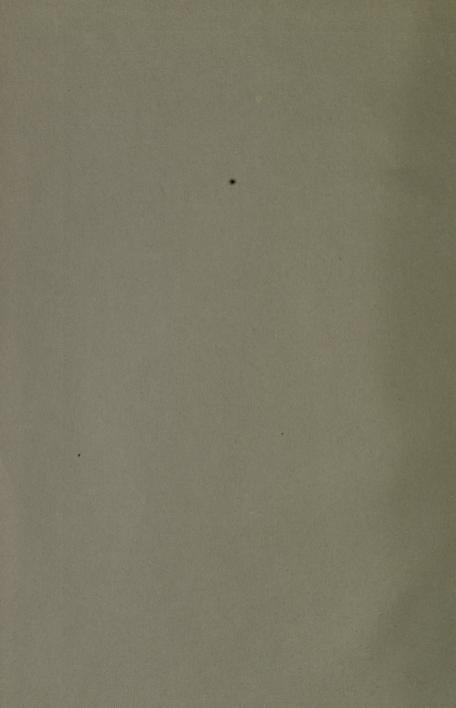


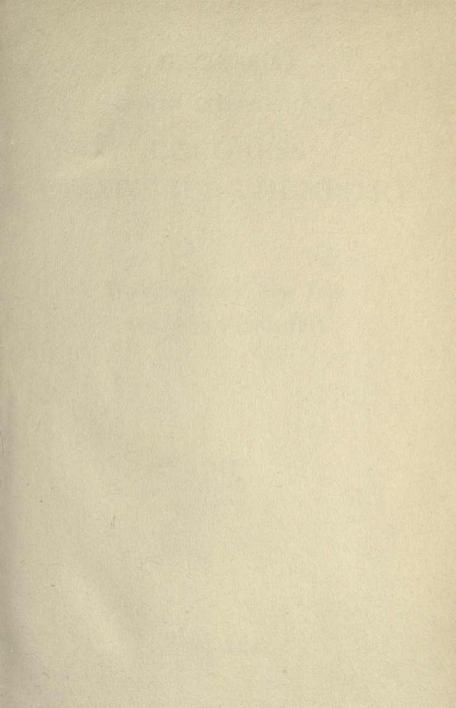
# DISCUSSIONS EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

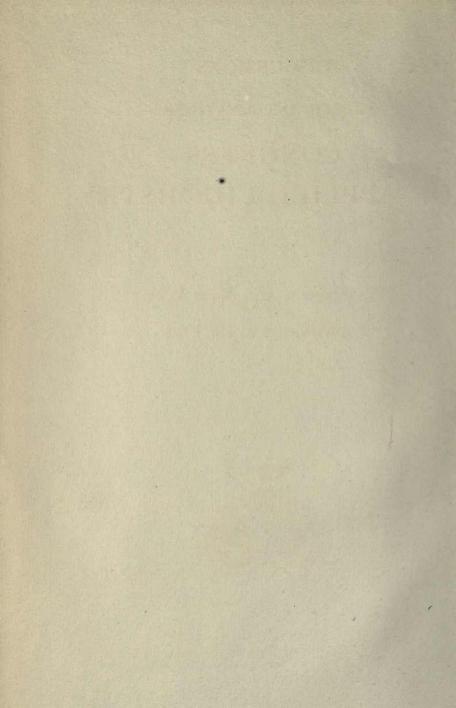
Washington and New York September 4 to 13, 1912



VOL. XXVII.

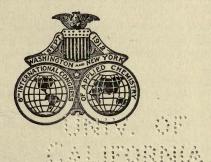






## DISCUSSIONS EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

## Washington and New York September 4 to 13, 1912



VOL. XXVII

The matter contained in this volume is printed in exact accordance with the manuscript submitted, as provided for in the rules governing papers and publications.

La matière de ce volume a êté imprimée strictement d'accord avec le manuscrit fourni et les règles gouvernant tous les documents et publications.

Die in diesem Heft enthaltenen Beiträge sind genau in Übereinstimmung mit den uns unterbreiteten Manuskripten gedruckt, in Gemässheit der für Beiträge und Verlagsartikel geltenden Bestimmungen.

La materia di questo volume e stampata in accordo al manoscritto presentato ed in base alle regole que governano i documenti e le publicazioni.

> THE RUMFORD PRESS CONCORD.N.H.U.S.A.

## VOLUME XXVII

## CONTENTS

DICE

INTRODUCTION		I AGE
INTRODUCTION NOTE		

## Section I. Analytical Chemistry

WALTER S. ALLEN AND RALPH M. PALMER. A Revised and Improved Method of Accurately Determining Arsenic Based on the Gutzeit Test.	
(Vol. I, p. 9.)	4
WALTER S. ALLEN. Rational Analysis of Nitrate of Soda. The Use of the Devarda Method vs. the Misleading "Refraction Method." (Vol.	
<i>I</i> , <i>p</i> . 19.)	6
W. S. ALLEN AND H. B. BISHOP. Method for the Determination of Sul- phur in Pyrites. (Vol. I, p. 33.)	8
WM. BLUM. The Determination of Manganese as Sulphate and by the Sodium Bismuthate Method. (Vol. 1, p. 61.)	9
PHILIP E. BROWNING AND SIMON KUZIRIAN. On the Detection and Sepa- ration of Aluminium and Beryllium by the Action of Amyl Alcohol on the Nitrates. (Vol. I, p. 87.)	11
THE CHEMISTS' COMMITTEE OF THE U. S. STEEL CORPORATION, J. M. CAMP, Chairman. The Methods of the United States Steel Corpora- tion for the Commercial Sampling and Analysis of Pig Iron. (Vol.	
<i>I</i> , <i>p</i> . 91.)	12
PONTUS H. CONRADSON. Apparatus for the Examination and Study of the Behavior of Valve and Cylinder Oils and other Petroleum Lubricants in Saturated and Superheated Steam, Carbon Dioxide, Air and other	10
Gases. (Vol. I, p. 127.) PONTUS H. CONRADSON. Apparatus and Method for Carbon Test and	13
Ash Residue in Petroleum Lubricating Oils. (Vol. I, p. 131.)	18
PONTUS H. CONRADSON. Apparatus and Method for Sulphur Determina- tion in Petroleum Illuminating and Lubricating Oils. (Vol. I, p.	
133.)	19
L. J. CURTMAN AND A. D. ST. JOHN. A Study of the Sensitiveness of the Bead and Lead Dioxide Test for Manganese, with Special Reference	
to the Interference of Iron. (Vol. I, p. 137.)	20
JOEL H. HILDEBRAND AND HERBERT S. HARNED. The Rapid Determina- tion of Magnesia in Limestone by Means of the Hydrogen Electrode.	00
(Vol. I, p. 217.)	20
111	

iv Contents		[VOL.	
		PAGE	
J. I. D. 1	HINDS. The Volatility of Arsenous Chloride. (Vol. I, p. 227.)	. 21	
HERMAN	N C. LYTHGOE. Refractometry. (Vol. I, p. 295.)	. 23	
	DU AND R. FOURET. Note sur le dosage de l'etain dans ses minerais		
(Va	bl. I, p. 373.)	. 23	
	RICHARDS. The Control of Temperature in Analytical Operations		
	<i>d. I, p. 403.</i> )		
	ICHARDS. The Measurement of Temperature in Analytical Opera		
tion	vs. (Vol. I, p. 411.)	. 24	
T. W. F	CICHARDS. Nephelometry. (Vol. I, p. 423.)	. 24	
	G. BREYER. A Proposed Standard Method of Analysis for Zind opendix, Vol. XXV, p. 7.)		
	G. BREYER. A Quantitative Estimation of the Small Amounts of Imium in the Dry Way. (Appendix, Vol. XXV, p. 1.)		
E. MEI	RKEL. Vorschläge für einheitliche Benutzung der Atomgewichts	3-	
tabe	ellen. (Appendix, Vol. XXV, p. 91.)	. 26	

## Section II. Inorganic Chemistry

WILDER D. BANCROFT AND J. M. LOHR. The Tensile Strength of Copper- Zinc Alloys. (Vol. II, p. 9.)	28
GREGORY P. BAXTER AND JAMES MOORE. A Revision of the Atomic Weight of Phosphorus. (Vol. II, p. 21.)	28
GREGORY P. BAXTER AND CHARLES R. HOOVER. A Revision of the Atomic Weight of Iron. (Vol. II, p. 37.)	28
A. BOUCHONNET. Sur l'Absorption des Matières Colorantes par les Ocres. (Vol. II, p. 53.)	29
PHILIP E. BROWNING AND GEORGE O. OBERHELMAN. On the Effect of Free Chlorine upon the Product of Hydrolysis of Tellurous Chloride.	
(Vol. II, p. 59.) EDWY GODWIN CLAYTON. Phosphorus and its Relation to the Manufac-	29
ture of Matches. (Vol. II, p. 75.)	31
ELWOOD HAYNES. The Alloys of Cobalt with Chromium and other Metals. (Vol. II, p. 119.)	32
WILLIAM WILKE. Combination of the Contact Process with the Ordinary Lead Chamber or Power Systems; an Improvement in the Manufacture of Sulphuric Acid. (Vol. II, p. 249.)	32
J. R. WITHROW. The Effect of Lime-Sulphur Spray Manufacture on the	
Eye-Sight. (Vol. II, p. 253.).	34
ALFRED H. COWLES. Alumina, Hydrochloric Acid, Caustic Alkalies and a White Hydraulic Cement by a New Process from Salt, Clay and Lime. (Appendix, Vol. XXV, p. 119.)	35

XXVII]

#### 'Contents

## Section IIIa. Metallurgy and Mining

J. O. HANDY. Sampling and Assaying Silver Ores Containing Co	obalt,
Nickel and Arsenic. (Vol. III, p. 89.)	
O. SIMMERSBACH. Koksöfen Gas zur Beheizung von Siemens-Martin	öfen.
(Appendix, Vol. XXV, p. 745.)	38

#### Section IIIb. Explosives

CHARLES P. BEISTLE. The Determination of Exudation of Nitroglycerine	
from Dynamite. (Vol. IV, p. 7.)	40
H. BRUNSWIG. Neue Initialzündung für Sprengstoffe. (Vol. IV. p. 19.).	40
THOMAS M. CHATARD. The Misuse of Explosives. (Vol. IV, p. 23.)	41
JAMES MOIR. A Plea for Improvement in the Methods of Chemical Test- ing of Mining Explosives. (Vol. IV, p. 79.)	42
ARTHUR LEE ROBINSON. Detonator Troubles Experienced in the Con- struction of the Isthmian Canal. (Vol. IV, p. 85.)	43
C. G. STORM. The Effect of Nitrotoluenes on the Determination of Nitro- glycerine by Means of the Nitrometer. (Vol. IV, p. 117.)	44
J. TAFFANEL AND H. DAUTRICHE. Recherches de la Station d'essais de Liévin sur les Explosifs de Surete pour Mines Grisonteuses et Pous-	
siéreuses. (Vol. IV, p. 127.)	45
H. C. WEBER. On a Modified Form of Stability Test. (Vol. IV, p. 147.)	47
COMMISSION Internationale pour l'Étude de l'Unification des Methodes D'Epreuves sur la Stabilité des Explosifs-Rapport Final. (Appendix,	
Vol. XXV, p. 255.)	48

#### Section IIIc. Silicate Industries

Α.	S. CUSHMAN	AND G. W	COGGESHAL	L. The	Production	of Available	
	Potash from	Natural Sa	ilicates. (Vo	l. V, p.	33.)		49

## Section IV. Organic Chemistry

F. W. BUSHONG. Isomeric Naphthenic Acids. (Vol. VI, p 57.)	51
F. D. DODGE. The Oxidation Assay of Essential Oils. (Vol. VI, p. 86.) .	51
H. W. DOUGHTY AND F. R. ELDER. The Reaction Between Selenic Acid and Toluene. (Vol. VI, p. 93.)	51
P. A. KOBER, J. T. MARSHALL, AND E. N. ROSENFELD. Phenolphthalein and Its Colorless Salts. Preparation of Monobasic Phenolphthalates.	
(Vol. VI, p. 157.)	52

v

DACE

vi Contents	[VOL.
	PAGE
S. P. MULLIKEN AND C. L. GABRIEL. A Study of the Lassaigne Reaction (Vol. VI, p. 208.)	
W. H. WARREN AND M. R. GROSE. The Possibility of Reducing the Co of Malic Acid. (Vol. VI, p. 265.)	
J. DUPONT AND L. LABAUNE. Observationes sur quelques dérivés hydrosu fonés de composés non saturés, constituants des huiles essentielle	8.
(Appendix, Vol. XXV, p. 357.) G. B. FRANKFORTER AND H. H. BROWN. The Chemistry of Wood. The	
Resins of the Douglas Fir. (Appendix, Vol. XXV, p. 359.)	
G. B. FRANKFORTER AND W. KRITCHEVSKY. Contribution to our Know edge of the Condensation Reaction by Means of Anhydrous Aluminu Chloride. The Action of Chloral and Aluminum Chloride on ti	m
Phenol Ethers. (Appendix, Vol. XXV, p. 361.)	
W. H. HUNTER AND J. D. EDWARDS. An Improved Apparatus for the Determination of Carboxyl Groups in Organic Acids. (Appendi	
Vol. XXV, p. 377.)	54
B. RASSOW. Ueber Rizinusoelsaeure. (Appendix, Vol. XXV, p. 421.)	. 54
E. E. REID. Studies in Esterification. The Esterification of Amides and Thioamides and the Formation of Dithio-Esters. (Appendix, Vo	ol.
XXV, p. 423.)	55
Section IVa. Coal Tar Colors and Dyestuffs	

TH. VALETTE.	Action des Alcalinoterreux sur la Laine. (Vol. VII, p. 29.)	56
E. E. SMITH.	Coal Tar Colors and Injury to Health. (Appendix, Vol.	
XXV, p.	473.)	56
L. DA COSTA	WARD. The Need of Official Tests in Dyeing and Textile	
Chemistry	(Annendir Vol XXV n 175)	56

## Section Va. Industry and Chemistry of Sugar

NOEL DEERR. The Status of Cane Sugar Manufacture in the Hawaiian Islands. (Vol. VIII, p. 7.)	59
H. D. GIBBS. Production of Alcohol and Sugar from Sap of the Nipa	00
Palm. (Vol. III, p. 13.)	60
T. DE GROBERT. Sur la Precipitation Incomplete par la Carbonate de Soude de la Chaux Combineé dans les jus Sucres. (Vol. VIII, p. 21.).	61
J. H. VAN LOON AND M. G. HUMMELINCK. How the Netherland Sugar- Fabricants are being kept Informed during Campaign about Quality of	
the Raw Sugar Produced. (Vol. VII, p. 29.)	62

XXVII]

#### Contents

vii

P	AGE
F. STROHMER AND O. FALLADA. Inversion von Rohrzuckerlösungen mittelst Chlorammonium. (Vol. VIII, p. 85.)	63
AUGUSTE AULARD. Quelques Particularités nouvelles sur l'emploi de l'anhydride Sulfureux et les Hydrosulfites dans l'industrie Sucrière. (Appendix, Vol. XXV, p. 501.)	64
(Ippendix, Vol. MIV, p. 601). AUGUSTE AULARD. L'emploi de la Cellulose (Pâte à papier) Comme Pro- duit Filtrant dans l'industrie Sucrière et Autres. (Appendix, Vol. XXV, p. 489.).	65
<ul> <li>AUGUSTE AULARD. Quelle que Soit la Temperature (90° a 150°C.) a Laquelle on Soumet les Solutions de Saccharose, Glucose, Maltose, etc., Pure ou Impure, ces Hydrates de Carbon Peuvent ils se Transformer en Caramel ou un de ses Derives en Milieu Humide a l'Abri de l'Air. (Appendix, Vol. XXV, p. 493.).</li> </ul>	66
<ul> <li>WILLIAM E. CROSS. Sour Cane in Louisiana. (Appendix, Vol. XXV, p. 531.)</li> </ul>	66
M. SAILLARD. Le Sucre Clerget des Melasses Normales du Betteraves par Double Polarization Neutre. (Appendix, Vol. XXV, p. 541.)	67

#### Section Vb. India Rubber and other Plastics

J.	G. FOL. On the Relationship between the Amount of Resin and the	
	Viscosity of Rubber Solutions. (Vol. IX, p. 71.)	68
L.	E. WEBER. The Action of the Resins in the Vulcanizing of Rubber.	
	(Vol. IX, p. 95.)	71
L.	H. BAEKELAND. Phenol-Formaldehyde Condensation Products.	
	(Appendix, Vol. XXV, p. 563.)	73

## Section Vc. Fuels and Asphalt

HERBERT ABRAHAM. The Classification of Resinous and Bituminous	
Substances. (Vol. X, p. 7.)	75
IRVING C. ALLEN AND T. W. ROBERTSON. Methods for the Determina-	
tion of Total Sulphur in Fuels, Particularly Applicable to Petroleum	75
Products. (Vol. X, p. 25.)	10
E. J. BABCOCK. Investigation into the Better Utilization of Non-Coking	_
Low Grade Lignitic Coals. (Vol. X, p. 41.)	76
W. F. HILLEBRAND AND W. L. BADGER. Errors in the Determination of	
Moisture in Coal. (Vol. X, p. 187.)	77
R. LESSING. A New Coking Test for Fuels. (Vol. X, p. 195.)	78
P. NICOLARDOT. Influence de la Grosseur du Grain dans l'analyse des	
Charbons. (Vol. X, p. 203.)	78

vii	i Contents [	VOL.
		PAGE
S.T	W. PARR. The Resinic Bodies in Bituminous Coal. (Vol. X, p. 225.)	79
R.	P. PERRY. Tar Distillation in the United States. General Development and Recent Progress. (Vol. X, p. 233.)	79
Por	RTER AND OVITZ. The Spontaneous Combustion of Coal. (Vol. X, p. 251.)	80
М.	TAFFANEL. De l'Alteration des Poussieres de Houille Exposées al'Air. (Vol. X, p. 277.)	82
Bυ	RRELL AND SEIBERT. Composition of Natural Gas Gasoline. (Appendix, Vol. XXV, p. 637.)	82
F. 1	C. PHILLIPS. The Determination of Soot in Mine Lamp Oils. (Appendix, Vol. XXV, p. 711.)	84
	Report of the Committee on Fuel Analysis. (Appendix, Vol. XXV, p. 41)	84
<b>E</b> .	C. UHLIG. The Analysis of Water Gas Purification Materials. (Appendix, Vol. XXV, p. 765.)	86
E. •	C. UHLIG. The Determination of Tarry Matter in Water Gas Purification Material. (Appendix, Vol. XXV, p. 769.)	87

#### Section Vd. Fats, Fatty Oils and Soaps

ARTHUR LOWENSTEIN AND LOUIS BOELIO. Experimental Data on the	
"Cold Test" of Oil. (Vol. XI, p. 17.)	89
FRANK N. SMALLEY. Factory Method for the Determination of Total Fatty	
Acids in Cotton-Seed Foods. (Vol. XI, p. 31.)	91
J. MARCUSSON. Die Bestimmung des Seifengehalts Konsistenter Fette.	
(Appendix, Vol. XXV, p. 777.)	91

## Section Ve. Paints, Drying Oils and Varnishes

GODFREY L. CABOT. Carbon Black and Lamp Black. (Vol. XII, p. 13.)	93
H. A GARDNER. The Rarer Paint Oils. (Vol. XII, p. 33.)	93
L. F. HAWLEY. Wood Turpentines. (Vol. XII, p. 41.)	93
C. H. HERTY. The Naval Stores Industry, its Past, Present and Future. (Vol. XII, p. 101.)	96
EDWIN F. HICKS. Shellac Analysis and the Detection of Small Amounts of Colophony in Shellac. (Vol. XII, p. 115.)	97
JOHN R. M. KLOTZ. Benzol and the Coal Tar Distillates and their Appli- cation in the Paint Trade. (Vol. XII, p. 123.)	97
V. P. KRAUSS, Cobalt Driers. (Vol. XII, p. 127.)	98
J. W. LAWRIE. Painting of Modern Steel Passenger Cars. (Vol. XII, p. 133.)	100

xxvII]

