, necessary to attain the stational state of polorisation phenomena, is the principal part of dielectric loss due to charge, and the change of the dielectric constant is also thought to depend on its orientation. On its release from the charging field, the inner polarisation does not instantly diminish; and the water molecule can attain by inner friction the stational state after a certain lapse of time. Therefore, the equivalent series electrostatic capacity, the equivalent series resistance and the dielectric loss decrease gradually, as residual phenomena.

According to our experimental results, the physically absorbed water and Langmuir's chemically absorbed water showed different behaviors. So far as our applied voltagh (2500 volt/cm) was concerned, the former showed a charging effect and might be regarded as "boundary water" while the latter did not show any noticeable charging effect and might be called "fixed water".

In conclusion, the author thanks Professor M. Shikata for his kind asistance during these experiments.

11. Effects of the Alternating Electric Field on the Dielectric Properties of the Colloidal Systems.

By **Shichiro Fukuwatari.**

Kwagaku, **7**, 272 (1933).

Some phenomena of fibrous particles containing moisture in a strong alternating electric field were reported.

12. Relation between the Absorption Spectrum of an Electromagnetic Wave and the Adsorbed Water Phase.

By **Masuzo Shikata** and **Shichiro Fukuwatari.**

Journal of of the Electrochemical Association ot Japan, **3**, 212 (1935).

To decide the numerical state of adsorbed water molecules in the organic material, we attempted to determine a characteristic constant due to the adsorbed water phase.

First, we studied the relationship between the adsorbed water contents of the fibrous material and the absorption spectrum of the electromagnetic wave in the frequency range from 20 to 6,000 cycles. For our experiments with the dielectric condenser we took the system of the wood flour dispersed in a benzene medium. Under about 3,000 cycles, the moisture contents influenced only the absorption values ($\tan \delta$) in simple relations.

Analogous to the anomalous dispersion of the ice condenser, we calculated the time required for the relaxation of water molecules distributed in the fibrous material to make a kind of fixed " pattern " electrically in that condenser. The values calculated are 10^{-5}—10^{-6} seconds, which correspond to the value of water molecules in the space lattice of ice crystal at a temperature of about $-5°C$.

Chapter IV. A Study of Pulp Woods and Cellulose Resources.

In the following papers, the results of chemical research on the pulp woods of Japan and Manchuria are described. The cooking methods for rayon pulp were also studies. Research concerning the new cellulose resources (cellulose producing plants) was also undertaken.

1. Chemical Research Concerning the Pulp Woods in Karafuto, Japan. Part I.

By **Masuzo Shikata** and **Michiya Ishizaki**

Cellulose Industry (The Journal of the Cellulose Institute, Tokyo, Japan.), 8. 121. (1932).

A chemical analysis of Karafuto spruce (Ezomatsu) (Picea ajanensis, Fisch.), Karafuto blue fir (Aotodomatsu) (Abies Mayriana Miyabe et Kudo) as well as of Karafuto red fir (Akatodomatsu) (Abies sachalinensis) was completed. When spruce and fir were digested in Ca-sulphite, Mg-sulphite as well as in a mixed sulphite solution, the Ca and Mg mixture showed the best results.

As to chemical pulp wood, Karafuto spruce gave a better result than did the Karafuto firs. This relation can also be seen by studying the results of the chemical analyses.

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2. Chemical Research Concerning the Pulp Woods in Karafuto, Japan. Part II. Digestion and Spinning Test of Karafuto Spruce.

By **Masuzo Shikata** and **Shohoku Ba.**

Cellulose Industry (The Journal of the Cellulose Institute, Tokyo, Japan.), **9**, 305 (1933).

Digestions of Karafuto spruce (Picea ajanensis Fisch) in Mg-sulphite and in ammonium sulphite solution were carried out.

These two modes of digestion gave about the same results.

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3. Chemical Research Concerning the Pulp Woods in Karafuto, Japan. Part III. The Chemical Composition of Karafuto Poplar and Willows.

By **Masuzo Shikata** and **Shohoku Ba.**

Cellulose Industry (The Journal of the Cellulose Institute, Tokyo, Japan.), **9**, 309 (1933).