## Contents

	PAGE
ERIK LIEBREICH. Können Anstriche Rostfördernd Wirken? (Vol. XII,	
<i>p.</i> 143.)	102
A. LUSSKIN. Herring Oil. (Vol. XII, p. 155.)	103
J. C. OLSEN AND A. E. RATNER. Decomposition of Linseed Oil during	
Drying. (Vol. XII, p. 165.)	104
J. A. SCHAEFFER. The Manufacture and Properties of Sublimed White	
Lead. (Vol. XII, p. 175.)	104
A. W. SCHORGER. The Examination of the Oleoresins from Several Species	
of Pine Native to the Western States. (Vol. XII, p. 181.)	106
J. CRUIKSHANK SMITH AND GASTON DE PIERRES. The Technology of	
Varnish Manufacture with Notes on an Improved Scientific Process.	
(Vol. XII, p. 185.)	106
HENRY WILLIAMS. Modern Painting Methods in the Navy. (Vol. XII,	
<i>p. 203.</i> )	107
GASTON DE PIERRES. The Struggle between White Pigments in Europe.	
(Appendix, Vol. XXV, p. 783.)	107
GUSTAVE W. THOMPSON. The Coating and Hiding Power of Paints.	
(Appendix, Vol. XXV, p. 795.)	107

## Section VIa. Starch, Cellulose and Paper

A. P. BRYANT. Composition of Commercial Glucose. (Vol. XIII, p. 47),	
and A. P. BRYANT and C. S. MINER. A Study of the Unfermentable	
Residue in the Hydrolytic Products of Starch. (Vol. XIII, p. 57.)	109
H. BUEL. A Study of some of the Physical Properties of Starches. (Vol.	
XIII, p. 63.)	109
MCGARVEY CLINE AND J. H. THICKENS. The Effect of Variable Grinding Conditions on the Quality and Production of Mechanical Pulp. (Vol.	
XIII, p. 83.)	110
A. L. DEAN AND C. R. DOWNS. Antiseptic Tests of Wood-Preserving	112
Oils. (Vol. XIII, p. 103.)	114
GEO. DEFREN. The Presence of Maltose in Acid Hydrolyzed Starch	
Products. (Vol. XIII, p. 111.)	114
WILLIAM RAITT. Bamboo Cellulose. (Vol. XIII, p. 219.)	115
E. SUTERMEISTER. The Consumption of Caustic Soda in Cooking Wood and the Influence of this Consumption on the Yield and Bleaching	
Properties of the Fibre Produced. (Vol. XIII, p. 265.)	115
H. F. WEISS. Tests to Determine the Commercial Value of Wood Preserva-	
tives. (Vol. XIII, p. 279.)	118

ix

## Contents

## Section VIb. Fermentation

ALFRED FISCHER.	The Analysis of Hops as Basis for their Valuation.	AUD
(Vol. XIV, p.	77.)	120

## Section VII. Agricultural Chemistry

GABRIEL BERTRAND. Emploi du Manganese Comme Engrais Catalytique.	
(Vol. XV, p. 39.)	121
P. E. BROWNING. The Conservation of Phosphates in the Urine. (Vol.	
XV, p. 41.)	122
F. K. CAMERON. Concentration of the Soil Solution. (Vol. XV, p. 43.)	123
B. E. CURRY AND T. O. SMITH. A Study of Soil Potassium. (Vol. XV,	
<i>p. 51.</i> )	123
R. O. E. DAVIS. Comparison of Rock Grinding with Balls and Cylinders.	
(Vol. XV, p. 73.)	126
R. O. E. DAVIS. Sponge Spicules in Certain Soils. (Vol. XV, p. 77.)	128
H. VON FEILITZEN. The Fertilizing Effect of Palmaer-Phosphate on Peat	
Soils. (Vol. XV, p. 85.)	128
G. S. FRAPS. Relation of Active Phosphoric Acid and Potash of the Soil to	
Pot and Field Experiments. (Vol. XV, p. 99.)	130
G. S. FRAPS AND J. B. RATHER. Composition and Digestibility of Ether	
Extract of Hays and Fodders. (Vol. XV, p. 105.)	131
B. L. HARTWELL AND P. H. WESSELS. The Effect of Sodium Manures on	
the Percentage of Sugar in Certain Plants. (Vol. XV, p. 129.)	132
H. A. HUSTON. Field Tests with Fertilizers. (Vol. XV, p. 139.)	132
F. W. MORSE. Some Effects of Fertilizers on the Growth and Composition	
of Asparagus Roots. (Vol. XV, p. 191.)	135
A. RINDELL. Remarks on the Theory Concerning the Action of Fertilizers.	
(Vol. XV, p. 209.)	135
W. O. ROBINSON AND W. H. FRY. The Use of Ground Rocks and Ground	
Minerals as Fertilizers. (Vol. XV, p. 215.)	136
WILLIAM H. Ross. The Extraction of Potash from Silicate Rocks. (Vol.	
XV, p. 217.)	138
OSWALD SCHREINER. Organic Soil Constituents in their Relation to Soil	
Fertility. (Vol. XV, p. 231.)	140
J. J. SKINNER. Effect of Histidine and Arginine as Constituents. (Vol.	
<i>XV</i> , <i>p</i> . 253.)	142
A. STUTZER. Die Steigerung der Wirkung des Cyanamids auf den Ertrag	
landwirthschaftlicher Kulturpflanzen unter dem Einfluss von Eisenoxyd.	140
(Vol. XV, p. 301.)	142

[VOL.

DIGE

xxvii] Contents	xi
	PAGE
M. X. SULLIVAN. Biochemical Factors in Soils. (Vol. XV,	p. 305.) 143
J. W. TURRENTINE. The Composition of Kelps. (Vol. XV,	p. 313.) 144
A. VIVIER. Recherches sur la Fumure Minerale de la Better	
(Vol. XV, p. 343.)	
L. D. HAIGH. A Study of the Variations in Chemical Compo Timothy and Wheat Plants during Growth and Ripening.	(Appendix,
Vol. XXVI, p. 115.)	145
S. L. JODIDI. Amino-acids in Soils. (Appendix, Vol. XXV)	I, p. 119.) 145
J. N. LE CLERC AND J. F. BREAZEALE. The Effect of Lime up	on the Alkali
Tolerance of Wheat-Seedlings. (Appendix, Vol. XXVI,	p. 135.) 146
J. A. LE CLERC AND P. A. YODER. Soil Exchange Exper	iments with
Wheat. (Appendix, Vol. XXVI, p. 137.)	146
L. E. MORGAN. The Composition of Beef Fat as Influences and Condition of the Animal and Location in the Body.	0 0
Vol. XXVI, p. 155.)	148
C. R. MOULTON. A Study of the Cost of Maintenance and C Changes in the Composition of the Mature Beef Anima	
Fattening Period. (Appendix, Vol. XXVI, p. 157.)	

## Section VIIIa. Hygiene

S. RIDEAL.	International	Standards for	Disinfectants.	(Appendix, Vol.	
XXVI,	p. 261.)				150

## Section VIIIb. Pharmaceutical Chemistry

MILLER AND BAKER. The Potency of First Year Cultivated Digitalis	
Leaves as Indicated by Physiological Assay. (Vol. XVII, p. 51.)	152
RANSOM AND HENDERSON. Belladonna. The Effect of Cultivation and	
Fertilization on the Growth of the Plant and on the Alkaloidal Content	
of the Leaves. (Vol. XVII, p. 63.)	153
G. L. SHAEFER. Quinine Alkaloid and Some of its Compounds. (Vol.	
XVII, p. 75.)	153

## Section VIIIc. Bromatology

H. A. BAKER. Special Adaptation of Iodine Ti	
mation of Tin, Especially in Connection v	with Determination of Salts
of Tin in Canned Goods. (Vol. XVIII, 1	5.35.) 155
H. A. BAKER. "Springers" in Canned Food	ls, Their Causes and Pre-
vention. (Vol. XVIII, p. 39.)	155

xii Contents	[VOL.	
	PAGE	
H. A. BAKER. The Disappearance of Oxygen in Canned Food Container.		
(Vol. XVIII, p. 45.)		
J. M. BARTLETT. Eggs Preserved With Silicate of Soda. (Vol. XVII. p. 51.)		
WILLIAM FREAR. Food Standards—Their Functions, History and Form (Vol. XVIII, p. 129.)		
H. H. HANSOM. The Packing of American Sardines. (Vol. XVIII, 1		
131.)	. 159	
YUZARU OKUDA. Quantitative Determination of Creatine Creatinine an Mono Amino Acids in the Flesh of Some Fishes, Mollusca and Cruste		
cea. (Vol. XVIII, p. 275.)		
K. G. BITTING. Method of Determining Antiseptic Properties. (Appendix, Vol. XXVI, p. 353.)		

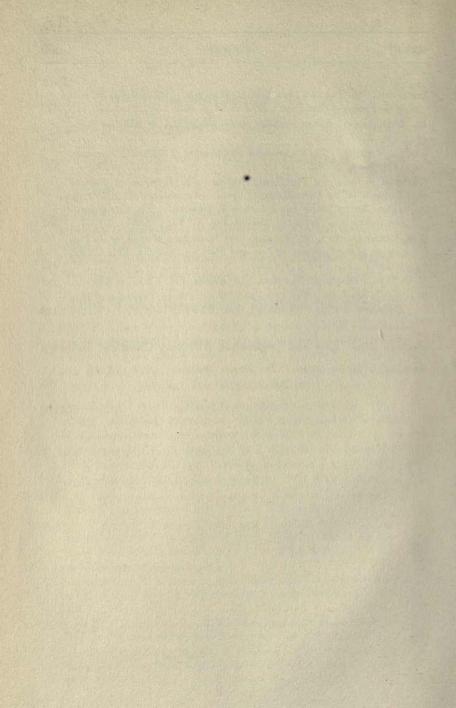
## Section VIIId. Biochemistry, including Pharmacology

Jow	ETT,	Pym/	AN AND	REMFR	y. The	Re	alation	between	n Ci	hemi	cal Consti	tu-
	tion	and	Physic	ological	Action	as	Exem	plified	by	the	Glyoxalin	les,
	Iso-	quino	lines ar	nd Acid	Amides	. (	Vol. 2	XIX, p	. 15	3.).		163

## Section Xa. Electrochemistry

RICHARD AMBERG. The Function of Slag in Electric Steel Refining. (Vol.	
21, p. 7), and Albert E. GREENE. Electric Heating and the Removal	
of Phosphorus from Iron. (Appendix, Vol. XXV, p. 191.)	164
W. D. BANCROFT, L. V. WALKER, AND C. F. MILLER. The Study of a	
Small Carborundum Furnace. (Vol. 21, p. 19.)	167
F. A. J. FITZGERALD. Heat Losses in Furnaces. (Vol. XXI, p. 37.)	167
HUGO H. HANSON AND WARREN K. LEWIS. A Method for Testing the	
Mutual Corrosive Effect of Metals. (Vol. XXI, p. 43.)	168
C. H. VOM BAUER. Electric Induction and Resistance Furnaces. (Appendix, Vol. XXV, p. 205), and PAUL HEROULT. Recent Develop-	
ments in the Electric Steel Furnace. (Vol. XXI, p. 59.)	168
Both papers were discussed together.	
E. P. SCHOCH AND D. J. BROWN. The Electroanalysis of Copper, Anti- mony, Bismuth and Tin with Acidified Chloride Electrolysis. (Vol.	
XXI, p. 81.)	170
WILLIAM H. WALKER AND RALPH E. GEGENHEIMER. Some Factors in	
the Cost of Sodium Hypochlorite Production. (Vol. XXI, p. 127.)	170
WILLIAM H. WALKER AND WALTER A. PATRICK. The Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace.	
(Vol. XXI, p. 139.)	172

XXVII	Contents	xiii
GEORG	E C. WHIPPLE AND MELVILLE C. WHIPPLE. Mill Scale as a Cause	PAGE
	the Pitting of Steel Pipe. (Vol. XXI, p. 155.)	172
M. WI	LDERMAN. Recent Progress in the Electrolysis of Alkaline Salts.	
(1	ol. XXI, p. 185.)	179
	WHITING. The Commercial Development of Chemical Processes.	
(1	ol. XXI, p. 203.)	180
E1 47 in	ES F. BURGESS AND JAMES ASTON. The Influence of Various ements on the Corrodibility of Iron. (Appendix, Vol. XXVI, p. 9.) JAMES ASTON AND CHARLES F. BURGESS. The Rate of Rust- g of Iron and Steel. (Appendix, Vol. XXVI, p. 453.)	181
	CLEMENT AND L. V. WALKER. An Electrolytic Method for the Pre- ntion of the Corrosion of Iron and Steel. (Appendix, Vol. XXVI,	
	491.)	187
C. G. 1	FINK. On Ductile Tungsten. (Appendix, Vol. XXVI, p. 503.)	188
WALTH	R B. SCHULTE. The Influence of Cinders on the Corrosion of Iron	
E	nbedded in Clay. (Appendix, Vol. XXVI, p. 555)	188
Sectio	on XIa. Law and Legislation Affecting Chemical Indu	stry
EDWAL	D J. McDERMOTT. "The Expert Witness." (Vol. XXIII, p.	189



#### INTRODUCTION

Discussion is said to be the raison d'être of congresses; and that is why men cross oceans and continents to attend them; the report of discussions may therefore be a proper measure of the value of the record of such gatherings. Therefore the officers of this Congress went to much additional labor and effort to make preparation for full discussion possible by printing in advance 560 papers (118 illustrated) in 24 volumes of a total of 4,950 pages and distributing all of them before the opening of the Congress to such members in attendance as cared to withdraw them; 1,322 members availed themselves of this opportunity. Ample stenographic service in the four official languages was provided at Columbia University for the use of members who desired to write their discussions out prior to delivery. For aid in reporting extemporaneous discussions months of effort were expended by Mr. Thomas A. Edison and his staff in originating a proper phonographic device, since ample competent stenographic service could be had under prohibitive terms only; each sectional meeting room was equipped with efficient apparatus and attendants and ample efficient transcribing facilities in the four official languages were provided; additional clerical help was kept accessible. This constituted the provisions, equipment and organization for the correct reporting of discussion.

No such effort in a gathering of this kind can be successful without coöperation of the participants in discussion; the coöperation asked was that they should leave their visiting or similar cards with the sectional secretaries, should speak from the rostrum loudly and clearly, so that those in the rear of the room could understand and should be prompt in correcting the transcript of their remarks or in providing a correct copy thereof to the sectional secretaries.

The records show that 332 papers were discussed, that 860 persons took part therein and that 30% of the total meeting time was devoted to discussion.

The following pages show 172 papers discussed with a total of 439 participants; none of these discussions seem to have been

#### Eighth International Congress of Applied Chemistry [VOL.

2

prepared in advance; many of them are edited copies of transcripts from good phonographic records but so altered as to show clearly that the authors of the extemporaneous remarks preferred not to go on record as they actually put the matter; the great majority of the indistinct phonographic records were so on account of the participants not speaking loudly nor clearly enough to be understood by their audience in the middle of the room: only a small part of the indistinct phonographic records were so because of defective operation and the remaining small part of the indistinct phonograph records were so because of the transcribers' non-familiarity with the technical subjects involved. This phonographic aid was used during the first three days only; for the last three days dependence was placed upon the participants sending in their remarks. Many of the participants did not return corrected or correct transcript of their remarks made either in the first or the last three days and in such cases the sectional secretaries reported the proceedings as well as circumstances would permit.

Absence of discussions from this report is because of failure of coöperation as above outlined or because their substance, however valuable it may have been at the moment, was not of sufficient importance or interest or too ephemeral in nature to warrant permanent embodiment in this report.

It should also be remembered that 514 of the 1,322 members who withdrew their copies of the first 24 volumes shipped them to points outside of New York City at once, thus leaving only 808 sets available to form a basis of discussion.

In measuring the value of the report of this Congress by the value of its discussions the above circumstances must be borne in mind.

> BERNHARD C. HESSE, Secretary.

3

#### NOTE

The discussions are arranged in the order in which the papers discussed appear in the Original Communications of this Congress, keeping those of each section together and in such consecutive order and not in the order of the program which in its very nature is ephemeral and very subordinate. This is done in the belief that in the printed proceedings only the substance of the discussion is desired and that its setting or surrounding is not, except in very extraordinary cases, essential or even desirable; wherever the contrary seemed warranted it has been done.

## SECTION I. ANALYTICAL CHEMISTRY

Walter S. Allen and Ralph M. Palmer. A Revised and Improved Method of Accurately Determining Arsenic Based on the Gutzeit Test. (Vol. I, p. 9.)

JOSEPH KAHN: I was very much impressed with the paper read by Mr. Allen. The quantitative determination of arsenic as described by Mr. Allen is quite simple, and, I hope will prove of great value to the chemist.

The modification of the Gutzeit method depends upon the behavior of  $AsH_3$  toward  $HgCl_2$ ; its accuracy—upon the rate of evolution of hydrogen and arsine.

• In my opinion, the state of solution of both the sulphuric acid in the hydrogen-generator, and the lead acetate in the upper tube, should have been taken in consideration with the other factors. According to the ionic theory, chemical reactions are ionic reactions; in dilute solutions the dissociation of a substance into free ions is most perfect.

In the ordinary Gutzeit test, which depends upon the behavior of  $AsH_3$  towards  $AgNO_3$ , the state of solution plays also a considerable part; with a concentrated solution a yellow compound is produced, while with a dilute solution, the yellow compound is not formed, as it is immediately decomposed hydrolytically, gray metallic silver being separated out.

In the improved test, the authors do not state the nature of the compound produced by the interaction of AsH<sub>3</sub> and HgCl<sub>2</sub> nor is the chemical effect of water upon it stated.

Another point of great importance omitted by the authors is the behavior of the test toward compounds of antimony.

W. S. ALLEN: The amount of water in the generator is always approximately the same. We use an amount of acid equal to 4 grams  $H_2SO_4$  and the total volume is always kept at about 40 cc., so that the water is always about the same amount.

In regard to the effect of antimony, I would say that we have very carefully looked into this matter. If antimony is present in excess of .0002 grams  $Sb_2O_3$  it will effect the stain. If it is less than that amount it will have no effect. It has the effect of making the stain longer and lighter in shade. We can tell whether we have antimony present or not by subjecting the stain to fumes of HCl; if antimony is present the stain will fade appreciably. The stain will be intensified if arsenic is present alone. It is very rarely the case that antimony is present in our line of work.

E. H. BAILEY: Have you studied the effects of manganese and alumina in the solution?

W. S. ALLEN: I have studied the effects of alumina but not of manganese. Alumina does not affect the stain in any way.

L. J. CURTMAN: Have you ever noticed any very great variation in results obtained when running blanks?

W. S. ALLEN: With the same lot and amount of reagents they are practically uniform.

A MEMBER: I did not catch the name of kinds of material the speaker experimented with or used in practising this method. I know a man who works a lot with arsenic in the laboratory where I am engaged and he can only use the Gutzeit method on certain classes of materials. This question has been discussed in our food work and some men claim that they are able to do all their work with the Gutzeit method and others claim difficulties, having to use the Marsh test.

W. S. ALLEN: We have rarely had to use the Gutzeit method for arsenic except in the analysis of ores and heavy chemicals of all kinds. It is applicable to every case where we use it and it is my opinion that it can be used wherever the Marsh test can be used. There are several things that have to be very carefully studied in order to have its use applicable: such as substances which may be composed largely of organic compounds. I am not certain just how to treat all of these materials: we know that certain organic compounds will very materially inhibit the evolution of arsine, and it is a question of properly preparing the sample so that the organic matter will be decomposed and none will be left to have any prohibitory action. Starch is converted to dextrose by boiling with a little HCl. Our experience with organic matter has been very limited and it is only in that field

## 6 Eighth International Congress of Applied Chemistry [VOL.

that further work should be done to make absolutely certain that this method is applicable.

A MEMBER: What effect has fluorine on the deposition of the stain?

W. S. ALLEN: When traces of fluorine are present there is no injurious effect. If it is present in larger amounts I do not see any objection to removing it. There is no trouble in getting rid of such impurities provided the arsenic is kept in the oxidized condition.

H. J. ROSIN: The speaker states that he discriminates between the stain produced by arsine and stibine by the action of HCl fumes on the stain. Fleishman has published a method whereby he boils the sample in an alkaline solution, thereby getting the arsenic stain alone. Could this apparatus be used in this case?

W. S. ALLEN: In the course of our investigation we tried the use of metals and alloys in an alkaline solution but were not at all successful when compared with the results obtained with an acid solution. If arsine could be produced in that way the apparatus would be entirely suitable to the Fleishman method. I much prefer the acid treatment.

Walter S. Allen. Rational Analysis of Nitrate of Soda: the Use of the Devarda Method vs. the Misleading "Refraction Method." (Vol. I, p. 19.)

 $\langle \diamond \rangle$ 

A MEMBER: I would like to ask Mr. Allen this question: How much difference is there between the results obtained by the Devarda method and the nitrometer?

The du Pont Powder Company is perhaps the largest, or one of the largest users of nitrate of soda in this country and for years we have been analysing our nitrate both by the West Coast and nitrometer, the former method because we purchased this material upon that basis, and the latter method because it is absolutely necessary that in order to run our plants efficiently we must know the exact nitrate value of the material we use. We have investigated the nitrometer method for quite a number of years and have worked out in detail every possible source of error in

## XXVII] Discussions: Section I. Analytical Chemistry

the method. We likewise require our other laboratories to check within .15% by the nitrometer; they usually check closer and to make sure that they are doing their work accurately we send out occasionally a check sample for analysis. It is inaccurate to state that it is unnecessary to make the analysis as accurately as Mr. Allen suggested. I think that the large commercial houses of this country realize that in order to work their plants efficiently they must analyse their material more accurately than any such method as the West Coast method. I think that we are about as much interested in this proposition as anybody in the country because we find, as Mr. Allen states, from 1 to  $1\frac{1}{2}\%$  and sometimes 2% difference between our analysis with the nitrometer and the analysis by the refraction method. Another objection I have to the refraction method is, that it includes the determination of moisture and I think anyone who has had experience in analyzing nitrates will agree with me that moisture plays an important part in analyzing nitrates. We always do our nitrometer determinations on the dry basis and make independent moisture determinations on a larger representative sample of nitrate and base our calculations on the two analyses.

W. S. ALLEN: In reply to the question of the last speaker concerning comparative results between the Devarda method and nitrometer, they agree very closely as a rule. We have here a summary of results from the analyses of 23 samples. Out of these 23, 22 agree within .5% and 18 within .3%. Out of these same 23 only 6 agree within .5% by the refraction method which shows again the great difference in results. The nitrometer method is exceedingly accurate but I think it requires a great deal of very careful manipulation and a lot of experience to get exceedingly accurate results, and in scattered laboratories such as we have in our company this is not always available.

Eighth International Congress of Applied Chemistry [VOL.

W. S. Allen and H. B. Bishop. Method for the Determination of Sulphur in Pyrites. (Vol. I, p. 33.)

8

J. B. F. HERRESHOFF: I would say that it has been the policy of the General Chemical Company and the Nichols Copper Company ever since their existence to encourage the use and application of research work as applied to the improvement of various analytical methods.

The character of the research work is plainly shown and well done by Mr. Allen and Mr. Bishop. The difficulty of all previous methods has been recognized and this new method has been very carefully considered by the principal analysts in New York City who are engaged in making analyses of this kind and they are reaching the point when they will adopt this method as a standard. I mention these facts especially for our foreign friends so that they may look into this method with a great deal of care and learn its advantages.

J. W. McKELVEY: Do marcasite and pyrite occur together? I understand that marcasite can be determined in pyrite by its different rate of oxidation. Are they both oxidized equally by the reagent bromine?

W. S. ALLEN: I cannot answer that definitely one way or the other. There is a great difference in the rate of oxidation of different grades of pyrites ore. We have no trouble in getting complete oxidation with either pyrites ore or marcasite.

JOSEPH W. RICHARDS: If there were a difference in the rate of oxidation of pyrite and marcasite the pyrite ore would take care of the marcasite.

L. M. LIDDLE: I wish to call attention to the recently published method of A. M. Smoot. Mr. Smoot, after dissolving the pyrite, precipitates the iron by electrolysis on a mercury cathode. The other heavy metals precipitate with it. This leaves practically only a pure diluted solution of sulphuric acid from which to throw down the barium sulphate. The advantage over the Allen & Bishop method is the smaller size of the beakers worked with, so that a man running 20 or 30 analyses can have them close together and right under his hand.

W. S. ALLEN: Mr. Smoot was kind enough to give me a copy

of his method some time ago and we have tried it out. We find that by electrolysis the iron is apparently driven into the mercury. I do not see any advantage in removing the iron when reducing it accomplishes the same results. A great many laboratories are not equipped with an electolytic apparatus to carry out Mr. Smoot's method.

L. M. LIDDLE: I believe one of the advantages is that he works with a much smaller sample than the method presented and 20 or 30 analyses can be made at the same time.

L. A. TOUZALIN: In the routine determination of sulphur in iron and steel by the volumetric evolution method, it may be of interest to know that at the South Chicago plant of the Illinois Steel Company we have experimented with an electric heater for this purpose. By means of such a heater the uniform heating while undergoing solution and final boiling is made as uniform as possible.

Wm. Blum. The Determination of Manganese as Sulphate and by the Sodium Bismuthate Method. (Vol. I, p. 61.)

٨

٨

MR. BRINKEN: If, as has been shown, the permanganate contains some substance which leaves a residue on filtering, may we not assume that this residue contains lower oxides of manganese? If this is true in the reduction and reoxidation proof given by Dr. Blum is it not possible that some tetravalent manganese is reduced and then oxidized to the heptavalent form by the bismuthate? If this were so to any considerable extent, it would tend to support my empirical factor.

W. F. HILLEBRAND: The Bureau of Standards is doing work of this kind. The question arose some time ago as to the necessity of using an empirical factor in calculating the results of the sodium bismuthate method, when the potassium permanganate solution is standardized by the use of sodium oxalate. It was found by the work of Dr. Blum that the empirical factor was not at all necessary.

A MEMBER: For the determination of manganese in low

manganese steel has any comparison been made between the Volhard and the sodium bismuthate methods?

W. F. HILLEBRAND: I do not believe that any comparison of these two methods has been carried out by the Bureau of Standards. I should like to point out further that it is quite unnecessary to use small amounts of the sample with the sodium bismuthate method. Larger amounts may be used equally well, as Dr. Blum has succeeded in demonstrating.

W. B. PRICE: I should like to ask whether the presence of vanadium has caused any difficulty in the determination of manganese by the bismuthate method? In our work on steel we have found the Ford-Williams method gives better results.

MR. BRINKEN: In this regard I should like to say that we have used the bismuthate method in determining manganese in steel where the amount of vanadium was as high as 0.15% and have found that the method gives very good results.

J. W. MCKELVEY: I should like to say with regard to the stability of permanganate solution that we have found the solutions to be very much more stable if they are kept slightly alkaline. Furthermore, permanganate solutions are quite stable in the light even for many months

E. W. MORLEY: The reason for the instability of permanganate solutions may be found in the water itself. If the water is very carefully purified from organic matter, permanganate solutions are very much more stable. I have a permanganate solution that I prepared over four years ago. I have standardized it several times every year and find that its oxidizing power actually increases, contrary to what we might expect. This is doubtless explained by the fact that a slight evaporation of the water takes place up past the sides of the stopper.

W. F. HILLEBRAND: Dr. Blum has made every effort to get rid of the stain on the asbestos, which always appears on filtering the permanganate, but his efforts have been futile in this respect. It has been found, however, that the amount is so small as to be quite negligible from an analytical standpoint.

J. W. MCKELVEY: The stain on the asbestos is not due to the presence of lower oxides of manganese. It is the effect of the asbestos upon the permanganate solution.

## XXVII] Discussions: Section I. Analytical Chemistry

۲

E. W. MORLEY: That the stain on the asbestos is not due to the presence of the lower oxides of manganese is readily demonstrated by the fact that no precipitate is formed in the permanganate solutions on standing.

Philip E. Browning and Simon Kuzirian. On the Detection and Separation of Aluminium and Beryllium by the Action of Amyl Alcohol on the Nitrates. (Vol. I, p. 87.)

L. J. CURTMAN: I should like to know whether there are practical difficulties in carrying out this operation, especially when applied to volatile determination. I should like to know especially whether there is any possible loss in the process of boiling.

P. E. BROWNING: I am glad to answer that question. I should like to say that it is necessary to evaporate the water to the smallest possible amount. The difficulty that most people have with these amyl alcohol methods is that they attempt to boil out a large amount of water through a small amount of alcohol, or use equal parts of water and alcohol. Of course, under these conditions, since the water is in the lower layer and the alcohol in the upper, it is a very few minutes before the alcohol is spread about the room, and very often fire breaks out. If you evaporate solutions to about a drop or a cubic centimeter, and then put on five cubic centimeters of amylalcohol, there is no difficulty whatsoever. I have used successfully the alcohol method for analytical purposes for over twenty years in the separation of strontium and calcium by a method that I worked out in 1892. Of course one may get into difficulties with this method by not following directions closely. Simply get the volume of water as small as possible, agitate the liquid in which case the water passes off very readily through the alcohol, and leaves the substance insoluble in the alcohol on the sides of the tube.

The Chemists' Committee of the U.S. Steel Corporation, J. M. Camp, Chairman. The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron. (Vol. I, p. 91.)

MR. RICH: I should like to call attention to a correction on page 120. "25 CC's of water," etc., should read: "One part of acid to three parts water." (Print of p. 120 is accurate to copy. B. C. H.)

QUESTION: Is it well to use cold or hot acid? Answer: It is advisable to use hot acid.

W. F. HILLEBRAND: Referring to Dr. Richards' remark on the importance of determining copper in present-day steel, I add my testimony to the same effect, having noticed lately as much as 0.34% copper in one of the steels issued by the Bureau of Standards. I would call attention also to the growing importance of making more detailed analysis than has been customary. especially perhaps with alloy steels. If this is not done errors of analysis are possible on account of the presence of small amounts of unexpected constituents; for instance nickel steel was found to contain 0.15% of tungsten, which probably was not derived from the iron or nickel ores which furnished the steel. As an illustration of the effect of one element on the determination I may mention the case that was recently settled at the Bureau of Standards, where wide discrepancies in the results of certain foreign chemists on the Chilean iron ore were traced to the apparently overlooked presence of two to three tenths of 1% of vanadium in the ore.

W. S. ALLEN: I should like to ask if the presence of arsenic has had any disturbing effects in the determination of phosphorus?

J. M. CAMP: There is usually very little arsenic in the ore itself. Arsenic is usually introduced in the scrap iron. With regard to the determination of phosphorus in the presence of arsenic we have followed the method given by Blair. The arsenic is reduced by hydrogen sulphide. Where the phosphorus is low and the temperature is kept down, results are fairly satisfactory. We have found that the reduction of the arsenic by the addition of oxalic acid is a very good method for the determination of phosphorus in steel.

F. G. BREYER: I should like to say that the methods of sampling of pig iron and steel differ considerably, because the composition of the spiegel iron differs in different layers. In certain cases tried, the content of manganese differed as much as 2%, while that of silicon often differed 1%. It is necessary to have a uniform method of sampling and to take samples from every bed.

J. M. CAMP: It is a well-known fact to chemists that the first cast differs very greatly from the last. Our samples are taken from the molten material and we take one sample from each ladle. A ladle contains about thirty tons. Each layer corresponds to one ladle and we therefore have a sample from each layer.

J. W. RICHARDS: It would seem that the method of sampling needs improving very much. In fact, the error introduced in sampling is often much greater than the error in analysis.

٨

Pontus H. Conradson. Apparatus for the Examination and Study of the Behavior of Valve and Cylinder Oils and other Petroleum Lubricants in Saturated and Superheated Steam, Carbon Dioxide, Air and other Gases. (Vol. I, p. 127.)

P. H. CONRADSON: After several years of carefully following up the matter of lubrication in actual service on railroads not only in connection with the saturator, superheated steam, but also in other directions, I have come to the conclusion that it is better to have a cylinder oil containing a certain amount of comparatively volatile matters at low temperatures. I have followed up an lubricating oil fed into locomotive boilers for the prevention of scale. About  $3\frac{1}{2}$  liters, one gallon, is fed. During the run of a locomotive over a division of say 100 miles it has been found that wherever this oil is used in connection with the prevention of scale in the boilers, it is much easier for the engineer to handle his throttle valve. That oil goes off in the

#### 14 Eighth International Congress of Applied Chemistry [VOL.

form of vapor with the steam, and the steam becomes lubricated. It is further demonstrated that the steam chests, cylinder holes and the piston rings are kept much cleaner and last longer where this oil is used showing that the theory, if we may call it such, has been borne out in actual practice: that the lubricating the steam is a good device. Last night I showed the president of a company who handles this device and he told me some interesting things in direct connection with what I have said. He gave me a sample of some locomotive statistics on two roads, one an Eastern and one a Southern road. They took two or three engines equipped with the introduction of this oil and the same class of engine having no oil introduced and they find that where they have introduced the oil in the boilers to bring the scale down they have much less trouble from the formation of carbonaceous matter than when they have no oil. This demonstrates the fact that the idea of lubricating steam seems to be correct from a practical standpoint.

G. R. PRENTICE: I simply wish to say that in addition to the oil preventing scale in locomotive boilers, the Chicago, Milwaukee & St. Paul Railroad has used crude petroleum oil as a means to prevent the water in the boiler from foaming, and where ordinarily the foaming in a boiler becomes very troublesome when the concentration of the salts in the water reaches 125 grains to the gallon, that by the use of crude petroleum oil we have been able to run engines where the water in the boiler has a concentration of 800 to 900 grains to the gallon without occasioning great trouble. In certain instances the concentration had reached 1400 to 1500 grains to the gallon and it is a fact that we have demonstrated for the past several years that the steam from the boiler does help the lubrication when oil is used in that way.

J. MOTION: I would like to ask whether or not crude lubricating oils from Pennsylvania and crude and lubricating oils from California have been compared by this method. For instance, suppose we take a Pennsylvania cylinder oil having a test something like 26 Be, gravity 122, viscosity 40 and a flashing point of about 500, and we compare that with an oil made from California having a gravity of about 18, viscosity of about 90, flashing about 400, how would these two oils compare? What results would he find if he has examined them? What would he expect to find?

P. H. CONRADSON: I have only examined cylinder oils made from Pennsylvania oil. I have no experience with Western oil and would be very glad if the gentleman would send me some samples for test. It would be very important in practical results and in commercial directions.

E. M. CHANCE: With regard to the purification of water, which I believe Mr. Motion just called to your attention, I say that it has been my misfortune on several occasions to be obliged at many of our collieries to purify our acid mine waters in order to keep our plants in operation. At each of these collieries we will require 200,000 to 300,000 gallons of water per day, and I thought perhaps it might be of interest to some of you to hear of our experience and I would also like to ask Mr. Prentice for any further details in regard to the foaming. These waters will contain about 1500 parts per million of SO<sub>3</sub>, so that you can realize after the treatment of these waters by the usual lime and soda method we have a vast quantity of dissolved salts remaining in the water. We experience considerable trouble in preventing foaming. It was necessary to blow our boilers at least once an hour or once every two hours on some occasions to permit of their being run at all. It was a decidedly unpleasant experience and I would like if possible to have some further data in regard to the use of the oil distillate in the obviation of this foaming. When you consider that we had 20 or 30 plants using 300,000 gallons per day each you will see what it means. I would like very much to have Mr. Motion give us a little further information in regard to the action of the oil in preventing the foaming.

P. H. CONRADSON: Perhaps I can say a few words in regard to this. The statement given by the gentleman for the Chicago, Milwaukee & St. Paul Railroad in regard to the use of crude oil for the prevention of the formation of scale, I think answers the question pretty well. However, I have had some experience in connection with this oil fed into the boiler of locomotives where the water had not a large quantity of salts which produced foaming, on a Western railroad where the oil was tried—say on an uphill grade. The locomotives, owing to the severe foaming, could only pull about 8 freight cars. After putting in sufficient quantity of oil, in fact, not a large quantity of this petroleum distillate, it could pull from 12 to 13 cars over the hill. This would indicate that petroleum distillate or petroleum oil would have a tendency to prevent foaming in the boilers. It is simply a matter of trying it. The following table bears on the question:

The following (table of comparative tests of five samples of cylinder oils, A, B, C, D, E, and F, a petroleum distillate,) is of interest in connection with the study of Cylinder Oils in Superheated Steam.

	1	1	1		1	
	A.	В.	C.	D.	E.	F.
	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.
The Devile a state of the	Turkier of			1.12		
Flash Point (open cup).	545°	550°	605°	595°	550°	365°
Burning Point	610	630	695	680	630	415
Gravity at 60°F. Baume		26.1	24.7	25.9		33.5
Sp. Gr. at 15°C	0.895	0.897	0.905	0.898		0.856
Color	Light	Dark	Dark	V. Dark		Yellow
Gas. Test Bef. Fire Test		Good	0.5cc.	4.cc		
Gas. Test Aft Fire Test	TILL STOLES	Good	Good	3.cc		
Cold Test Flows	+55°F.	+32°F	+45°F	+34°F	+30°F	the second se
Saponifiable Fats	Trace	Trace	Trace	Trace	15%	None
Vis. Saybolt at 212°F	133 sec	146 sec	215 sec	216 sec		
(60 cc.)		ALL REAL PROPERTY	Chen Arthurs			District
Barbey Ixomot 500°F	45 sec	51 sec	61 sec	60 sec		
(180  units = 30 cc.)				Sector Sector		
Hot Air test at 540°E	15%	11%	2.5%	5.5%		
(Loss)		e and the for	CERT DATA	24.98.27	S. States	
Gas. test after	Good	Good	0.5cc.	3.5cc		
Carbon test Residue	2.51%	2.70%	4.90%	5.10%		
SO, in Residue	0.023%	0.03%	0.03%	0.04%		
Loss Sup. steam 400°F.	0.0%	.0%	0.0%	0.0%	0.0%	32%
Loss Sup. steam 500°F.	5.0	4.0	1.5	1.0	5.0	67
Loss Sup. steam 600°F.	18.5	18.0	6.5	8.5	21.5	
Loss Sup. steam 700°F.	44.0	34.0	32.5	40.5		
Same Discont Station and Station of						
Total Loss up to 700°F.	67.5	56.5	40.5	50.0		
Gas test of Oil						
Residue from 700° Test	Good	Good	1.5cc.	3.0cc.		
	日本にある		COLUMN.	The share	81-2-1	10 15

Hot Air Test = 13 grams oil in shallow round flat bottom iron dishes exposed six hours at 540°F. in a specially designed air bath.

Gasolene Test = 10 cc. oil 90 cc. Petroleum ether 0.65 sp. gr. (from Pennsylvania crude) in graduated flat precipitating tubes, taking reading after one hour's standing.

Carbon Test using 35 grams oil, according to Conradson's apparatus and method.

Superheated-Steam Test = 13 grams of oil used.

Sample "A" in a superheated steam test at 800°F. (427°C.) left no residue. Sample "C" left 2.5% dry carbonaceous residue.

Sample "E" containing 15% of saponifiable fats subjected to the superheated steam test lost 26.5% up to  $600^{\circ}$ F.,—the oil residue from this test contained 17.5% saponifiable fats, this indicates that the petroleum oil stock (B used) goes off with the steam somewhat faster in proportion to the fat oil up to  $600^{\circ}$ F. ( $350^{\circ}$ C.).