The results of the chemical analysis of Doroyanagi (Populus Suaveolens Fisch.), Onoeyanagi (Salix Opaca Anders.) and Bakkoyanagi (Salix Caprea L.) are given.

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4. A Study of the Pulp Woods in Karafuto, Japan. Part IV. Cooking and Spinning Tests of Karafuto Fir.

By **Masuzo Shikata** and **Takeo Kohsaka.**

Journ. agri. chem. Soc. Japan, **10,** 557 (1934).

Cooking and spinning tests of Karafuto red fir (Abies sachalinensis Fr. Schem.) were carried out.

It was proved that this fir can be used as a rayon pulp wood, although it is inferior for this purpose to Karafuto spruce (Picea ajanensis, Fisch.).

5. On the Future Problem of Rayon Pulp in Japan.

By **Masuzo Shikata.**

Journal of Forestry, Japan, **16,** 69 (1934).

The author summarised his research concerning the chemical composition of spruces and firs in Japan and Manchuria.

The spruces examined were

Tohi (Picea hondoensis, Mayr.) (from Naganoken)
Ezomatsu (Picea ajanensis Fisch.) (from Karafuto)
„ („) (from Manchuria)
Chōsenharimomi (Picea Schrenkiana Rupr.) (from Manchuria)

The firs examined were

Aotodomatsu (Abies Mayriana, Miyabe et Kudo) (from Karafuto)
Akatodomatsu (Abies sachalinensis, Mast.) (from Karafuto)
Shirabe (Abies Veitchii, Lindl.) (from Naganogen)
Oshirabiso or Aomoritodomatsu (Abies Mariesii Mast.) (from Naganoken).
Urashiromomi or Dakemomi (Abies brachyphylla Maxim.) (from Naganoken).
Toshirabe (Abies nephyrolepis Maxim.) (from Manchuria).

It was found that the spruces are more suitable as rayon pulp woods than are the firs, although both can be used as rayon pulp woods.

Because of the rapid development of the rayon industry in Japan, the author drew attention to the necessity for studying the other natural resources for rayon pulp, such as larch and hard woods and certain agricultural products such as stalks and stems.

6. A Study of Viscose Pulp and Viscose Pulp Woods. Part I. Japanese Beech as a Pulp Wood.

By **Masuzo Shikata** and **Isamu Tsuchiyama.**

Journal of the Japanese Forestry Society of Japan, **16,** 259 (1934).

The chemical analysis of Japanese beech (Bunanoki) (Fagus Sieboldi, Endl.) was carried out. The total cellulose was 58.14% and α cellulose was 45.85% in absolutely dry matter. The soda processes were applied for the cooking test. The best cooking conditions among our experiments are the following:

Cooking liquor. 7.0% NaOH with Na_2CO_3 0.6% solution. The Na_2O employed was 25% to the chip weight. By the titration after cooking, it was found that 7 to 11% Na_2O for the chip was consumed.
Main cooking temperature: 160°C.
Main cooking time: 6 hours.
Pulp yield to the dry wood: 46.55%.
This pulp contained 93.46% α-cellulose and its copper number was 0.63.

In order to improve the quality of the pulp, it was again cooked with dilute NaOH solution (2-6%). However, under proper cooking conditions, we can obtain rayon pulp without after-cooking. As a result of the viscose spinning test, it was found that the beech pulps were slightly inferior to the commercial rayon pulps. The cooking method must be improved in order to obtain rayon pulp from Japanese beech.

7. Study of Viscose Pulp and Viscose Pulp Woods. Part II. On the Two Kinds of Manchurian Spruces.

By **Masuzo Shikata, Shokoku Ba** and **Kazuhiko Akagi.**

Cellulose Industry (The Journal of the Cellulose Institute, Tokyo, Japan.), **10,** 92 (1934).

We have undertaken a chemical study of the two kinds of Manchurian spruces—Gyorinsyo (Picea ajanensis Fisch.) and Sansyo (Picea Schrenkiana Rupr.) —as raw material for the rayon industry.

1. Chemical Composition.

The two kinds of spruce were subjected to an analysis by the same methods as are reported in this journal.

We can see from the above results that there is no great difference between E and F in their chemical compositions with the exception that the total cellulose and α-cellulose are 2 to 3 percent higher in F; Sansyo is rich in resinous matter and contains less total cellulose, α-cellulose and hemicellulose than Gyorinsyo.

Table 1. The Chemical composition of Gyorinsyo and Sansyo.

	Gyorinsyo E	Gyorinsyo F	Sansyo
1. Alcohol-benzene extracts	1.87	2.90	5.38
2. Cold water soluble matter	2.57	1.65	4.85
3. Hot water soluble matter	7.99	5.45	5.95
4. 1% NaOH soluble matter	14.19	14.82	15.45
5. Total cellulose	59.96	61.42	55.51
6. α-cellulose	33.94	36.92	32.12
7. β-cellulose	16.41	15.30	13.67
8. γ-cellulose	9.61	9.20	9.72
9. Lignin	27.97	30.40	30.06
10. Pentosan	12.32	12.22	9.97
11. Mannan	6.05	8.41	6.99
12. Calactan	0.71	0.62	0.34
13. Hemicelluloses	19.08	21.25	17.30
14. Nitrogen	0.05	0.07	0.05
15. Crude protein	0.31	0.46	0.31
16. Ash	0.57	0.22	0.34
17. Methoxyl	5.96	5.83	5.31
18. Methoxyl/Lignin×100	15.20	14.40	16.61

(where Gyorinsyo E and F are of the same species but differ only in their individuality)

In α-cellulose content, both the Manchurian spruces are inferior to Karafuto spruce, but Gyorinsyo is superior to Karafuto fir, and Sansyo should be put in the same class.

2. Cooking Experiments.

We carried out a series of experimental cookings by the sulphite process and observed the influence of alkali after-cooklngs on the qualities and yield of pulp.

(1) Cooking with Magnesium bisulphite and Magnesium, calcium-mixed bisulphite liquors.

a. Composition of the cooking liquor

Total	6%
MgO or MgO+CaO	1% (In the case of MgO+CaO, MgO : CaO=1 : 1)

b. Cooking conditions

Weight of chis	100 g
Volume of cooking liquor at start	1.3 *l*
Maximum temperature	155°C
Maximum pressure	6.4 atm p.
Mean temperature	145°C
Mean Pressure	5.6 atm. p.
Cooking duration	8 hrs.

(2) After-cooking with 1% NaOH.

The after-cookings took place at 135°C (4 atm. p.) for 1 and 4 hours using fifteen times the amount of 1% NaOH to partially bleached sulphite pulps.

Table 2. Analytical data of prepared pulps.

Pulp No.	Kinds of woods	Cooking methods	Yields kg/m³ wood	Pulp qualities			
				moisture	α-cell.	β-cell.	γ-cell.	ash
1.	Gyorinsyo E	Mg-sulphite process	220	5.68	84.86	6.88	8.26	0.53
2.	,,	,, (Alkali after-cooking 1 hr.)	190	7.24	88.72	8.46	2.82	0.75
3.	,,	,, (Alkali after-cooking 4 hrs.)	170	5.32	67.55	24.67	7.78	4.01
4.	,,	Mg, Ca-mixed sulphite process	220	12.02	87.63	6.88	5.49	0.57
5.	Gyorinsho F	Mg-sulphite process	220	6.62	86.33	9.29	4.38	0.51
6.	,,	Mg, Ca-mixed sulphite process	220	19.64	86.66	9.58	3.76	0.39
7.	,,	,, (alkali after-cooking 1 hr.)	190	8.20	89.36	8.40	2.24	0.47
8.	Sansyo	Mg-sulphite process	190	6.30	73.91	18.76	7.33	2.73
9.	,,	,, (alkali after-cooking 4 hrs.)	165	6.54	86.09	9.21	4.70	1.85
10.	,,	Mg, Ca-mixed sulphite process	190	7.70	72.21	21.30	6.47	3.92
		Kipawa (from Canada)		7.27	88.08	3.31	8.61	0.68

The pulp yields are about 220 kg per 1 cubic meter wood, but lower yields are obtained by alkali after-cookings. In case only the sulphite methods applied Gyorinsyo yields a pulp of a high quality, containing 86 to 87 present α-cellulose, but Sansyo yields an inferior quality containing only 72 to 73 percent α-cellulose. When partially bleached sulphite pulps are cooked further with 1% NaOH for 1 hour at 135°C (4 atm. p.) the pulp is propery refined, but if the cooking duration is extended to 4 hours, the residual pulp with the exception of Sansyo becomes of an inferior quality.