The steam pressures used in these tests was about ten to twelve pounds per square inch. Large volume of superheated steam passing through the apparatus during the tests (about 40 cc. condensed steam  $H_2O$  per minute).

In these superheated steam evaporating tests about 13 grams of oil were weighed into the small dish placed inside the steam vessel D. (The capacity of the small iron dish is 50 cc. having a diameter of about 480 mm. and 300 mm. high, with flat bottom.)

The steam vesel with the oil in the dish was heated up to about  $350^{\circ}$ F. (176°C.) passing a slow current of natural gas through the apparatus, then superheated steam was admitted, the gas shut off, and the temperature raised up to the required degree and kept constant for about 75 minutes;—the volatile matter in the oils at the given test temperature generally were carried over with the steam inside of 60 minutes, allowing about 15 minutes extra steaming. At the end of each given temperature test the steam and heat were shut off:—after cooling the dish containing the oil was weighed and replaced into the steam vessel and the operation repeated for the next temperature test and so on.

### 18 Eighth International Congress of Applied Chemistry [VOL.

Pontus H. Conradson; Apparatus and Method for Carbon Test and Ash Residue in Petroleum lubricating oils. (Vol. I, p. 131.)

P. H. WALKER: I would like to know what figures you would consider limits for the various types of special gas and automobile cylinder oils—what would you consider the limits that should be put on the carbon tests as applied to this apparatus and also how the results agree with different operators working on the same oil at a different time using this test? It would be interesting to know how close agreement can be had. The work that we have done on the test has been the old method of distilling in a glass retort and I must say that we do not come near to getting duplicates. We do not know whether we do not know how to make the test or whether it is due to the imperfection of the apparatus, and I would like to know what kind of duplicate determinations can be made under the conditions of a different operator working at different times on the same oil.

P. H. CONRADSON: As regards the first part of the question, the limit of the carbonaceous matter that is left in this distillation process or any other distillation used in laboratories, I give you the same answer as previously. This is simply a method and how much and what limits can be given I do not know. The less carbon residue you get the better the results in service. Dr. Day has called attention to carbon tests, etc., for automobile oils and some oils give very little carbon in tests, little residue in the carbon tests give poor results in the service. On the other hand, a man who understands how to run his automobile can have lots of carbon and get good results. It depends upon the practical handling of the oil in the lubrication of automobiles and this is much more important than any chemical tests in the laboratory.

P. H. WALKER: How about duplicate tests?

P. H. CONRADSON: As regards duplicate determinations I only worked this myself and from time to time made duplicate tests of the same oil. For instance, an oil containing between 3 to 4% of carbon residue in this method I may get  $r_{00}^{2}$  of 1% difference in the results, sometimes a little higher.

## XXVII] Discussions: Section I. Analytical Chemistry

Pontus H. Conradson; Apparatus and Method for Sulphur Determination in Petroleum Illuminating and Lubbricating Oils. (Vol. I, p. 133.)

P. H. WALKER: I want to ask Mr. Conradson in regard to the interpretation of sulphur values rather than the method of making the determination. Our trouble with the examination of oils is not in making the determination. We can make a whole lot of determinations on oils but what do they mean when we get them? Could you tell us what would be the limits that you have determined them, *i. e.*, what percentage of sulphur would be admissible in oil, for example? What would be the limits of sulphur in various grades of lubricating oil? Those are the points that we want to know, rather than the method of determination.

P. H. CONRADSON: This question is a good one and a practical one. Of course, as you understand, this is simply methods to bring out discussion. How much sulphur should be present in oil simply so far as sulphur is concerned, I cannot tell. That depends on the process of refinement. Do you mean a compound of oil with petroleum oil; or do you mean a straight petroleum oil such as is used on railroads on track signals?

P. H. WALKER: I mean straight oil used on track signals.

P. H. CONRADSON: I will give you an illustration which will give Mr. Walker an idea that his question cannot be answered offhand and perhaps cannot be answered at all. However, in the Pennsylvania oils containing the crude oil probably not more than 3-100ths of 1% of sulphur is present. That amount of sulphur in properly refined signal oil such as used by railroads for important tests is all right if the sulphur is present in the form of sulphur that goes off with combustion in the apparatus. On the other hand, if the sulphur amounts to 300 to 400 thousandths of a percent is present as sulphates in the oil it indicates a poorly refined oil and you may have poor results. About a year or a year and a half ago I had a sample of Western oil from a gentleman; that oil burned about two days and went out. It was no good. The sulphur was about 13-100ths of 1%. I told him that his method of refining must be improved. So this year he

came back at me again with the same oil and perhaps 3-100ths of 1% of sulphur in the sample sent this year and the oil burned six days. I do not attribute the difference in burning 3 days and 6 days to the 3-100ths of 1% of sulphur, but he had improved the process in another direction. At present we have no accurate information as to how much sulphur might be allowable in a burning oil. On the other hand take a lubricating oil; take, for instance, the first one with a sulphur content of 2-100ths of 1%. of sulphur. That is brought to 25-1000ths of 1% of sulphur. That is a long story but with the gentleman's approval I will simply say two words against it. It has been found that in the oil used over and over again it became bad. Therefore, it would follow that it is advisable to use oil with lower sulphur contents.

L. J. Curtman and A. D. St. John. A Study of the Sensitiveness of the Bead and Lead Dioxide Test for Manganese, With Special Reference to the Interference of Iron. (Vol. I, p. 137.)

۲

۲

۲

E. B. SPEAR: In making qualitative tests for small amounts of manganese in steel, I found it advantageous to dissolve the steel in concentrated nitric acid, add lead peroxide, boil a few minutes, pour off the liquid and add equal amounts of water and dilute nitric acid. On boiling again, very small amounts of manganese can be detected because most of the iron has been poured off.

Joel H. Hildebrand and Herbert S. Harned. The Rapid Determination of Magnesia in Limestone by Means of the Hydrogen Electrode. (Vol. I, p. 217.)

J. H. HILDEBRAND: I should like to say that this will compete, as far as I can see, with ordinary methods for the analysis of limestone with the ordinary manipulator. Of course, when you are titrating with normal alkali you cannot get an accuracy for more than two tenths of a cc. which I think is in the first place, sufficient for the purposes. All that I claim for this method is ٨

that it is useful in technical analysis. Of course it is also useful for preliminary analysis; for publication, other analysis must be resorted to. Suppose a man is making cement, buying limestone, and wants to know whether he is buying 2 or 5% of magnesium. This method is applicable, and saves the tieing up of large amounts of limestone waiting for analysis. With regard to the accuracy, you can determine the end point to about two tenths of a cc. That would correspond to about 200 milligrams with normal alkali.

J. I. D. Hinds. The Volatility of Arsenous Chloride. (Vol. I, p. 227.)

L. J. CURTMAN: As I understand it, the paper just read by Dr. Hinds was the outcome of an attempt to secure a definite acidity in the precipitation of the arsenic group. To attain a definite acid concentration of HCl by boiling, it was feared that some arsenic would be lost by volatilization. Regarding the first point, namely, that of a definite acidity, I should like to know what objection there is to neutralizing the solution directly with NH<sub>4</sub>OH and then adding a definite quantity of standard acid. The NH<sub>4</sub>Cl formed would not interfere with the analysis, as the test for NH<sub>4</sub> is always made on a separate portion of the original solution; moreover by assisting in coagulating the precipitated sulphides, the NH<sub>4</sub>Cl would seem to be favorable rather than detrimental to the analysis. Concerning the method employed by Dr. Hinds in determining the quantity of arsenic which distilled over, I should like to ask whether more accurate results would not have been obtained, if the arsenic were determined in the solution before and after the distillation, the loss would then be represented by the difference in the amounts found. It seems to me that this method would yield more reliable results, particularly if the losses so found, were checked by the figures obtained in the analysis of the distillates. I should think that some volumetric method, such as the iodine method employing a 1-100 N. solution and making due allowance for the volume consumed in affecting the indicator, would give reliable results.

### 22 Eighth International Congress of Applied Chemistry [VOL.

While I do not doubt the accuracy of Dr. Hinds's method, it is somewhat novel as applied to the determination of small amounts of arsenic; and in view of this, it is to be regretted that Dr. Hinds did not check his method against solutions of known strength.

J. I. D. HINDS: In regard to the first point in Mr. Curtman's inquiry I reply that the object of the evaporation is to secure sufficiently high acid concentration for the ready precipitation of quinquivalent arsenic and the subsequent dilution is to secure a sufficiently low acid concentration for the complete precipitation of the other members of the group.

As to the second question, I reply that the quantity of arsenic lost was so small that to determine it in the residue would have required a quantitative analysis, while in the distillate a close approximation was easily and readily obtained by the colorimetric and nephelimetric comparison with solutions of known concentrations, as indicated in the paper. Such comparisons were more rapid than volumetric determinations and equally as accurate.

MR. HOWE: This work of Dr. Hinds has interested me very much, especially one phase which led, as I understand, to the work, namely the precipitation of arsenic in its quinquivalent form by hydrogen sulphide. Dr. Hinds finds that at a special concentration and by boiling a certain time, or by boiling away a certain portion of the liquid the arsenic in its quinquivalent form is readily precipitated by hydrogen sulphide.

In a previous discussion, at another consideration of this same paper, I made the suggestion that possibly the reason for this was that the hydrochloric acid on being boiled with the quinquivalent arsenic was oxidized and the arsenic reduced to its trivalent form. I merely want to state this morning that I have since carried out a number of experiments along this line, and find no change in the quinquivalent arsenic on boiling hydrochloric acid, but it does appear to be a fact that at certain concentrations on boiling a certain length of time the arsenic is much more easily precipated. Why I hope Dr. Hinds is going to be able to tells us, but it appears not to be owing to the reduction of the quinquivalent arsenic.

#### Herman C. Lythgoe. Refractometry. (Vol. I, p. 295.)

L. W. ANDREWS: I should like to remark that the refractometric method is conveniently applicable to the determination of small amounts of water in organic liquids; particularly in such as are miscible with water to only a limited degree. These solutions are in general more refractive than the organic liquid in a pure state. The process has been found useful in the estimation of small amounts of water in alcohol or ether.

O. RAUBENHEIMER: I should like to point out that the refractive index method has been used in pharmacy for a long time. In fact, the first table was prepared by pharmaceutical chemists. Revision of tables and uniform international methods are extremely desirable.

H. Milou and R. Fouret. Note sur le dosage de l'etain dans ses minerais. (Vol. I, p. 373.)

J. W. RICHARDS: With regard to the sulphuric acid and zinc method it is found not to work well on cassiterite. Potassium cyanide worked badly on tin ores low in the percentage of tin. The potassium cyanide must be kept pure and must not contain carbonates or cyanates.

T. W. Richards. The Control of Temperature in Analytical Operations. (Vol. I, p. 403.)

٨

A MEMBER: I should like to ask whether these temperatures are measured with a Beckmann thermometer, or with the resistance thermometer, or by a thermal element?

T. W. RICHARDS: The temperatures in the thermostat were measured by several kinds of standard mercury thermometers and also with a thermal element made by Dr. White of the Geophysical Laboratory of the Carnegie Institution. It is true of course that the apparatus must be protected from evaporation if you want to get the most accurate results. We have found, however, that with active stirring, using water with oil on top of it, one may obtain results within this degree of accuracy (that is, within  $0.001^{\circ}$  or  $0.002^{\circ}$ ), provided that the barrel is carefully insulated from outside thermal effects by a thick coating of felt.

T. W. Richards. The Measurement of Temperature in Analytical Operations. (Vol. I, p. 411.)

F. C. BREITHUT: I want to ask whether variation in atmospheric pressure had been taken into account and the effect of exterior pressure on the thermometer bulb.

T. W. RICHARDS: You will find that matter alluded to in the printed paper. In taking any temperature with a mercury thermometer one must take into account not only the varying atmospheric pressure, but also the pressure of liquid above the thermometer bulb, when this is immersed to determine the total effect of external pressure upon the thermometer bulb; this effect with a thin-bulbed thermometer may amount to several thousandths of a degree. One must also take into account the internal pressure, and various other effects on the thermometer bulb which I omitted in speaking, partly because they are described in the paper and partly because they are pretty generally known.

#### T. W. Richards. Nephelometry. (Vol. I, p. 423.)

٨

W. H. WALKER: I should like to ask Professor Richards whether the instrument is looked at with both eyes or with one only. Is it binocular or monocular? Another point is, how close can one come to the amount present?

T. W. RICHARDS: I am glad to answer these questions. We have the instrument arranged to use only one eye. There is a case or box above the prisms with a hole in the top; no lens is necessary. The height of the orifice must be adjusted so as to get the half shadow effect with one eye. The height would vary, of course, with the angle of the prisms. A little trial soon determines the proper arrangement. With regard to amounts of

## XXVII] Discussions: Section I. Analytical Chemistry

material:--the solutions which we have used are generally those of silver salts. These give precipitates which are opalescent in small quantities, and peculiarly slow about settling. The process works very well with mixtures containing anything between one half a milligram and three milligrams of silver to the liter. When the mixture becomes more concentrated, some of the substance may settle out, so that it is not safe to have more than two or three milligrams of material to the liter. But of course the instrument is only devised for very dilute suspensions. With regard to the percentage accuracy:--that varies greatly with the experience of the experimenter. At first, perhaps, a beginner at this sort of work could get no nearer than within one half a centimeter in a single setting. The sliding shades being about 10 cm. long, that would be within 5%. If he made 20 settings, even such a man would probably get within 1% of the true amount of material. With more skill, more practice in the judging of those delicate differences of shades you can perhaps estimate the individual settings within 2% and get your final results within one half of 1% of the amount present. You can thus probably get within 0.005 milligram in a liter, but this would require very careful work. Almost any one could get within 0.02 milligram, in a mixture containing a milligram of silver per liter.

Frank G. Breyer. A Proposed Standard Method of Analysis for Zinc. (Appendix, Vol. XXV, p. 7.)

۲

E. J. ERICSON: I might mention that I have for several years been adding two drops of 0.25% solution of ferric chloride to serve as an auxiliary indicator and then finished by uranium nitrate or ammonium molybdate on a plate. However, when the zinc in solution is less than 200 mgs. the bluish tinge and its disappearance is not very distinct.

I consider Waring's formic acid separation for zinc satisfactory, although cadmium is not completely removed by aluminum, but since it is always very low no serious error results.

I did not agree with the previous speaker that the gravimetric

## 26 Eighth International Congress of Applied Chemistry [VOL.

determination of zinc as phosphate is unreliable. I admit that it is a sensitive method and requires very careful manipulation.

Frank G. Breyer. A Quantitative Estimation of Small Amounts of Cadmium in the dmy way. (Appendix, Vol. XXV, p. 1.)

F. G. BREYER: I might add that anyone interested in this problem of analysis for cadmium or for separating cadmium, will find that the hydrogen sulphide precipitation is about one of the least possible for separating cadmium in the determination of arsenic. I tried a half dozen different hydrogen sulphide methods and in no case did I get the accuracy that I did with the simple electrical precipitation on a copper electrode coated with copper. In other words, cadmium can be precipitated from sulphuric acid solution up to 10% sulphuric acid, and you can get a more accurate result than with the hydrogen sulphide method, and in a great deal less time in every case. I thought I would just bring out this point in connection with good results. It is necessary to say that the determination is more accurate than three tenths of 1%. Some of the methods with hydrogen sulphide may be within one tenth of 1%. The electrolytic method gives results within two one-hundredths of 1%.

### E. Merkel. Vorschläge für einheitliche Benutzung der Atomgewichtstabellen. (Appendix, Vol. XXV, p. 91.)

٨

٨

MR. WILLS: I certainly do not wish to disagree at all with this report, but it has occurred to me that if this report is adopted, you have made a law which will be binding on all chemists for five years. I can conceive that conditions might arise that make it desirable to change possibly some one atomic weight in the meantime. It seems to me that it would be possible if the emergency arose to make such individual alterations, it would give a little elasticity to this resolution.

MR. BRINTON: The one point that struck me was the educa-

# XXVII] Discussions: Section I. Analytical Chemistry

tional standpoint of adopting this at the first of January. I can see in that the same trouble we have had in the past with the atomic weights. Once every five years, we shall have to start in at the first of the school year with the old atomic weight table, and in January come to the new one. Would it not be just as useful to have this revision take place at the first of September which would suit both the German and American Universities and start the educational year with the fixed set of atomic weights instead of having to break as would be the case, if we started on the first of January.

#### SECTION II. INORGANIC CHEMISTRY

Wilder D. Bancroft and J. M. Lohr: The Tensile Strength of Copper-Zinc Alloys, (Vol. II, p. 9.)

W. D. BANCROFT: The tensile strength of many metals varies directly with the size of the crystals. Zinc when cast has a strength of only 5,000 pounds per square inch, but if extruded through a die up to 23,000 pounds. If we chill cast metal fast, while it is solidifying we stop more or less the growth of crystals and can get metal with excellent qualities.

J. W. RICHARDS: Is it not probable that some of the wonderful results produced by adding very small amounts of one metal to another are to be accounted for by the added metal acting somewhat similarly to a colloid in a solution, and inhibiting the growth of crystals of the other metal? The qualities of some steels like those of nickel and vanadium, point to some such explanation of their exceptional qualities.

W. D. BANCROFT: It is undoubtedly the fact that many metals are prevented from crystallizing and improved in quality in just this way. Phosphor- and silicon-bronze may be cases in point, in addition to the steels mentioned by Dr. Richards.

Gregory P. Baxter and James Moore. A Revision of the Atomic Weight of Phosphorus. (Vol. II, p. 21.)

 $\langle \diamond \rangle$ 

٨

٨

Gregory P. Baxter and Charles R. Hoover. A Revision of the Atomic Weight of Iron. (Vol. II, p. 37.)

F. W. CLARKE congratulated Professor Baxter on his two communications upon atomic weights, and expressed his belief that the values for phosphorus and iron were now fairly well settled. He suggested, however, that the new iron value should be substituted in the ratios previously determined for ferrous bromide, thereby giving new and independent values for silver

## XXVII] Discussions: Section II. Inorganic Chemistry

and bromine. Their agreement with other standard determinations would give an excellent check on the accuracy of the whole group of measurements.

A. Bouchonnet. Sur L'Absorption des Matières Colorantes par les Ocres. (Vol. II, p. 53.)

M. CHABRIÉ: On m'a fait l'objection que, dans sa note sur l'absorption des couleurs organiques par les ocres M. Bouchonnet avait dit que les couleurs obtenus par lui étaient resistantes à la lumière, mais qu'il n'avait pas expliqué comment il avait verifié cette propriété. J'ai répondu que M. Bouchonnet avait teint des étoffes et des papiers blancs avec ses couleurs et qu'il avait exposé longtemps ces papiers et ces étoffes au soleil et avait constaté que leur teinte n'était presque pas affaiblie sans ces conditions.

Philip E. Browning and George O. Oberhelman. On the Effect of Free Chlorine upon the Product of Hydrolysis of Tellurous Chloride. (Vol. II, p. 59.)

۲

P. E. BROWNING stated that after the publication of the preliminary paper on the complexity of Te in 1909 with Flint, it was agreed that the completion of the problem so far as the hydrolysis of the chloride was concerned should be turned over to Flint.

Later when delays in publication caused comment, Browning suggested that he continue the investigation in part, but Flint requested that the previous agreement hold and that he assume full responsibility.

Browning promised then to leave this problem, (the attempt to show complexity by fractional hydrolysis of the tellurous chloride) entirely in Flint's hands. Browning stated further that the experimental work described in the preliminary paper was done entirely by Flint.

He further stated in reply to Dr. W. C. Morgan's communi-

cation that it seemed to him that further evidence would be necessary, in view of these conflicting results, to determine the questions of the complexity of Tellim. The statement was also made by Browning that the tellurium with which Flint worked, after purification by known methods including two distillations in hydrogen, was examined spectroscopically and found to be free from impurity.