3. Spinning Tests of the Pulps.

5 g. of air dried pulps were mercerized with 50 g. of 17.5% NaOH solution at about 15°C overnight, pressed to about 14 g., and matured at 15°C for two to three days placed in a tightly stopped bottle; and then were added 2.5 g. of carbon disulphide. The xanthogenate thus obtained was dissolved in a dilute caustic soda solution, making a viscose of 7% cellulose and 6% sodium hydroxide, and the viscose was then subjected to ripening at 15°C. After 4 to 5 days the viscose was placed in an ice refrigerator and spun according to Dr. Tomihisa's bobbin spinning apparatus, using the following coagulating liquor.* The spinning velocity of 46 to 47 m/min. was maintained throughout the

* Composition of the coagulating liquor:

H_2SO_4	8%
Glucose	10 ,,
Na_2SO_4	12 ,,
$ZnSO_4$	1 ,,
H_2O	69 ,,

experiments. The following table illustrates the strength of viscose threade obtained by this process:—

Table 3.

	Kinds of pulps	Strength (g/denier)
1.	Gyorinsyo E, Mg-sulphite pulp	0.90
2.	,, ,, (alkali aftercock 1 hr.) pulp	1.07
3.	,, ,, (alkali aftercook 4 hrs.) pulp	1.09
4.	,, Mg, Ca-mixed sulphite pulp	1.36
5.	Gyorinsyo F, Mg-sulphite pulp	0.97
6.	,, Mg, Ca-mixed sulphite pulp	1.14
7.	,, ,, (alkali aftercook 1 hr.) pulp	1.32
8.	Sansyo, Mg-sulphite pulp	1.18
9.	,, ,, (alkali aftercook 4 hrs.) pulp	1.18
10.	,, Mg, Ca-mixed sulphite pulp	0.72
	Kipawa (from Canada)	1.20

We can see from the above table that the threads are of a strength comparable to Kipawa viscose thread with the exception of No. 10. It is an interesting fact that Gyorinsyo-Mg, Ca-mixed sulphite pulp and the same when refined with 1% NaOH for one hour at 135°C yield a stronger silk than Kipawa. This fact seems to throw some light on the problem of how to produce a viscose pulp for the future.

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8. A Study of Viscose Pulps and Viscose Pulp Woods. Part III. Chemical Compositions of Manchurian, Karafuto and Japanese Inland Larches.

By **Masuzo Shikata** and **Shokoku Ba**

Cellulose Industry (The Journal of the Cellulose Institute, Tokyo, Japan). **10**, 148 (1934).

We have analysed three kinds of larches, Hwanghwasoon (Manchurian larch, Larix dahurica Turcz.), Guimatsu (Karafuto larch, Larix kamtschatica Carr.) and Karamatsu (Japanese inland larch, Larix leptolepis, Gord.) mainly according to Schorger's method. The analytical data are tabulated as follows:—

(expressed in percentage of even dry (105°C) samples)

	Karafuto Larch	Japanese Inland Larch	Manchurian Larch	Karafuto Spruce	Karafuto Fir
1. Alkohol-benzene extracts	4.24	4.42	3.43	1.89	3.20
2. Cold water soluble matter	17.68	11.24	7.95	2.20	2.03

3.	Hot water ,,	18.63	14.38	10.00	1.84	3.93
4.	1% NaOH ,,	28.95	24.71	18.17	15.02	14.50
5.	Galactan	12.98	7.89	6.16	0.35	0.78
6.	Mannan	4.59	7.14	6.34	6.92	7.16
7.	Pentosan	10.72	10.37	11.82	14.45	9.39
8.	Hemicellulose (5+6+7)	28.29	25.40	24.32	21.72	17.33
9.	Lignin	25.10	25.59	29.13	26.47	28.76
10.	Total cellulose	48.26	53.04	53.11	59.54	57.45
11.	α- ,,	30.54	32.96	34.54	48.83	32.23
12.	β- ,,	5.37	7.94	3.88	10.76	25.22
13.	γ- ,,	12.35	12.14	14.69		
14.	Nitrogen	0.07	0.05	0.07	0.07	0.12
15.	Crudeprotein	0.43	0.32	0.45	0.45	0.75
16.	Ash	0.46	0.22	0.31	0.29	0.49
17.	CH_3O	3.68	3.81	3.31	5.12	5.48
18.	CH_3O/Lignin ×100	14.60	14.80	11.40	19.30	19.00

The total cellulose contents of the three kinds of larches are less than that of Ezomatsu (Karafuto spruce, Picea ajanensis, Fisch.) and Todomatsu (Karafuto fir, Abies Sachalinensis, Mast.) which are used in the Japanese pulp industry. However, the α-cellulose contents of these larches are less than that of Ezomatsu but similar to Todomatsu.

It is a noticiable fact that these larches are rich in galactose and water soluble components compared with the other pulp woods; the water soluble matter seems to be occupied chiefly by galactose.

A. W. Schorger and D. F. Smith (*Ind. Eng. Chem.*, 8, 494 (1916)) isolated water soluble ε-galactose from the western larch (Larix occidentalis) which contains 8 to 17% galactose, and recently Louis E. Wise, Philip L. Harmer and Floyed C. Peterson (*Ind. Eng. Chem.*, 184~187) pointed out that the water-soluble galactose from the eastern larch (Larix laricina (DuRou) Koch) is an arabogalactose (which consists of 12.0% anhydroarabinose and 82.1% annydro-galactose) and its physical properties are similar to the water-soluble ε-galactose from the western larch. Accordingly it may be expected that the galactose in the three kinds of larches is a water-soluble galactose having an arabogalactose form.

From the point of view of α-celluose content, we may conclude that the three kinds of larches are much inferior to Ezomatsu. Further, among these larches, Manchurian larch is best as a pulp wood and Karafuto larch is most inferior.

9. A Study of Viscose Pulp and Viscose Pulp Woods. Part IV. Cooking Tests with Karafuto and Japanese Inland Larches.

By **Masuzo Shikata** and **Shokoku Ba.**

Cellulose Industry (The Journal of Cellulose Institute, Tokyo, Japan.), **10**, 150 (1934).

Although larch is said to be unsuitable for viscose pulp wood, their rapid growth and easy planting make them worthy of consideration. Cooking was carried out by sulphite and sulphate (kraft) methods with Karafuto and Japanese inland larches.

I. Cooking Karafuto larch with magnesium bisulphite liquor. In this case 100 g of air dry chips were digested with 1.3 liters of cooking liquor (6% SO_2 and 1% MgO) for 5 hours at a mean temp. of 147±1°C. The residual pulps, however, were not completely pulped, and so we cooked again the partially bleached pulps with 500 g of 1% NaOH at 135°C (4 atm p.) for 4 hours. The qualities of the residual pulps and their viscose threads are tabulated in table 1.

Table 1. Quality of pulps and Viscose Threads.

	Pulp yield kg/m³ woods	Quality of Pulps					Strength of Viscose Threads (g/denier)
		Moisture	α-cell.	β-cell.	γ-cell.	Ash	
Larch pulp prepared by authors' methon	180	7.36	81.55	14.20	4.25	6.40	0.75
Larch pulp prepared experimentally by Nihonjinken Pulp Co.	—	8.24	91.00	—	—	—	0.92
Kippawa	—	7.27	88.08	3.31	8.61	0.68	1.20

It seems to be difficult to cook larches with only sulphite liquor; and even though alkali is applied after cooking, this treatment did not give unusually good results.

The strength of viscose threads given in Table 1 was obtained by making viscose silk from these larch pulps, using Kippawa pulp as the standard. This method is far from being absolute, but we tried to apply it.