VICTOR LENHER: While in our laboratory considerable work has been done with tellurium, the particular problems which Browning and Flint have studied have not been repeated by us consequently we cannot pass on their work. The purity of the tellurium that all in recent years have worked with can hardly be questioned as we all use the same processes of purification. In the hydrolysis of tellurium tetrachloride and of the nitrate of tellurium, the retention of chlorine in the one case and of the oxides of nitrogen in the other can be suggested. What bearing this would have on the atomic weight can only be answered by an atomic weight determination which would insure observations in which such a factor would not appear.

W. C. MORGAN: The data which I shall present to you by way of discussion of Dr. Browning's paper would have been presented as an individual paper had I expected to be present at this Congress.

During the last year at the University of California I have been working in the problem of the complexity of tellurium and have repeated the work of Flint in the hope of confirming his results. We purchased 10 pounds of tellurium from the American Smelting and Refining Company of Omaha, and had for our work many times as much material as Flint had. He states that the fractional hydrolysis of tellurium tetrachloride is one of the best methods of purifying the element and our results seem to confirm his statement. We started with more than 3 kilos of somewhat impure tellurium tetrachloride and fractionally hydrolyzed it ten times. By this method Flint claims to have reduced the atomic weight of tellurium to 124.3. Our material after treatment gave an atomic weight of 127.2.

Wishing to test the effectiveness of fractional hydrolysis as a method of purification we then submitted our ten-times-hydrolyzed material to the standard methods of ultimate purification. After precipitation with sulphur dioxide, fusing with potassium cyanide and precipitating with air twice, the atomic weight was still 127.2. Some of the material was then distilled in hydrogen; its atomic weight was unchanged by distillation.

Now, having abundant evidence of the purity of our material, we submitted it to fractional hydrolysis ten times repeated once more, but the atomic weight was unchanged from 127.2. In short, we were unable to duplicate Flint's results in any respect.

Our work was not directed toward atomic weight determination of the highest degree of accuracy, but rather to test the question of the complexity of tellurium. We chose the rapid permanganate method in analyzing our material knowing that it was sufficiently delicate to detect one tenth of the difference for which we were looking. Our results run constant at 127.2 which is 0.3 lower than the accepted atomic weight of tellurium. We did not have time to investigate the reason for this difference, but checked up our volumetric determinations by the gravimetric basic nitrate method which gave us 127.5 as a result.

Flint's directions are to dissolve the dioxide "in the smallest possible amount of hydrochloric acid" and then dilute with water. In our results when we used "the smallest possible amount" of acid, we invariably precipitated a larger fraction of the material than Flint did, thus indicating that his directions are inexact in certain particulars. The same fact has recently been pointed out by Pellini who was also unable to produce any reduction of the atomic weight of tellurium by Flint's method.

## Edwy Godwin Clayton. Phosphorus and its Relation to the Manufacture of Matches. (Vol. II, p. 75.)

۲

JEROME ALEXANDER: I think it should appear on the records of this Congress that last year The Diamond Match Company, one of the largest manufacturers of matches in the world, voluntarily surrendered for cancellation its American patents for the use of the non-poisonous sesquisulphide of phosphorus in the manufacture of matches, and at the same time, gave out a prac-

tical formula for using it, so that this material is now available to all of its competitors.

Such public-spirited action on behalf of a large corporation in thus deliberately relinquishing valuable patents, is particularly praiseworthy, and shows that although corporations are supposed to be soulless, here is a corporation with a soul and officers who consider the public welfare as well as dividends.

It was this action of The Diamond Match Company that made possible the passage by the United States Congress of the Hughes-Esch bill during March, 1912, which lays such a prohibitive tax on the manufacture of poisonous white phosphorus matches, that none of them will be made in this country after July 1st, 1913.

Elwood Haynes. The Alloys of Cobalt with Chromium and other Metals. (Vol. II, p. 119.)

٨

C. L. PARSONS: High speed tool steel is estimated to be saving to the world \$100,000,000 per year. If these alloys are an improvement on high-speed tool steel, their industrial value is very great.

J. W. RICHARDS: Are the alloys shown heat-treated in any way, or can they be improved by heat treatment? What do they cost?

E. HAYNES: We are selling the tool-steel alloy at \$5 per pound. These alloys have not been heat-treated, but we are experimenting in that line to see if they can be thus improved. They are not attacked by perspiration or by sea-water. I wrapped a piece in paper soaked with sea-water, and it was unaffected.

William Wilke. Combination of the Contract Process with the Ordinary Lead Chamber or Power Systems; an Improvement in the Manufacture of Sulphuric Acid. (Vol. II, p. 249.)

Henry Bowen asked if the plant referred to by Mr. Wilke in his paper was that of the Contact Process Company at Buffalo, N. Y.

## XXVII] Discussions: Section II. Inorganic Chemistry

W. WILKE: As to the question whether my paper refers to a particular local installation or plant I would say No—the first application of the principle I made in Buffalo in an experimental crude way, but it proved all that I claim for it, since then I have greatly improved the construction in detail and the installation in volume II, page 250, shows the design which I now use in general.

MR. BOWEN then said that some eight or nine years ago Mr. Wilke installed a Mannheim Contact Process for the Schoellkopf, Hartford and Hanna Company at Buffalo and subsequently built a chamber plant, in connection with which an iron oxide contact shaft was installed. This entire acid plant was later acquired by the Contact Process Company.

The iron oxide contact shaft, as originally installed in the chamber plant and operated by Mr. Wilke until his connection with the company terminated, did not produce results. It was finally condemned as a complete failure, torn out and replaced by another iron oxide shaft embodying material changes designed by the present superintendent, Dr. von Rucker, which were suggested by the previous experience.

It should be borne in mind that the operating conditions in a chamber plant are quite different from those in a contact plant. Because of this fact the results obtained in the iron oxide shaft in the complete contact process are not obtainable in a similar shaft used in connection with chambers. While some benefit was derived from the new shaft, we have thus far failed to obtain such results as Mr. Wilke mentions in his paper. According to our experience the capacity of the chamber plant was not increased 30%; the conversion of SO<sub>2</sub> into SO<sub>3</sub> varies considerably and has not averaged 30%; the elimination of arsenic contained in the burner gases is between 80% and 85%; the saving of nitre has not amounted to 30% of that consumed in the ordinary plant.

Regarding Mr. Wilke's statement that warm or cold weather makes no difference in the conversion, it is our experience (confirmed by Dr. von Rucker) that the conversion is much greater in winter than in summer.

A careful perusal of the paper clearly shows that the installation

<sup>3</sup> 

referred to was the first of its kind undertaken, and inasmuch as it was at the plant in Buffalo (although the illustration given is not of this Buffalo plant), it is quite plain that this is the plant referred to, notwithstanding Mr. Wilke's statement to the contrary. He himself says in the closing paragraph of his paper "since constructing the above described plant, the iron oxide contact shaft has been introduced in other existing chamber plants, etc." The paper as printed states that "thirty-six lump burners were installed, each able to handle from 900 to 1200 pounds ore daily, and four standard Herreshoff fines burners." As a matter of fact, O'Brien not Herreshoff fines burners were installed in the Buffalo plant.

## J. R. Withrow. The Effect of Lime-Sulphur Spray Manufacture on the Eye-sight. (Vol. II, p. 253.)

۲

٨

J. R. WITHROW: In reply to the question as to whether the author has observed any effect of fine or powdered sulphur on the eyes, he would reply no. He has heard workmen speak of irritation of the eyes due to this cause, but probably owing to the fact that we loaded the cars of sulphur in sacks the trouble did not become serious enough to attract personal attention. It would be interesting to know from any how have experienced the powdered sulphur difficulty whether it is one resulting from the sulphur as a dust or whether it is due to the acids probably present on the particles. The action of "lime-sulphur" is probably different. It appears to be essentially corrosive. One chemist has informed me that he had lost in large part the coating over the eye on two occasions. The trouble with "lime-sulphur" comes from the vapors arising during boiling. Alfred H. Cowles. Alumina, Hydrochloric Acid, Caustic Alkalies and a White Hydraulic Cement by a New Process from Salt, Clay and Lime. (Appendix, Vol. XXV, p.119.)

A MEMBER: Has any attempt been made to catch and utilize the CO?

A. H. COWLES: No. This may eventually be done in the same manner as CO is utilized from blast furnaces. To remove a small amount of HCl from it, it should be passed through a proper scrubber.

R. C. PURDY: What use has been made of the white cement. Has the same been made?

A. H. COWLES: White cement has high value for use in decorative work. No; we have only made the di-calcium silicate. Adding one molecular weight of CaO to the same we know that we fall within the formula discovered by Dr. Arthur Newbery for the strongest hydraulic cement, which formula permits up to several per cent. of  $Al_2O_3$  to be present in tri-calcium silicate, and if iron oxide be absent this produces a strong white cement.

A. S. CUSHMAN: Are the reactions theories or have they been worked out on a large scale? Why does not the NaCl distill off? At what temperature does the final reaction take place?

A. H. COWLES: Answering the first question the reactions have been worked out on a large experimental scale during three years work previous to our starting to erect our plant at Sewaren, N. J. I expected to have converted briquetts from a channel furnace one hundred and eighty feet long here this morning, the first from the new plant. Yesterday morning an engine cylinder went to pieces that operated our generator which furnished current to the motors driving the blowers connected with the furnace. This stopped the furnace with the bricks just approaching the hottest zone in the furnace. Acid was condensing in our condensing system at this time.

The NaCl is decomposed by superheated vapor of water before it has a chance to distill off. Some will vaporize in the hot zone of the furnace and be carried over the loaded cars. For about ninety feet the hollow briquetts act as a scrubber and carry the sublimed salt back towards the hottest zone of the furnace. Using too high a percentage of NaCl in the briquetts might clog the furnace for it would be capable of forming more Na<sub>2</sub>O than the clay would be able to absorb. The limit above that required to place 33% of Na<sub>2</sub>O in the product will probably be higher with our large furnace than with the small furnaces that we formerly employed.

Answering the third question. The reaction begins lower than the vaporizing temperature of salt. Day before yesterday the hottest part of our large furnace was  $1450^{\circ}$ F., and acid fumes so strong were passing through our condensing pipes that it was with difficulty that U pipes were connected between one set of upright acid ware pipes to permit the fumes to pass through the other sets and weak acid was drawn from the condensers. After we pass the vaporizing temperature of NaC1, about  $1700^{\circ}$ F., the reaction goes on very rapidly. The higher the A1<sub>2</sub>O<sub>3</sub> in the clay the higher can the temperature be carried without melting the briquetts.

L. P. BROWN: What purity of clay is required?

A. H. COWLES: The purer the better, as the presence of ironoxide leads to a larger amount of iron chloride and loss of pure acid. If the iron chloride were used for leaching ores or otherwise, then its presence would not be so detrimental. The moraine clays contain an undesirable amount of iron oxide and are most too low in alumina for best results.

H. W. CHARLTON: Would it work in an electric furnace with steam passed through a hole in the electrode?

A. H. COWLES: It would not work economically. Neither clay, silica nor alumina will be fluxed by boiling salt. Vapor of HCl would come out of such a furnace and could be detected but it would be associated with sublimed salt and solid matter without complete transformation of the latter.

G. W. COGGESHALL: In the first reaction in Mr. Cowles process in which NaCl acts upon clay, the general clay formula of  $Al_2O_3$ ,  $2SiO_2$  is given and Mr. Cowles says that feldspar may also be thus acted upon by this process. As feldspar contains  $6SiO_2$  to each  $Al_2O_3$ , would not the formation of the "sodium, silico, aluminate," as shown by the written reaction, be disturbed by the large proportion of silica. I would like to ask if Mr. Cowles has carried on this reaction, using feldspar in place of clay, and if the process with feldspar, works out on the lines given by these reactions.

#### SECTION IIIA. METALLURGY AND MINING.

J. O. Handy. Sampling and Assaying Silver Ores Containing Cobalt, Nickel and Arsenic. (Vol. III, p. 89.)

L. M. LIDDLE: It is open to question whether Mr. Handy's last remark is universally true. A correct method will give correct results, but the reaction may not be reversible. Concordant results may only indicate a consistent method of doing things inaccurately.

Many assayers have difficulty with the "wet-and-fire assay," mentioned by Mr. Handy. This seems to be due to a precipitate of arsenious oxide on the beaker which cannot be wiped off, and which occludes silver chloride. The difficulty is avoided by rinsing the beaker with caustic alkali, acidifying with nitric acid, adding one drop HCl, and adding the precipitate formed to the regular assay.

Personally, I advocate machine sampling rather than hand, both for cheapness and accuracy. As Mandy says: Hand sampling is good sampling only as it becomes mechanical, hence good machine sampling is preferable to hand. Machine sampling is being practiced on the Cobalt ores with good results both in the United States and Canada, where the purely mechanical Campbell-Deyell mill seems to represent the best practice. The high-grade ores, however, we shall probably continue sampling by hand, as we cannot risk salting a big sample with such abnormally rich material.

O. Simmersbach. Koksöfen Gas zur Beheizung von Siemens-Martinöfen. (Appendix, Vol. XXV, p. 745.)

٨

۲

٨

W. M. CRAFTS: Is any change necessary, when using cokeoven gas, in the height of the roof or the angle of incidence of the ports?

K. QUASEBART: Der Simmersbachsche Vortrag enthält die interessante Feststellung, dass das Ofengewölbe durch Koksofengas nicht stärker angegriffen worden ist, als durch Generatorgas. Da lange Zeit in Stahlwerkskreisen die Ansicht vertreten war, dass ein Gas mit mehr als 12% H<sub>2</sub> schädlich für die Ofenzustellung sei, so wäre es wichtig zu erfahren, ob die Haltbarkeit der Ofenköpfe durch das Koksofengas nicht beeinträchtigt worden ist.

W. N. CRAFTS: In 1900 we tried coke-oven gas in a 20-ton acid-lined open-hearth furnace at Cleveland, Ohio. The furnace was built to work on producer gas. We found the coke-oven gas to hug the roof, and had difficulty in obtaining the necessary heat. We concluded that the roof should be made lower, in order to hold the flame down on the bath.

J. W. RICHARDS: The problem appears very similar to that of using natural gas. It does not pay to pre-heat the gas, because you lose as much heat by diminished calorific power of the gas as you gain by its sensible heat when hot. Our open-hearth furnaces at Pittsburgh are run with natural gas, the air only being pre-heated, and such practise should be at once applicable to using coke-oven gas in similar furnaces.

O. SIMMERSBACH: Es bedarf im allgemeinen keiner besonderen Aenderungen hinsichtlich des Neigungswinkels und der Dimensionen der Gas und Luftzuführungen, nur müssen die Calorienzahlen des Gases und der Luftbedarf berücksichtigt werden. Dies war auch der Grund dafür, dass im Anfang die Ofenköpfe und das Gewölbe bei Verwendung von Koksofengas mehr oder weniger angegriffen wurden, weil man eben die ersten Versuche mit solchen Martinöfen anstellte, die für Generatorgasbeheizung gebaut waren; zudem mussten die Arbeiter erst sich an die neue Betriebsweise gewöhnen. Auf die Resultate der Koksofengasbeheizung der erwähnten sauren 20 t Ofens kann ich leider nicht eingehen, da mir die Details hinsichtlich Construction und Betrieb fehlen. Im Uebrigen hat Professor Richards vollkommen Recht, wenn er sagt, dass die Beheizung der Martinöfen mit Koksofengas der mit Naturgas sehr ähnelt. In Deutschland, speciell in Rheinland-Westfalen werden jetzt auf den grossen Hüttenwerken die Martinöfen zumeist mit Koksofengas und Hochofengasbeheizung eingerichtet, man rechnet bei den dortigen 100 t Oefen mit c. 31 Mk prot Stahl Ersparnis.

#### SECTION IIIB. EXPLOSIVES

Charles P. Beistle. The Determination of Exudation of Nitroglycerin from Dynamite. (Vol. IV, p. 7.)

C. G. STORM: The test for exudation employed by the Bureau of Mines is a modification of the test originally used by Mr. In this modification as worked out by Dr. W. O. Beistle. Snelling, the radius along which the centrifugal force acts is constant; i.e., the dynamite, instead of resting upon a perforated disc supported on a compressible wad of absorbent cotton, is placed in Gooch crucibles hung in rigid metal stirrups. Below the Gooch crucibles are hung small porcelain crucibles containing cotton for holding the nitroglycerin forced out of the dynamite. The crucibles, containing the dynamite samples are weighted before and after rotating for 5 minutes at 600 r.p.m., the loss in weight being the exuded nitroglycerin. The speed and radius being constant, the centrifugal force is necessarily constant. It has been found necessary to maintain uniform conditions of temperature in order that results may be comparable. Under such conditions the method gives good results. This test is applied to all dynamite manufactured for use on the Panama Canal.

H. Brunswig. Neue Initialzündung für Sprengstoffe. (Vol. IV, p. 19.)

C. G. STORM: One of the most frequent causes of poor results in the use of blasting explosives, especially in this country, is the use of a detonator of insufficient strength. In such cases the explosive does not attain its maximum rate of detonation and frequently detonates only partially, in either event failing to perform the full amount of work of which it is capable. In such operations as quarrying, where relatively insensitive explosives are often used in very large charges, it has been my opinion that much greater efficiency and economy might result from the use of detonating fuse as an imitator of detonation, and it certainly seems reasonable to expect that the method described by Dr. Brunswig should give a still higher efficiency.

ARTHUR M. COMEY stated that the same idea that had been suggested at the Eastern laboratory of the du Pont Company some time ago, and experiments had been carried out along the same lines as those mentioned by Dr. Brunswig without, however, obtaining any marked increase in velocity of detonation or strength as shown by any test. It was difficult to see what caused this difference, but it might be due to the fact that the regular Dautriche fuse was used at the Eastern laboratory, which has a velocity of detonation of 5,000 meters per second, whereas Dr. Brunswig used a fuse of smaller diameter, which he states has a higher velocity, *i.e.*, 7,000 meters per second.

Thomas M. Chatard. The Misuse of Explosives. (Vol. IV, p. 23.)

CHARLES L. REESE: It hardly seems to me that the proposition made by Dr. Chatard in his paper requires any action by this Congress. Many foreign countries are overridden with such laws as are proposed by Dr. Chartard, some more and some less stringent.

In Germany the laws are of such nature as materially to hamper the economic production of high explosives and also increase their cost to the consumer and in spite of these very stringent laws as has been brought out by a previous speaker, outrages have not been prevented since few criminals are restrained by fear of comparatively light punishment incident to the detection of illegal possession.

Although I am not opposed to proper laws restricting the possession of high explosives, I do not believe it is the proper function of the Congress to formulate laws to be presented to the various governments, in fact, I believe it is against the rules governing this Congress.

### 42 Eighth International Congress of Applied Chemistry [VOL.

James Moir. A Plea for Improvement in the Methods of Chemical Testing of Mining Explosives. (Vol. IV, p. 79.)

C. G. STORM: My experience with the potassium-iodidestarch heat-test confirms many of the objections of Dr. Moir to this method of testing the stability of most mining explosives. In the case of nitrocellulose and nitroglycerine, I consider the heat-test of great value in the factory as a test for proper purification, but owing to the fact that its results are affected in one way or another by many of the constituents of smokeless powders and mining explosives, its value as an indication of the real stability of such explosives is doubtful. It is important to note. however, that an explosive showing a poor heat-test should at least be regarded with suspicion. In regard to the effect of sunlight on the stability of explosives, I have never observed an instance where "one minute's exposure of an explosive to the sun will ruin its heat-test," and have personally noted cases where several days exposure had no material effect on nitroglycerine explosives.

I have never been able to discover any relation whatever between variations in the heat-test period and atmospheric pressure, and have noted opposite effects of the addition of woodpulp to nitroglycerine, *i. e.*, a decrease rather than an increase in the time of test.