II. Cooking Japanese inland and Karafuto larches by the sulphate method.

It is preferable to apply the sulghate method for larches, because larches contain much resinous substance and alkali soluble matter. Moreover larches are relatively hard among coniferous woods. That is to say, larch may be ranked as a hard wood rather than as a soft wood. We carried out these test as follows:

Series 1. Cooking Japanese inland larch with 1 liter of 3% digestion liquor (total alkali being NaOH 25.6 g) per 100 g bone dry chips at 160°C for 6 hours.

Series 2. Cooking Japanese inland and Karafuto larches with 600 g of 5% digestion liquor (total alkali being NaOH 25.6 g) per 100 g bone dry chips at

Table 2. Cooking Data, Yield and Quality of Bleached Pulps.

No. of Pulp	Kind of Woods	Weight of Bone Dry Chips (g)	Composition of Cooking Liquor					Cooking Conditions				Pulp Yield, wt. %	Pulp Yield, Kg/m³ woods	Pulp Qualities				
			Total Chemicals (g)	NaOH (g)	Na_2S (g)	Total Alkali as NaOH (g)	Liquor Concentration (%)	Temp. (°C)	Press. (atm. p.)	Duration (hour)	Remarks			Moisture	α-Cellulose	β-Cellulose	γ-Celluiose	Ash
1	J.I.L.	100	30	21	9	25.6	3	160	7.0	6(8)	Chips were extracted in hot water for 2 hours	37	222	8.04	76.19	15.68	8.13	0.41
2	,,	100	30	21	9	25.6	3	160	7.2	6(8)	Chips were dipped into cold water 2 days	37	222	17.86	74.54	16.87	8.59	0.38
3	,,	100	30	21	9	25.6	3	160	6.6	6(8)		—	—	Patiailly Pulped				
4	J.I.L.	100	34	24	10	29.0	5	160	7.2	6(8)		34	204	7.39	82.83	7.14	10.03	0.45
5	K.L.	100	30	21	9	25.6	5	160	7.2	6(8)	Temp. was raised up about 185°C in the course of cooking	33	198	2.24	90.77	1.57	7.66	0.23
6	J.I.L.	100	30	21	9	25.6	5	160	7.8	6(8)		36	216	11.77	74.78	17.08	8.14	0.11
7	K.L.	100	30	21	9	25.6	5	160	6.6	5(7)	Chips were extracted in hot water for 2 hours	30	180	9.09	85.70	3.32	10.98	0.34
8	K.L.	100	30	21	9	25.6	5	165	8.4	5(7)		32	192	10.77	82.37	9.18	8.45	0.31
9	K.L.	100	30	21	9	25.6	5	170	9.3	5(7)		31	186	4.49	75.20	11.86	12.94	0.37
10	J.I.L.	100	30	21	9	25.6	5	170	9.3	5(7)		32	192	4.82	74.36	14.02	11.62	0.64
11	K.L.	100	25	17.4	7.6	21.3	5	170	9.8	5(7)		31	186	6.21	85.68	2.68	11.64	0.33
12	J.I.L.	100	25	17.4	7.6	21.3	5	170	9.8	5(7)		31	186	3.29	89.49	1.36	9.15	0.25
13	K.L.	100	25	17.4	7.6	21.3	5	160	7.2	6(8)		32	192	5.24	77.27	12.10	10.63	0.10

Where { J.I.L. and K.L. mean Japanese inland larch and Karafuto larch respectively.
Figures in the brackets show the total cooking times.

Chips were extracted in hot water for 2 hours. ..... Pulp No. 1 remark.
Chips were dipped into cold water for 2 day. ..... Pulp No. 2 remark.
Temperature was raised to about 185°C in the course of cooking. ..... Pulp No. 5 remark.
Chips were extracted in hot water for 2 hours. ..... Pulp No. 7 remark.

160°C for 6 hours.

Series 3. Cooking Karafuto larch with 600 c.c. of 5% digestion liquor (total alkali being NaOH 25.6 g) per 100 g bone dry chips at 165°C for 5 hours.

Series 4. Cooking Japanese inland and Karafuto larches with 600 c.c. of 5% digestion liquor (total alkali being NaOH 25.6 g) per 100 g bone dry chips at 170°C for 5 hours.

Series 5. Cooking Japanese inland and Karafuto larches with 500 c.c. of 5% digestion liquor (total alkali being NaOH 21.3 g) per 100 g bone dry chips at 170°C for 5 hours.

Series 6. Cooking Karafuto larch with 500 c.c. of 5% digestion liquor (total alkali being NaOH 21.3 g) per 100 g bone dry chips at 160°C for 6 hours.

Among this series it is noticeable that the second (Pulp No. 4, 5, 6 & 7), the third (Pulp No. 8) and the fifth series (Pulp No. 11 & 12) give pulps of high quality. Especially in the fifth series, cooking with less chemical at high temperature for a short time is the most suitable process. It is not good to cook with a dilute digestion liquor or with a great quantity of chemicals at a high temperature as in the first and in the fourth series.

In these cookings we could find no differences between Karafuto larch and Japanese inland larch.

The results of the examination of these pulps as viscose pulps will be given in the coming series of papers.

10. A Study of Viscose Pulps and Viscose Pulp Woods. Part V. On the Microbiological Decay of Japanese Beech.

By **Masuzo Shikata** and **Isamu Tsuchiyama.**

Journ. agri. chem. Soc. of Japan, **10,** 557 (1934).

In Part I of the present report we pointed out that we might be able to get good soda pulp from Japanese beech (Fagus Sieboldi, Endl.). One of the serious defaults of Japanese beech as pulp wood is the ease with which beech is attacked by micro-organisms. In the present paper the results of the chemical analyses as well as the cooking test were described. It was found that rot, when it dose not go so far as to give zone lines to the wood, does not cause serious damage to the pulp qualities, but results in a poorer pulp yield than does ordinary wood.

11. A Study of Viscose Pulps and Viscose Pulp Woods. Part VII. The Chemical Composition of Birches.

By **Masuzo Shikata** and **Hideo Onishi.**

Journ. agri. chem. Soc. Japan, **11,** 836 (1835).

The chemical composition of the birches of Japan and Manchuria were given.

The birches analysed were:

Sōshikamba (Betula Ermanii, Champ var. communis Koids.) from Karafuto).

Shirakamba (Betula japonica, Sieb) (from Karafuto and Manchuria).

The chemical composition of the sap and heart wood of the birches were compared. Their chemical composition was not much differ from that of the Japanese beech, studied in the Part I of these paper.

12. A Study of Cellulose Resources. Part I. The Chemical Composition of Deccan Hemp and Indian Mallow Cultivated in Manchuria.

By **Masuzo Shikata, Kazuhiko Akagi** and **Nobukiyo Urano.**

Journ. agri. chem. Soc. Japan, **11,** 621 (1934).

In search of new cellulose resources (new cellulose producing plants) the present study was undertaken. A chemical analysis of the basts and stalks of Deccan hemp (Hibiscus cannabis L.) and Indian mallow (Abutilon Avicennoe Jaertn.) was carried out. The crude cellulose content of bast was always higher than that of the heart stalks. However, quite contrary to our expectations, there was not much difference in the crude cellulose parts of the bast and heart stalk. The pith of Deccan hemp contained only 29.48% of cellulose in its dry matter, so that this part could not be used as a cellulose source.

13. A Study of Cellulose Resources. Part II. The Properties of α-Celluloses from Various Plants.

By **Mamoru Watanabe.**

Journ. agri. chem. Soc. Japan. **11,** 624 (1935).

A comparison of α-celluloses of various sources (cotton seed hairs, cotton bast fibre, Deccan hemp and Indian mallow) was given.

The method proposed by R. A. Gortner (Ind. Eng. Chem., **25**, 505 (1933)) was applied.

The chief process according to this method is the measuring of the loss of α-cellulose during repeated treatments with 17.5% NaOH. It is worth noticing that the α-cellulose of the wood part of the cotton stalks was not inferior to that of cotton bast, when they were treated in the same way.

14. A Study of Cellulose Resources. Part III. Rayon Pulp from Cotton Stalks.

By **Masuzo Shikata** and **Kazuhiko Akagi.**

Journ. agri. chem. Soc. Japan, **11**, 635 (1935).

Pulp preparations from the cotton stalks were made. It was found that the whole of cotton stalks, that is, the bast as well as the wood part, is suitable as a source of pulp.