ARTHUR M. COMEY raised the question as to the advisability of considering improvements in the Abel test as applied to nitroglycerine and nitroglycerine explosives, as he did not consider this test of any value whatsoever in determining the stability of such substances, citing experiments with nitroglycerine of low heat test (one or two minutes) which, when exposed to the direct rays of the sun for several months, showed no visible decomposition, while a similar sample of nitroglycerine having a heat test of 40 to 60 minutes was decomposed completely in a few days. Further in a test resembling that proposed in the report of the International Committee on Test for Stability of Explosives, in which the explosive was exposed to a temperature of 60°C in a tightly closed tube containing a piece of litmus ٨

paper moistened with glycerine suspended over the explosive, nitroglycerine and nitroglycerine explosives caused reddening of the litmus after varying lengths of time, which showed no relation to the heat test.

Arthur Lee Robinson. Detonator Troubles Experienced in the Construction of the Isthmian Canal. (Vol. IV, p. 85.)

WALTER O. SNELLING: The development of the waterproof detonator came about in a most interesting way. At first the difficulties on the Panama Canal were attributed to faulty insulation of the wires, but when gutta-percha covered wires, with insulation tested to over 1,000,000 ohms were tried, and found also to fail, the fault was traced to the detonator itself. At the suggestion of Dr. Charles E. Munroe I had a pipe 30 feet long arranged vertically outside one of the windows of the laboratory, and had it filled nearly to the top with salt water. I placed detonators of different kinds in the pipe over night, and after ten or twelve hours immersion practically all types except the very expensive gutta-percha covered detonators were found to be wet inside. It then occurred to me to mix fulminate with paraffine or vaseline, so as to make a mixture that would repel water. I tried it, and found that I could only explode detonators containing such treated fulminate by means of a small amount of ordinary dry fulminate. To keep the priming charge dry was, of course, as difficult as protecting the whole mass, so the plan was clearly a failure.

I then tried the effect of different viscous, water-resisting materials placed just over the sulphur plug, reasoning that under the conditions existing in the detonator one fluid could not by hydraulic pressure penetrate another fluid. By such use of simple plugs of viscous water-resisting materials I made a number of detonators which fired after immersion for 48 hours in 30 feet of water. I then made systematic tests of the different materials suitable for the purpose of forming the plug, making small balls of each material, and laying them upon strips

43

### 44 Eighth International Congress of Applied Chemistry [VOL.

of blotting paper over night. Some materials which were suitable as far as viscosity and water-resisting properties are concerned, failed because of being drawn by capillary attraction into the fulminate. With the blotting paper test, however, by simply noting the materials which were most fluid as shown by their flattening out on the paper, and yet which did not "grease through," it was a comparatively simple matter to find the types of asphalt and petroleum residue best adapted for the purpose.

At the present time more than a million of these detonators are used each year on the work of the Panama Canal alone, and the failure of a detonator, even under rather extreme conditions of immersion, is unusual.

 $\langle \mathbf{A} \rangle$ 

C. G. Storm. The Effect of Nitrotoluenes on the Determination of Nitroglycerine by Means of the Nitrometer. (Vol. IV, p. 117.)

J. MOIR: I do not wish to discuss the paper, as I agree with the results given in it, from experiments I did last year. I wish to ask a question on a cognate subject, namely,—what is the "liquid trinitrotoluene" of commerce? Has any quantitative analysis of it ever been published. I have only been able to analyse it *qualitatively*, as a mixture of 2-4-6-trinitrotoluene with two of the dinitrotoluenes.

C. G. STORM: To confirm this and that from nitrogen content it must contain somewhere about 80% of trinitrotoluenes and that it is most remarkable that it should be a liquid. The amount of mononitrotoluene is under 1%.

J. MOIR: I got the same kind of figures, but am still puzzled because the amount of solid trinitrotoluene which can be extracted from it by freezing (or by means of its compound with alphanaphthylamine) is much under 80%. There must be another isomer of trinitrotoluene, one not in the literature.

A. M. COMEY: There is undoubtedly an isomer of TNT other than the 2-4-6-variety, though it has not been isolated.

### xxvII] Discussions: Section IIIb. Explosives

J. Taffanel and H. Dautriche. Recherches de la Station d'essais de Liévin sur les Explosifs de Surete pour Mines Grisonteuses et Poussiéreuses. (Vol. IV, p. 127.)

M. V. WATTEYNE: La très intéressante communication de M. Taffanel met en lumière, et commente, divers faits relatifs aux différences, dans la manière de comporter des explosifs vis-à-vis du grisou et des poussières, suivant que les charges sont tirées dans telles ou telles conditions.

J'ajouterai, à l'appui de ce qu'il a dit, que nous avons aussi, au Siège d'expériences de Frameries, constaté ces différences; nous en avons même déjà fait l'objet de communications sommaires aux précédents congrès, de Rome et de Londres.

Pour éliminer, dans la mesure du possible, les causes d'erreur, ou plutôt d'écarts, résultant des conditions de l'expérience, nous avons entrepris depuis peu, près de Frameries, le creusement d'une galerie dans les roches mêmes du terrain houiller. De cette façon, nous creuserons, chargerons et tirerons les mines dans les conditions de la pratique.

Nos essais ne sont pas encore assez avancés pour que je puisse en donner des résultas. Ce sera pour un prochain congrès.

Je dirai seulement, dès à présent, que nous avons constaté une énorme différence entre les mines faisant canon (blown out shot) et les mines qui "travaillent."

Lors du voyage que j'ai fait dans les mines américaines, il y a 4 ans, j'ai constaté que les exploitants américains se préoccupaient beaucoup d'empêcher les "*Blown out*" ou "Windy shots." Ils ont raison: ce ne sont pas les seules mines dangereuses, mais ce sont, de beaucoup les plus dangereuses.

En attendant que toutes les incertitudes soinent levées, (le seront-elles jamais?) quant à la sûreté des explosifs, nous nous trouvons bien en Belgique de l'emploi des explosifs dont nous avons déterminé les charges limites vis-à-vis du grisou et des poussières (explosifs S. G. P.). Un fait encourageant, c'est que depuis les quelques années que cet emploi s'est répandu, nous n'avons plus en Belgique une seule explosion. Et je ne pense pas qu'il y en ait eu non plus dans les autres pays, avec ces explosif employés au-dessous de la charge limite.

Et si l'on emploie, en outre, le "bourrage extérieur" en poussières incombustibles, la sécurité du tir des mines sera encore augmentée.

Je rappellerai que le "bourrage extérieur" consiste simplement dans l'accumulation de quelques kilos de poussières incombustibles devant le trou de mine.

M. l'ingénieur Principal Lemaire et moi avons publie un premier rapport sur les effets de ce bourrage. Nos expériences continuent. Jusqu'ici, *aucune explosion* n'a eu lieu, même avec de fortes charges d'explosifs dangereux, lorsque ces poussières sont employées dans les conditions que nous avons indiquées.

Il y a donc là un nouveau moyen, très commode et très économique, de renforcer la sécurité du tir des mines.

M. TAFFANEL ajoute au texte de sa communication la remarque suivante.

La compression du mélange d'air et grison a lieu par onde de choc, et l'élévation de température t est liée à l'accroissement de pression p par la formule.

$$\frac{\mathrm{t}}{\mathrm{To}} = \frac{\gamma - 1\,\mathrm{p}\,1 + \frac{1}{2}\frac{\mathrm{P}}{\mathrm{Po}}}{\gamma\,\mathrm{Po}\,1 + \frac{\gamma + 1}{2\,\gamma}\frac{\mathrm{P}}{\mathrm{Po}}}$$

dans laquelle  $\gamma$  désigne le rapport des chaleurs spécifiques Po la pression initiale et To la température initiale, en degrés absolus.

La detente ramène ensuite le mélange grisouteux à la pression initiale Po; mais la relation entre les variations de température et de pression n'est pas la même; c'est celle des ondes continues et l'one a la formule:

$$\frac{\mathrm{To}^{1}}{\mathrm{To}+\mathrm{t}} = \left(\frac{\mathrm{Po}}{\mathrm{Po}+\mathrm{p}}\right)\frac{\gamma-1}{\gamma}$$

où To désigne la température finale, à la fin de la détente. To est supérieur à To.

La température To+t atteinte à l'instant de la compression peut être très élevée, mais elle ne dure, comme la pression, qu'on temps extrèmement court et il es possible que la propriété bien connue due retard à l'inflammation; mais il pourra arriver que la température finale après détente complète, soit supérieure à ٨

la température d'inflammation du grison; il suffit pour cela que l'onde de choc ait réalisé une pression instantanée superiéure à une cinquantaine d'atmosphéres. En ce cas, independamment de tout mélange avec les gaz de la détonation, et à la condition qu'il n'y ait pas de refroidissement notable par les parous, l'inflammation a lieu nécessairement, avec un retard plus ou moins prononcé, suivant la valeur de la pression instantanée réalisée par l'onde de choc.

H. C. Weber. On a Modified Form of Stability Test. (Vol. IV, p. 147.)

W. O. SNELLING: The defects of the Abel test are so clearly recognized that any new method that promises better results is of great interest to us. I am at present experimenting with such a method, based upon principles different from any of the former stability tests.

The new test depends upon the electrical conductivity of a drop of distilled water placed in a tube with the explosive under examination. As is well known, the electrical resistance of a drop of pure water is practically infinite, but the presence in the water of any material which undergoes electrolytic dissociation in solution, has the effect of allowing an electric current to pass.

In my present experiments I am making use of a tiny piece of ground glass to hold the drop of water, and the electrical resistance is measured at intervals of one minute. Even at low temperatures the decomposition of unstable explosives is readily shown, and the record of increasing decomposition at elevated temperatures is beautifully obtained by this method.

A preliminary note on this new test will be published in the near future.

### 48 Eighth International Congress of Applied Chemistry [VOL.

Commission Internationale pour L-Étude de L'Unification des Methodes D'Épreuves sur la Stabilité des Explosifs-Rapport Final. (Appendix, Vol. XXV, p. 255.)

EBERHARD KAYSER: Die Bleiblockprobe bleibt immer noch die zuverlaessigste und einfachste Probe zur Pruefung der Leistungsfachigkeit von Sprengstoffen, weil sie der praktischen Arbeitsleistung der Sprengstoffe am naechsten kommt, wachrend den anderen Pruefungsmethoden in dieser Beziehung erhebliche Maengel anhaften. Falls es richtig ist, dass die im Trauzlzylinder unterzubringenden Sprengstoffmengen zu gering sind, um die maximale Detonationsgeschwindigkeit und vollkommene Zersetzung zu erreichen, koennte man ja die Dimensionen des Bleiblockes nach international festzulegenden Vereinbarungen vergroessern.

Dass die Bleiblockprobe aber auch unter den jetzigen Verhaeltnissen Ergebnisse von genuegender Genauigkeit liefert, beweisst der Umstand, das theoretisch berechnete Maximum der Arbeitsleistung eines Sprengstoffgemisches auch mit der Bleiblockprobe nachzuweisen. Es empfiehlt sich, einen Vergleichssprengstoff, wie reines Trinitrotolnol zu verwenden, und die Ausbauchung des zu untersuchenden Sprengstoffes in Prozenten desjenigen des Vergleichssprengstoffes auszudruecken. Einen so grossen Einfluss der Korngroesse des Ammonium Nitrates in Ammonsalpetersprengsstoffes auf die Bleiblockausbauchung habe ich nicht gefunden.

#### SECTION IIIC. SILICATE INDUSTRIES

A. S. Cushman and G. W. Coggeshall. The Production of Available Potash from Natural Silicates. (Vol. V, p. 33.)

A. S. CUSHMAN: I wish to point out that this important subject may be considered in three separate aspects: scientific, commercial and political. Now, I have been working over these problems studying them and dreaming about them for a number of years. It is, of course, quite possible that, however successful we may consider ourselves to have been in the scientific aspect. that our product will not come into general use owing to purely commercial conditions. If, however, some of our friends on the other side of the Atlantic Ocean should fall into very serious differences of opinion, it is not at all impossible that the potash fertilizer requirements of our agricultural country would be seriously interfered with. We, on this side of the Atlantic, cannot view without some anxiety even a remote danger of interference with the successful growing of our crops. From this point of view, at least, it is satisfactory to be able to report that at least we have a process which has already been worked out on the large mill scale of operations.

As far as costs are concerned, we feel certain that this material can be produced in very large quantities for a price not to exceed that at which Portland cement is now manufactured in rotary kilns, so that in summing up my remarks, I merely wish to emphatically reiterate my belief that until some better process is evolved, we shall continue to hope that our method insures an American supply of water-soluble potash in a perfectly practical form, for use in American agriculture which may be useful under any conditions, but which would certainly be valuable in case any political upheaval should for any extended period of time interfere with the supplies of necessary potash.

G. W. COGGESHALL: In discussion, replying to questions as to costs and comparative values. In a process for making potash

in silicate rocks available for fertilizing purposes, we concluded that to be a commercial success the operations must be conducted on a large scale, by a continuous process, in a dry way, avoiding both volatilization of the potash and fusion of the silicates. All the operations in this process are those now commonly used in making Portland cement except the "clumping" process and our apparatus permits this operation to be done at an exceedingly low charge per ton. Portland cement is now made at very low cost. This rock potash fertilizer can be made by this process at a cost which may perhaps bring it into large use in this country. Several hundred tons of the product are now undergoing field trials at Experiment Stations and by large growers of fruits, vegetables, etc.

And I wish to say that it seems to me that the question as to agricultural value and the question as to its commercial possibilities must be decided by the results of field trials now going on and by the call for the product as a result of these trials and these are not questions which can be decided by us in debate. The product contains  $4\frac{1}{2}$ % water-soluble potash and from 12 to 16% lime and will probably be used in the same way wood ashes is now used.

#### SECTION IV. ORGANIC CHEMISTRY

F. W. Bushong. Isomeric Naphthenic Acids. (Vol.VI, p. 57.)

H. T. BUCHERER spoke of his synthesis of hexahydrobenzoic acid in the laboratory of Wislicenus and inquired as to its relation to the naphthenic acids. This point is fully treated in the complete paper as printed.

G. KOMPPA mentioned the necessity of steam distillation for the separation of the naphthenes from the soaps of the naphthenic acids. (This method was used by F. W. Bushong.)

S. F. ACREE asked if there is much difference in the optical activity in the methyl and ethyl esters.

F. W. BUSHONG replied that they run parallel, and that he can locate a maximum and a minimum, as shown in the paper.

٨

۲

۲

F. D. Dodge. The Oxidation Assay of Essential Oils. (Vol. VI, p. 86.)

٨

٨

M. T. BOGERT asked how delicate was the method and what percentage petroleum can be detected in the adulterated turpentine.

F. D. DODGE answered that 2% is readily detected. He had not tried the method on smaller amounts.

٨

H. W. Doughty and F. R. Elder. The Reaction Between Selenic Acid and Toluene. (Vol. VI, p. 93.)

In the discussion H. W. DOUGHTY brought out the fact that the seleninic acid irritates the skin, due probably to reduction and separation of metallic selenium. P. A. Kober, J. T. Marshall, and E. N. Rosenfeld. Phenolphthalein and Its Colorless Salts. Preparation of Monobasic Phenolphthalates. (Vol. VI, p. 157.)

M. GOMBERG said that the subject of color formation is clearer by assuming that there are two tendencies in the molecule, (1) to tautomerize, and (2) because of the carboxyl, to form a lactone. These two tendencies counteract each other. He also spoke on the ionization theory, saying that ionization does not produce the color, but that ionization follows the production of the color.

S. P. Mulliken and C. L. Gabriel. A study of the Lassaigné Reaction. (Vol. VI, p. 208.)

 $\langle \rangle$ 

 $\langle \diamond \rangle$ 

۲

٨

M. O. FORSTER asked if the iron tube had enough advantages that the clean test-tube should be superseded, and also if it enables one to recognize nitrogen in basic compounds, dyes, etc., that the ordinary method does not show.

C. L. GABRIEL replied that sodium often attacked the glass and that the glass tubes crack. It is better to vaporize the sodium and this can be done best in an iron tube. In the method outlined they were unable to detect nitrogen in diazo-compounds, but azo-compounds gave a positive test.

W. H. Warren and M. R. Grose. The Possibility of Reducing the Cost of Malic Acid. (Vol. VI, p. 265.)

M. T. BOGERT: Is there any extensive commercial use of malic acid?

E. MALLINCKRODT, JR. Not at the present time.

L. H. FRIEDBURG: What is the total annual amount?

W. H. WARREN: According to the available statistics 500,000 pounds of baking powder could be made annually from the malic acid.

M. GOMBERG: Is it optically active? ANSWER: Yes.

MR. PHELPS: Is it the laevo-form?

٨

۲

ANSWER. Laevo and dextro, depending on the concentration. MR. PHELPS: It might be used in pharmaceutical preparations. d-Tartaric acid is not readily oxidized in the body; 40-50% being eliminated as a salt; whereas malic and succinic acids are readily oxidized.

W. H. WARREN added that he believed the malic acid is in some way responsible for the formation of the sugar in the tree.

٨

J. Dupont and L. Labaune. Observationes sur quelques dérivés hydrosulfonés de composés non saturés, constituants des huiles essentielles. (Appendix, Vol. XXV, p. 357.)

F. D. DODGE: The combination of citral and sodium hydrogen sulphite was first noticed by myself and published in the *Journal* of the American Chemical Society, and this was later used by Tiemann and adopted as a method of determination of citral in essential oils. We found in citronella oils that it was almost impossible to get good results and we had to give up the method. This article clears up the difficulty. Further, this paper will clear up many discrepancies and phenomena that have been observed before.

G. B. Frankforter and H. H. Brown. The Chemistry of Wood. The Resins of the Douglas Fir. (Appendix, Vol. XXV, p. 359.)

MR. KREMERS mentioned the importance of proper technic and said that distillation under diminished pressure of an amorphous resinous mass often yields a crystalline product. Optically inactive derivatives of terpenes crystallize better than the active forms. The inactive resin acids are better crystalline than the active. Fractional precipitation may give no crystalline product when carried out in the ordinary way. Alcoholic hydrochloric acid often gives good crystals.

G. B. Frankforter and W. Kritchevsky. Contribution to our knowledge of the Condensation Reaction by Means of Anhydrous Aluminum Chloride. The Action of Chloral and Aluminum Chloride on the Phenol Ethers. (Appendix, Vol. XXV, p. 361.)

M. GOMBERG said that aluminum chloride has a tendency to split off carboxy and methoxy groups.

G. B. FRANKFORTER replied that it was apparently a question of temperature. All his work was done at zero degrees.

W. H. Hunter and J. D. Edwards. An Improved Apparatus for the Determination of Carboxyl Groups in Organic Acids. (Appendix, Vol. XXV, p. 377.)

M. T. BOGERT: How long does it take to carry through the test?

ANSWER: Three-quarters of an hour after the apparatus is set up: An hour and a half in all.

W. A. Noves. Does this method have any advantage over direct titration?

ANSWER: No advantages.

٨

B. Rassow. Ueber Rizinusoelsaeure. (Appendix, Vol. XXV, p. 421.)

۲

S. E. WISE: Dr. Rassow's research explains a result which I noted in the case of the analysis of an insulating compound which had been produced at a fairly high temperature and which contained castor oil as one of its component parts. By fusing the compound with potassium hydroxide, I obtained the characteristic odor-test for a secondary octyl alcohol  $C_6H_{13}$  (CH<sub>3</sub>) CHOH, (which together with the potassium salt of sebacic acid is formed when potassium hydroxide reacts with ricinoleic acid). I was much surprised to find that the ricinoleic acid had apparently not been changed by the heat to which the compound had been

subjected in the process of manufacture. As I understand it, Dr. Rassow has shown that only higher polymers of ricinoleic acid are formed when the acid is subjected to reasonable heat and that these may again be converted to ricinoleic acid. This probably accounts for the fact that ricinoleic acid could readily be detected in the mixture.

#### ٢

E. E. Reid. Studies in Esterification. The Esterification of Amides and Thioamides and the Formation of Dithio-Esters. (Appendix, Vol. XXV, p. 423.)

E. BIILMANN, speaking of the reaction in which the thio-ester had not been isolated,

$$C_6H_5 - CS - NH_2 + HOC_2H_5 \rightleftharpoons C_6H_5C \bigvee_{OC_2H_5}^S + NH_3$$

pointed out that the following reactions go quantitatively to the right within one hour. He said in the comparison of compounds where nitrogen was replaced by oxygen, that the cases were not identical, but might be analogous:

 $C_{2}H_{5}OCS - NH_{2} + ICH_{3} \rightarrow O = C \left\langle \begin{array}{c} SCH_{3} \\ NH_{2} \end{array} + C_{2}H_{5}I \right\rangle$ 

Similarly with IC<sub>2</sub>H<sub>5</sub>

 $C_2H_5OC \cdot S \cdot S \cdot CH_2COOH$ 

 $+\mathrm{ICH}_{2}\mathrm{CH}_{2}\mathrm{COOH} \rightarrow \mathrm{O} = \mathrm{C} \underbrace{\mathsf{SCH}_{2}\mathrm{COOH}}_{\mathrm{SCH}_{2}\mathrm{CH}_{2}\mathrm{COOH}} + \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{I}$ 

#### SECTION IVA. COAL TAR COLORS AND DYESTUFFS

Th. Valette: Action des Alcalinoterreux sur la Laine. (Vol. VII, p. 29.)

A. G. GREEN: I would like to call attention to the interesting fact, judging from the dyed samples presented, that the depth of shade is in direct proportion to the molecular weights of the oxides used.

E. E. Smith. Coal Tar Colors and Injury to Health. (Appendix, Vol. XXV, p. 473.)

۲

٨

٨

MR. DURFEE: I would like to know whether comparisons had been made in toxic effects of the known toxic essential oils allowed and the non-toxic colors not allowed.

E. E. SMITH: The answer to that question is twofold. In the first place the essential oils are themselves food, that is they belong to the class of food condiments, condimental food. Therefore, their use is not regulated under the Pure Food Law. What, or how much shall be consumed of a food is optional with the consumer.

It is to be granted that they are injurious, it is to be granted that they are probably very much more injurious than any of the colors that are made use of, but their comparison does not seem called for under the present conditions, because they are themselves food and the law does not take them into consideration.

MR. DURFEE: Color is a condiment to the eye.

### L. Da Costa Ward. The Need of Official Tests in Dyeing and Textile Chemistry. (Appendix, Vol. XXV, p. 475.)

W. LIVERMORE: Experience with tests based on official specifications seems to show that in textile work tests cannot be made by specification alone, owing to wide variation in individual

XXVII]

circumstances and handling, and in individual judgment as to results. What seems a satisfactory test for light fastness to a class of workers interested in one branch of the textile trade might and probably would be regarded as poor or even bad by a branch whose requirements were greater. The same is true of fulling and other tests. In the case of specifications given by the Government for army colors, experience shows that to be free from error in judgment, it is often essential to make tests in direct comparison with tests made at the same time on a standard Therefore it seems to me that in order to form proper sample. judgment from any suggested official code of tests, that the result must be reported in comparison with results obtained under identical conditions and at the same time with coloring matters selected as standards and representing a good range of fastness in the various important qualities. If it were possible to select and make general the recognition of such a scale of standard I believe a very important step would be accomplished in the intelligent discussion and comparison of dyestuffs. I feel, however, that such a step would probably have to be accomplished by agencies interested in the use rather than in the manufacture of colors.

L. DA COSTA WARD: It would be a difficult matter to arrive at definite methods of testing without cooperating with textile manufacturing associations, so that certain arbitary tests might be introduced.

H. A. METZ: Without desiring to prolong the discussion of Dr. Ward's paper, it does appear to me that while a standard of fastness would be desirable, it would be a hard thing to establish.

I had an experience personally, some time ago, when I was acting as arbitrator of a question which arose between a cloth manufacturer and a clothing manufacturer. The goods in question were a mixture of worsted and cotton. The worsted had been dyed with the well-known acid alizarine after-chrome colors, which are probably the fastest to light shades known to the art, and usually satisfactory for men's wear. The cotton was a fancy thread dyed with the usual developed substantive dyestuffs.

The peculiar part was that the dyed worsted when exposed

by itself would stand very well, but when exposed with the cotton it faded considerably. Whether this had any effect on the fastness or not, I do not know, but it certainly raised an interesting question.

The manufacturer guaranteed his goods to be fast and was justified in such guarantee, in that he had used the fastest color known to the art for this specific purpose and it had been properly and correctly dyed.

The suit of clothes in question had been brought by a gentleman who wore it during his vacation on a yacht, where they were exposed to the sunlight, if not twenty-four hours in the day, at least as many hours as the sun was up. If he had worn the same suit to his office there would probably have been no complaint. So it makes a difference what treatment a garment is subjected to.

In another garment, also submitted in the controversy, were a pair of trousers, which I concluded, as the seat was not as much faded as the rest of them, they had been worn by a rider, and upon being dusted a great deal of alkaline dust was removed, and probably a rider on the plains in the West. Here again the objection would not have been raised if they had been worn in Wall Street instead of in Colorado.

All of which indicates that what may be fast in one section of the country may be very fugitive in another and that hardly any standard which could possibly be fixed would satisfy all conditions.

H. T. BUCHERER: Ich weise darauf hin, dass ueber denselben Gegenstand in Deutschland ausgedehnte Besprechungen stattgefunden haben, die die grossen Schwierigkeiten erkennen lassen, die sich der Aufstellung von Pruefungsvorschriften entgegensetzen.

Auf der Hauptversammlung in Freiburg des Vereins deutscher Chemiker wurden Methoden der Pruefung in Vorschlag gebracht durch den Echtheitsausschuss—Fachgruppe fuer Chemie der Farbstoff und Textilindustrie.

### SECTION VA. INDUSTRY AND CHEMISTRY OF SUGAR

Noel Deerr. The Status of Cane Sugar Manufacture in the Hawaiian Islands. (Vol. VIII, p. 7.)

H. C. PRINSEN GEERLIGS called attention to the statement of Mr. Deerr that "sand as a filtering material has been replaced in the many cases of wood shavings" and asked Mr. Walker if the use of wood shavings for filtering juices had given favorable results in the Hawaiian Islands. To his knowledge the filtration of defecated cane juice through cloth, cork, sand, etc., had failed; a clean and well-settled juice did not need filtration, while a badly settled one will clog up the interstices of the filtering material and cause a rapid cessation in the flow of liquid.

HERBERT WALKER replied that this was also found to be the case with shavings and that a clear filtrate was obtained only with juice of superior quality.

F. G. WIECHMANN asked if infusorial earth was ever used for filtering the raw juice.

HERBERT WALKER replied that he knew of no such experiments having been made.

M. G. HUMMELINCK added a few words regarding the physical and technical requirements of sand filtration, more especially in sugar refineries. Among the important requirements for successful sand filtration the following were named: (1) Absence of vibration; (2) Constant speed of liquid; (3) Sand grains of uniform size; (4) Absence of air bubbles in the sand which might retard the speed of the liquid.

MR. PERKINS asked Mr. Hummelinck at what density and temperature the molasses should be filtered through the sand and also what were the principal mechanical impurities removed.

M. G. HUMMELINCK stated in reply that the molasses should be filtered at a density of about 60° Brix and at a temperature of 90°C. The chief mechanical impurities eliminated were ultramarine particles, suspended mineral matter, oil and gums.

# 60 Eighth International Congress of Applied Chemistry [VOL.

# H. D. Gibbs. Production of Alcohol and Sugar from Sap of the Nipa Palm. (Vol. III, p. 13.)

H. C. PRINSEN GEERLIGS stated that he was not so optimistic as Mr. Gibbs regarding the utilization of the Nipa Palm for sugar manufacture. This palm has existed for centuries in the midst of an industrious native population and the fact that the latter had never attempted to utilize the Nipa Palm for sugar manufacture shows that there is manifestly some natural obstacle in the way, as regards habits of growth, character of juice, etc. Other palms in these same countries, on the contrary, are utilized for making sugar.

He further mentioned in this connection the utilization for sugar manufacture of the Sago or Buri Palm. The latter lives for about 35 years and during this time stores up a large amount of starch as reserve material in the trunk. At the end of its life the tree flowers, fruits, and dies. If an incision be made in the top of the tree below the bud a pure juice can be collected which contains as much as 18% of sucrose. From 300 to 250 pounds of sugar can be obtained in a season from a single tree. The sucrose thus formed is derived from the starch, the latter being found to disappear from the top of the trunk downward. This conversion of starch into sucrose was ascribed by Mr. Geerligs to a specific enzyme but attempts to isolate it in a pure condition were not successful. An enzyme, which was separated, was found to convert starch into dextrose and not into sucrose.

F. STROHMER mentioned, in connection with the attempts to discover new sources of sugar, the recent experiments which had been made in Hungary with maize. The Stewart process of plucking off the young ears was tried and it was found that the stalks thus treated stored up a considerable amount of sucrose. The expressed juice, however, was of such low purity that the utilization of maize for sugar production did not appear feasible.

H. C. PRINSEN GEERLIGS stated that he had made similar experiments with maize and that the expressed juice upon evaporation always give a thick mass of pudding-like consistency which would not crystallize. The large amount of gums and

#### XXVII]

۲

Discussions: Section Va. Industry and Chemistry of Sugar

other impurities in maise juice seem to prevent the crystallization of the sugar.

T. de Grobert. Sur la Precipitation Incomplete par la Carbonate de Soude de la Chaux Combineé dans les jus Sucres. (Vol. VIII, p. 21.)

M. G. HUMMELINCK: I do not altogether agree with the conclusions of Monsieur de Grobert regarding the use of sodium carbonate in sugar factories. Many experiments have been performed upon the reaction between the various salts of calcium and carbonate of soda, but these experiments, for the most part, have made been upon a small laboratory scale and have not been carried out in a factory.

While the attempt to precipitate the excess of calcium from juices with sodium carbonate is a failure at the final stages of clarification, this is not the case if the sodium carbonate be added previously in the lime mixers where its influence will be felt during the whole process of carbonatation.

The composition of the raw juice after the addition of the lime may be represented roughly as follows:

Sugar + organic K salts + organic Ca Salts + Ca  $(OH)_2$ .

If the requisite amount of sodium carbonate be now added to the above there will be obtained

Sugar +  $\begin{cases} \text{organic K Salts} \\ " \text{Na Salts} \end{cases}$  +  $\begin{cases} \text{KOH} \\ \text{Na O H} \end{cases}$  + Ca C<sub>3</sub>O necessary precipitate alkalinity

If this process is followed, the juice after the second carbonatation will be entirely free of calcium, none of the soluble organic Ca salts being left in solution. The sodium carbonate should be added in calculated quantity so that the proper alkalinity is obtained.

This method has been used by several sugar factories in Holland during the campaign of 1911–1912, with excellent results. Less molasses was obtained, and the clarified juices and syrups were of excellent quality and color.

L. R. COOK: In Michigan, in spite of the use of carbonate of

61

soda and liberal sulphitation it has frequently been found impossible to rid the juices of lime salts. So high has the hardness run at times that the boiling has been seriously interfered with and the work of the entire sugar house cut down in consequence. I have seen a low grade pan usually boiled in ten hours refuse to boil at all after seventeen hours treatment, the pan being only two thirds full. Ebullition simply stopped and this in spite of a high vacuum and sixty pounds steam pressure. A hint from some writer on sugar house work led to the trial of cotton seed oil which was partially successful in restoring normal ebullition; but the boiling was still slow. The oil was then saponified with caustic soda and the results were electrifying.

A pan that merely simmered with a high vacuum, when treated with about ten pounds of the saponified oil responded within five minutes or as soon as the soap became mixed through the massecuite. The vacuum would fall rapidly requiring more water at the condenser, the heat of course rising in proportion until the additional water again raised the vacuum.

By the use of this soap frequently pans were boiled in two thirds the time otherwise required and with the attending better results. The beneficial effects were noted in high grade pans as well as in the low grades, although the high grade massecuites would not exhibit the extreme difficulties which of course accumulate in the low grades. Nevertheless a proportional benefit is remarked. The most economical place to use the soap is in the thick juice and syrups when being heated the last time before final filtration, but inasmuch as the amount used is so insignificant the vacuum pan itself is an effective point for its introduction.

J. H. Van Loon and M. G. Hummelinck. How the Netherland Sugar-Fabricants are being kept Informed during Campaign about Quality of the Raw Sugar Produced. (Vol. VII, p. 29.)

F. STROHMER stated that the method recommended by Mr. Hummelinck was a very good one but doubted whether it could be introduced in Austria. Raw sugars there had long been XXVII]

Discussions: Section Va. Industry and Chemistry of Sugar

bought and sold by rendement (polarization less five times the percentage of ash) and, since long established commercial usages are hard to change, it is not probable that the rendement method of valuing sugars will be abandoned immediately. Previous attempts have been made to displace the rendement method and among the substitutes proposed were named the old method of Payen and its modifications by Scheibler and Koydl, in which the crystal content of the raw sugar was determined by washing out the molasses with solutions of alcohol saturated with sucrose. The use of numerous alcoholic washing fluids was time-consuming. however, and also attended with several sources of error, so that the old rendement method was still in general use. A more promising substitute for the Payen methods, is the recent method of Herzfeld and Zimmermann in which the raw sugar is simply shaken up with a saturated solution of sugar in water and then spun out in a small centrifugal; this new method, however, has not been sufficiently tested to pronounce upon its merits.

H. C. PRINSEN GEERLIGS observed in reply to Geheimrat Strohmer that the rendement test was also used in Holland and that the method described by Mr. Hummelinck was not intended to displace the rendement test but simply to be used in connection with it and supply its deficiences.

AUGUSTE AULARD confirmed the conclusions of Mr. Hummelinck and added that the use of sulphurous acid had favorable results in securing white sugar.

٨

F. Strohmer and O. Fallada. Inversion von Rohrzuckerlösungen mitteslst chlorammonium. (Vol. VIII, p. 85.)

E. SAILLARD. Vous venez d'entendre les interessantes observations de M. Strohmer. Comme lui nous avons cherché une autre voie pour pratiquer l'inversion Clerget des mélasses de betteraves. Apres avoir étudié l'action de quelques sels et de quelques acides sur le pouvoir rotatoire du saccharose, du sucre inverti, et des matières azotées de la mélasse nous sommes arrives à la méthode suivante, dont l'étude n'est pas encore terminée.

(a) Prendre 50cc. de solution normale de mélasse déféquée (sans plomb) et neutre; completer a 100cc avec une solution de NaCl apportant en NaCl l'equivalent de HCl qu'on emploiera pour l'inversion. Polariser.

(b) Prendre 50cc de la même solution normale; ajouter l'acide chlorohydrique; faire l'inversion; neutraliser avec de la soude; completer a 100cc; potariser.

Appliquer la formule  $S = \frac{(A+B)200}{Constante - \frac{1}{2}t}$ 

Constante. On l'établit en suivant la même marche qui vient d'être indiquée.

Je viendrai sur la question dans ma communication du Mercredi prochain.

Auguste Aulard. Quelques Particularités nouvelles sur l'emploi de l'anhydride Sulfureux et les Hydrosulfites dans l'industrie Sucrière. (Appendix, Vol. XXV, p. 501.)

E. SAILLARD stated that when sulphur is burned in air in a furnace the escaping gas should contain theoretically 21% of  $SO_2$ ; in actual practice, however, the yield does not exceed 14% and sometimes sinks as low as 4% or 5%. The difference between the actual and theoretical yield is uncombined oxygen and it seems possible that when this mixture of  $SO_2$  and O is forced into a juice that a little  $SO_3$  may possibly be formed to the great detriment of the sugar in the juice. Experiments seemed to indicate, that the sugar and other substances of the juice act as negative catalyzers and thus prevent the oxidation of the  $SO_2$  to  $SO_3$ .

E. VOTOCEK called Professor Saillard's attention to some work previously done in Ostwald's laboratory where it was found that the oxidation of  $SO_2$  by oxygen was prevented by the presence of alcohols, sugars, and other organic substances. These latter all forming ester-like combinations with the  $SO_2$ .

E. SAILLARD inquired whether these experiments were carried out at room temperature and high concentration, or at high

65

temperature and low concentration, since the factors of temperature, concentration and time all play an important rôle.

E. VOTOCEK stated that the experiments had only a theoretical interest and were not carried out with reference to sugar manufacture.

E. SAILLARD stated in addition that the gas produced by a sulphur furnace may contain  $SO_3$  owing to the presence of moisture in the air used for combustion. This  $SO_3$  can be removed by passing the gas through washers containing a solution of sodium bisulphite, but as this process causes an entrainment of liquid he recommended as much better passing the gas from the sulphur furnace through scrubbers filled with dry coke.

H. C. PRINSEN GEERLIGS asked what results had been obtained in the United States in the experiments upon the injurious effects of sulphites in molasses.

W. D. HORNE stated in reply that experiments by Dr. Wiley in Washington indicated that the presence of sulphites in food tended to diminish the number of red and white corpuscles in the blood of the subjects experimented upon. Other injurious effects were also noted, Subsequently other experiments carried out by other investigators in New Orleans showed that negroes, which were fed upon molasses containing rather large amounts of sulphites, suffered no material injury in health. The question was still undecided as to the amount of sulphites which should be permitted in molasses and sirups when used as human food.

Auguste Aulard. L'emploi de la Cellulose (Pâte à papier) Comme Produit Filtrant dans l'industrie Sucrière et Autres. (Appendix, Vol. XXV, p. 489.)

۲

۲

H. C. PRINSEN GEERLIGS stated that the experiments in Java with the Perrin filter made at Wonopringgo, were not altogether conclusive as this factory employed carbonatation. Other experiments made in factories where the juices were defecated in the ordinary way showed that the Perrin filter gave very good results with badly filtering juices.

XXVII]

5

Auguste Aulard. Quelle que Soit la Temperature (90° a 150°C.) a Laquelle on Soumet les Solutions de Saccharose, Glucose, Maltose, etc., Pure ou Impure, ces Hydrates de Carbon Peuvent ils se Transformer en Caramel ou un de ses Derives en Milieu Humide a l'Abri de l'Air. (Appendix, Vol. XXV, p. 493.)

E. SAILLARD corroborated in general the statements of Mr. Aulard stating, however, that he preferred not to exceed a temperature of 110°-112° during the evaporation. The discoloration of sugar solutions was due more to the action of heat upon glucose and other impurities than upon the sucrose itself, which in pure solution is not discolored. An alkaline reaction always tends to promote darkening and if the juices remain too long in the evaporators discoloration is certain to follow.

William E. Cross. Sour Cane in Louisiana. (Appendix, Vol. XXV, p. 531.)

۲

G. P. MEADE asked: Of what value is the acidity determination as a basis for accepting or rejecting cane? Since Dr. Cross says that a high acidity with a high purity should be accepted and a low purity and low acidity should be rejected is not the purity the actual basis of determination?

W. E. CROSS: I admit that the acidity value has not much significance in ordinary cases. It is useful, however, in certain instances, especially where the dextran fermentation is not giving much trouble. We must remember that the acid produced by fermentation produces highly melassagenic salts, and these must be taken into some account in judging the cane. As I said, purity, acidity and gum content are the guiding criteria. M. Saillard. Le Sucre Clerget des Melasses Normales du Betteraves par Double Polarization Neutre. (Appendix, Vol. XXV, p. 541.) 67

L. R. COOK: It is well known that the action of NaCl upon pure sugar solutions is to diminish the reading. If NaCl is added to the solution for direct polarization the polariscope reading would be too low. It would seem that allowance would have to be made for this diminution in the direct reading.

The action of NaCl upon the inverted solution would scarcely be of the same effect and so would not offset the difference made in the direct reading.

E. SAILLARD replied in answer to Mr. Cook: Il est vrai que le chlorure de sodium change le pouvoir rotatoire du saccharose; mais cette cause d'erreur se trouve éliminée par ce fait que pour établir le coefficient d'inversion à appliquer, nous operons de la même façon c'est'-à-dire que nous ajoutons du NaCl, pour faire la polarisation directe, et que nous neutralisons apres inversions pour faire la polarisation à gauche.

#### SECTION VB. INDIA RUBBER AND OTHER PLASTICS

J. G. Fol. On the Relationship between the Amount of Resin and the Viscosity of Rubber Solutions. (Vol. IX, p. 71.)

E. MARCKWALD: Nach meinen Erfahrungen lassen sich aus der Viskositaet einer Kautschukloesung Schluesse auf den Harzgehalt des Kautschuks nicht ziehen. Von etwa 60 letzthin von mir untersuchten Manihot Kautschuken gaben mehrfach gerade die mit einem sehr geringen Harzgehalte eine niedrige, dagegen die mit relativ hohem Harzgehalte eine hohe Viskositaet. In den meisten Faellen liess die Viskositaet jedoch einen richtigen Schluss auf die Qualitaet des Kautschuks zu. Gewisse Abweichungen beduerfen noch der Erklaerung. Fest steht dass in jedem Falle eine unguenstige Koagulationsmethode oder eine falsche Behandlung des koagulierten Kautschuks dessen Viskositaet herabsetzt. Ebenso geben unausgereifte Kautschuke eine niedrige Viskositaet. Bei einigen Manihot-Kautschuken, die durch Verduennen der Milch mit Wasser gewonnen werden, habe ich vielfach wiederholt gefunden, dass die Kautschuke nicht in Loesung zu bringen waren, sondern bruechige Ausscheidungen gaben. Die Qualitaet dieser Kautschuke ist gering. Eine Erklaerung fuer die Erscheinung habe ich bisher nicht finden koennen. Vielleicht kann der Herr Vortragende dieselbe geben. Lebhaft bedauern moechte ich dass es bisher nicht gelungen ist, eine internationale Einigung auf eine bestimmte Metode der Viskositaetsbestimmung herbeizufuehren. Der Wert dieser Pruefungsmetode, die an sich nur relative Werte geben kann, ist dadurch erheblich herabgesetzt. In Deutschland hat das von Dr. Frank und mir konstruierte Viskosimeter, Modell II. mit 6 mm. Ausflussoeffnung jetzt fast allgemein Eingang gefunden. Die Viskosimeter werden saemtlich geaicht da schon geringe Abweichungen im Bau erhebliche Differenzen bedingen, die leicht zu Trugschluessen fuehren koennen.

J. G. Fol: I am glad to hear from Dr. Marckwald that accord-

XXVII

ing to his experiments there is no correlation between the amount of resins and the viscosity of the solutions of Manihot rubber. Just before I left Holland I found the same for solutions of Hevea rubber. Some of them, though they contained only a small amount of resins showed a low viscosity whilst others with a large percentage of resins were very viscous.

I quite agree with Dr. Marckwald that in order to get comparable results a uniform method for the determination of the viscosity of rubber solutions is wanted. In regard to the viscometer suggested by Dr. Frank and Dr. Marckwald I am very sorry to say that I got bad experience with this apparatus. The diameter of the tube, through which the solution is flowing is too large to get reliable results. When the rate of flow exceeds a certain speed we get a turbulent flow as has been pointed out by Osborne Reynolds. Only in case of a parallel flow we can determine the exact viscosity of a solution. Moreover, the great speed of flow of the solution in the viscometer, mentioned above, makes a correct determination of the rate of flow sometimes practically impossible.

I should be glad to hear from Dr. Weber how he could explain why the sample A, that contained only a very small amount of resins, could not be vulcanized.

E. MARCKWALD: Ich moechte die Ausfuehrungen des Herrn Dr. Weber noch besonders unterstreichen. Es ist nicht richtig, aus dem Harzgehalte an sich auf die Guete eines Kautschucks zu schliessen. Deshalb ist es meines Erachtens auch nicht angebracht, fuer gewisse industrielle Verwertungsgebiete, den Harzgehalt nach oben zu begrenzen. Das muss dazu fuehren, anstelle guter, etwas harzreicher Produkte, schlechte entharzte Kautschuke zur Anwendung zu bringen.

F. W. HINRICHSEN: Es besteht kein Zweifel, dass eine direkte Kautschukbestimmung, zum beispiel nach der Brommethode, von ausserordentlicher Bedeutung fuer die Analyse von Caoutchuc und Caoutchuc Waren sein wird. Ich kann heute noch nicht ueber die Arbeitsweise von Herrn Boggs sprechen, weil ich nach dieser Methode noch keine Versuche gemacht habe.

Wohl aber bin ich seit mehreren Jahren mit dieser Frage beschaeftigt und stehe mit Herrn Boggs auf dem Standpunkt, dass

### 70 Eighth International Congress of Applied Chemistry [VOL.

es moeglich sein wird, eine solche direkte Bestimmung zu erhalten. Andererseits stimme ich mit Herrn Boggs auch darin ueberein, dass die bisher in der Literatur zu diesem Zwecke vorgeschlagenen Verfahren ungeeignet sind, dies Ziel zu erreichen. Auch wir haben z. B. nach der Huebnerschen Methode stets zu hohe Werte erhalten, was in erster Linie auf die Einwirkung hoeherer Temperatur, und eines zu grossen Ueberschusses an waesseriger Bromloesung bedingt ist.

Wir haben systematische Versuche gemacht, um den Einfluss der einzelnen Fehlerquellen fest zustellen und haben gefunden, dass es moeglich ist, ein Bromid von normaler Zusammensetzung, entsprechend der theoretischen Formel C10H16 Br4 zu erhalten, wenn die Bromierung bei niedriger Temperatur in Chloroform-Loesung vor sich geht. Man muss also sowohl Wasser wie auch den Bromueberschuss und hohe Temperature vermeiden. Das Arbeiten mit Chloroformloesungen hat nach unseren Erfahrungen sowohl bei Rohcaoutchouc wie auch bei vulkanisiertem gute Resultate geliefert. Wenn man Rohcaoutchouc oder vulkanisierten Caoutchouc mit Brom in Chloroformloesung behandelt, so tritt eine vollstaendige Loesung ein. Man faellt nachher das Bromid z.B. mit Benzin aus, und bestimmt Bromgehalt nach Schmelzen mit Alkalikarbonat in aehnlicher Weise wie es auch Herr Boggs beschrieben hat. Wir arbeiten dann so, dass wir etwa O, 1 Gramm Caoutchouc mit einem geringen Ueberschuss von Brom (etwa ½ cm) in etwa 25 ccm Chloroform unter Eiskuehlung versetzen, dann lassen wir einige Zeit unter Eiskuehlung stehen. In diesem Falle ist es gleichgiltig, ob man eine Stunde, oder 6, oder 24 Stunden oder zwei Tage stehen laesst. Man bekommt nach unseren Versuchen stets den theoretischen Bromgehalt. Wir haben die Versuche noch nicht abgeschlossen, aber soweit wir bis jetzt sehen koennen, glauben wir doch, dass es auf diesem Wege moeglich sein wird, mit der Zeit zu einer brauchbaren direkten Kautschukbestimmung zu gelangen. Vorlaeufig jedoch, solange die Versuche noch nicht abgeschlossen sind, muessen wir der indirekten Analyse noch groessere Zuverlaessigkeit zusprechen.

L. E. Weber. The Action of the Resins in the Vulcanizing of Rubber. (Vol. IX, p. 95.)

G. H. SAVAGE: The results of the experiments described by Dr. Weber relate specifically to the resins of "Highlands Sheet," which is the one rubber that most nearly resembles "fine Para" in its botanical origin and mode of preparation. Now the term "rubber resin" is most commonly used to denote merely that part of the crude rubber that is soluble in acetone. Although there seems to have been comparatively little study as yet of the properties of the resins of different kinds of rubber, the term "rubber resin" is such a familiar one that it is very apt to be used as if it meant a definite chemical substance having identical. or at least closely similar chemical properties wherever found. In fact, without some such assumption it would be impossible to draw very definite conclusions from the behavior of the resins of one rubber as to the behavior of rubber resins in general. Such an assumption is unsafe in view of some of the apparently different properties of these "resins" and the widely differing botanical origin of some of them, and there is a possibility of some divergence in their behavior.

Considerably over a year ago a series of experiments was reported in the *Gummi-Zeitung* which seemed to prove conclusively that in the vulcanization of "fine Parà" in the presence of litharge a reaction takes place in which the resin, litharge, and sulphur are all involved, and that the heat of reaction is sufficient to raise the temperature of the mixture considerably above that of the vulcanizer. As I recall it, it was reported that the resins of certain African rubbers did not react in this way, but that there was evidence in these cases of the presence of bodies other than resins and that these bodies did. I believe nothing further has been reported with regard to the other resins, and I should like to ask if Dr. Weber has made any observations as to the behavior of other resins than those mentioned.

I have recently obtained some results in the analysis of a series of rubber mixtures that bear somewhat on the question of a chemical reaction involving resin and litharge. The mixtures analyzed all contained just 30% of crude rubber. Experiments

# 72 Eighth International Congress of Applied Chemistry [VOL.

were made with "fine Parà" with various changes in the mineral ingredients and with a limited number of other rubbers. The samples were vulcanized at various degrees of steam pressure and extracted with acetone and then with chloroform. Particular care was taken with the "fine Parà" used in the different experiments to obtain a sample of uniform resin content throughout.

The "fine Para," mixtures containing litharge showed a uniform chloroform extract of about 0.4% when cured at indicated steam pressures from fifteen pounds up to thirty pounds per square inch, with a possible slight tendency to increase at the highest pressures. As shown by mechanical tests the rubber was decidedly undervulcanized at fifteen pounds and overvulcanized at thirty pounds. In the absence of litharge the chloroform extract was considerably higher, even when cured at temperatures sufficient to effect a satisfactory cure from a mechanical standpoint. The mixture containing litharge also showed a much lower quantity of acetone-soluble resins than did the others. Apparently the changes effected by the vulcanization in the mechanical properties and in the solubility in chloroform are somewhat independent of one another, and it would seem that the litharge, while accelerating both, has the more marked effect on the solubility in chloroform. It is evident, too, that in vulcanization in the presence of litharge a portion of the resin is either destroyed or rendered insoluble in acetone.

In the case of other rubbers that I have tried up to the present time, which include extracted "guayule" with two to three percent (2-3%) resin content and rubbers closely related to "fine Parà," such as "Cametà," "Up River Coarse" and "Highland's Smoked Sheet," the chloroform extract insoluble in acetone of samples vulcanized with litharge varied considerably but was in no case so low as for "fine Parà." In some cases it was much higher. The fact that the litharge does not cut down the chloroform extract so much for these other rubbers as it does for "fine Parà" might conceivably point to a difference in the nature of the "resins" to the presence of other bodies or to differences in the condition of the rubber hydrocarbon. The evidence so far obtained as to which of these causes to assign it to is inconclusive. L. H. Baekeland. Phenol-Formaldehyde Condensation Products. (Appendix, Vol. XXV, p. 563.)

MR. ANDREWS: The question which I would like to put to Dr. Baekeland is whether he regards Bakelite "C" as being essentially a chemical compound or whether he regards it as having rather the nature of an alloy or mixture of different compounds?

L. H BAEKELAND: Dr. Raschig has suitably pointed out a few days ago, in his lecture that when you are working with variable amounts of phenol, or specially when you are working in different conditions, or when you are using commercial mixtures of phenols, several reactions can occur at the same time. At any rate, it does not matter very much whether the final product is a chemical unit or not. In most cases it is desirable to have a slight excess of phenol, or a slight excess of any other substance which can make a solid solution with the final product. because the presence of such substances which form colloidal solid solutions, enhances certain of the technical qualities of the product. With phenol, you may obtain a product which afterwards can be purified by washing and treating it with acids. But there again it is questionable whether the final product you obtain is a unit. It is one of the difficult problems of organic chemistry; one of those problems which have been very much neglected by the average chemist, who has the habit of kicking out of his laboratory anything which does not crystallize in nict crystals. Kleeberg, for instance, as soon as he found his produce would not crystallize and could not be nicely purified, and finding, furthermore, that his product was contaminated with a lot of side products, dismissed the whole subject in one paragraph and busied himself with the study of other condensation-products of polyphenols which were crystalline and could easily be isolated.

E. F. HICKS: I want to ask Dr. Backeland if it is possible to produce infusible, insoluble condensation products by means other than the alkaline condensing agents or excess of formaldehyde, or its technical equivalents, that is, by means of acids or neutral salts as condensing agents?

XXVII]

L. H. BAEKELAND: It is possible to obtain in the condensation product "C" (the polymerized resistive product "C") by using an acid condensing agent, or acid salt. This was done as far back as 1891 by Kleeberg, but the product obtained under such conditions does not have the properties which make it suitable for technical purposes. Furthermore, whenever you use an acid medium, the reaction is not a clear cut reaction. Several side products are formed which verge more towards group II.

R. B. CHILLAS, JR.: I would like to know whether the products that have been mentioned can be used as a protective coating for materials of a hydroscopic nature, which are also alkaline? The latter products contain a mixture of sodium and potassium carbonates, could bakelite be painted over these products and have it form a protective coating, also where there was lime present.

L. H. BAEKELAND: In the publications on the subject, you will find that some varieties of this material can be made to resist alkalies; for instance, carbonate of sodium and carbonate of potassium, but the material is not so resistive against caustic soda and caustic potash as against ammonia. It is attacked also by bromine but not so easily by chlorine; it is attacked also by nitric acid but not by hydrochloric acid.

I ought to mention, however, that resistivity against alkalies depends very much on the raw material which is used. One of my pending patents covers this subject, and I can take the liberty of saying that meta-cresol in presence of a sufficient amount of formaldehyde or its equivalents gives a final product which is considerably more resistant to alkalies than if you use phenol, ortho-cresol, or para cresol.

#### SECTION Vc. FUELS AND ASPHALT

Herbert Abraham. The Classification of Resinous and Bituminous Substances. (Vol. X, p. 7.)

C. R. DOWNES: I would like to ask Mr. Abraham if it is not a mistake to classify watergas-tar and watergas-tar pitch among the substances which result from bituminous coal. As far as I am aware only anthracite or coke is used for the production of watergas. The watergas-tar results from the "cracking" of the gas oils used for carburretting the watergas. These substances should therefore be classed only among those products resulting from petroleum.

J. M. WEISS:—I feel that it is a mistake to consider watergastar as originating from bituminous coal in any way. If any coal gas is made then the product would be a mixed tar and not a true watergas-tar.

E. J. BABCOCK stated that olefines and terpenes on interaction are liable to produce spontaneous combustion as found in Western coals.

H. ABRAHAM replied that Wagner states that bituminous coal is used for making water gas in Europe.

۲

٨

Irving C. Allen and T. W. Robertson. Methods for the Determination of Total Sulphur in Fuels, Particularly Applicable to Petroleum Products. (Vol. X, p. 25.)

I. C. ALLEN: One thought should be mentioned here that sulphur in burning will give a bad odor in a closed room, but how much I cannot say. Also with respect to lubricating oil, sulphur indicates an acid which will, of course, cut open a journal and it should not be in lubricating oil. The amount of water allowable in oil is also a question. We have considered 2%. One of its damages in burning oil is to reduce its calorific value to a large degree.

G. W. GRAY: I noticed in going over the article by Mr. Allen

on the sulphur determination that in giving credit you spoke in that article of absorbing sulphuric acid and titrating back with caustic soda. The method which has been in use for about 22 or 23 years was burning it in the ordinary apparatus, absorb it in carbonate of soda and titrate in sulphuric acid similar to what Mr. Allen described, they used at the Bureau of Mines. I think you mentioned about the quantity of sulphur permissible in fuel oil. I have oil burned under a boiler which ran as high as 15% of sulphur, or a total of probably 40% of SO<sub>3</sub> of combined sulphur in the oils. This would be a sludge product and I have seen that sludge product which would contain at least 40% of SO<sub>3</sub> burned under boilers with no harmful effect.

T. T. GRAY states that Mr. C. I. Robertson of the Standard Oil Company, and not Mr. Burton, as stated in the original paper, was the first to determine the percentage of sulphur in lamp oil by burning it in a lamp and eventually absorbing the sulphur fumes in alkalies.

I. C. ALLEN: What Mr. Gray has said regarding the burning of a refinery residue containing 40% of SO<sub>3</sub> without injury to the boilers is interesting. On the other hand, I know of a case in California where an oil containing one half of 2% of total sulphur was burned under a water tube boiler. There was formed a marked incrustation of iron sulphate upon the tubes and some of the tubes were very much pitted. In fact, in some cases so seriously that it was found necessary to replace them.

E. J. Babcock. Investigation into the Better Utilization of Non-Coking Low Grade Lignitic Coals. (Vol. X, p. 41.)

F. SCHNIEWIND asked about the percentage of sulphuretted hydrogen in the gas.

E. J. BABCOCK: The sulphur content is very low, not sufficient to give, usually, any marked lead test.

A. H. ELLIOT said that this gas would be a very excellent fuel if freed from  $CO_2$  if it were reduced to CO by passing it through the retorts again. That it would be more profitable

## XXVII] Discussions: Section Vc. Fuels and Asphalt

to convert the lignite all into fuel for power purposes rather than to make briquettes out of it. The tar seemed to be very rich in phenols from its odor which would make it valuable.

W. F. Hillebrand and W. L. Badger. Errors in the Determination of Moisture in Coal. (Vol. X, p. 187.)

HORACE C. PORTER: In behalf of the United States Bureau of Mines laboratories and in the absence of Mr. A. C. Fieldner, who is in charge of coal analysis at those laboratories I may say that our laboratories are studying carefully this question of moisture determination. In the routine work, modifications of the Official Method are used which increase the accuracy, in particular the passage of a current of dry, pre-heated air over the coal.

Our investigations emphasize the extreme hygroscopicity of dried coal. Dried coal recombines chemically with water and produces heat thereby.

Specific heat measurements on dried and undried coal show that the specific heat of the latter is considerably less than it would be theoretically on the basis of the dried coal value and of the value 1.0 for water. In other words, the water, even that which is driven out at ordinary temperature in vacuo; is present partly in combined form, not as free water.

Drying in carbon dioxide has been suggested but cannot be used since coal absorbs this gas materially. Nitrogen is well adapted, however, for the purpose.

There should be emphasized the wide variation between different types of coal as to oxydizability, some coals showing a rate of oxidation ten times that of others. The amount of methane expelled from any coal is not sufficient to be of any importance in connection with moisture determination.

77

R. Lessing. A New Coking Test for Fuels. (Vol. X, p. 195.)

F. SCHNIEWIND: Is the piston also of metal? Would not a non-conducting piston be best?

H. C. PORTER: Would not a strongly-expanding coal push the piston out of the crucible?

A. H. ELLIOTT: We are now using in America much poorer coal than heretofore; we used to get anthracite with 5% of ash, and now we have to be content with coal having 10 to 12% ash. Dr. Lessing's method imitates the best commercial practise, in that it cokes the coal in a confined space, just as in a coke oven. The weight upon the piston should be constant in order to get constant results.

R. LESSING: The crucible is of quartz glass, in order to avoid contraction and expansion; and the coke does not stick to it, but comes out clean. The piston is hollow, so that it can be weighted with the proper weight of quartz powder. The coal expanded too much in our early work, but we correct that by using less coal. We have now added to the apparatus gas-collecting tubes, so as to catch and analyze the gases evolved. We are pleased to be able to state, that on a very carefully prepared one-gram sample of a coal we obtained exactly the same yield of gas as was obtained from the *annual* average of that coal in a large works.

P. Nicolardot. Influence de la Grosseur du Grain dans l'analyse des Charbons. (Vol. X, p. 203.)

۲

٨

R. LESSING said that he also experienced differences in composition of coal fractions of varying size. He put it down to the hardness of coal being determined by the composition. This is brought out both by moisture and volatile constituents, but more particularly by the ash contents. S. W. Parr. The Resinic Bodies in Bituminous Coal. (Vol. X, p. 225.)

H. C. PORTER: Is the chemical nature of the so-called resinic bodies existing in coal similar to that of bitumen or artificial tars? Or are they more highly oxygenated substances? By studies of the distillation products from coal it is indicated that two classes of substances exist in coal, (1) those yielding chiefly paraffin hydrocarbons on heating, and (2) those yielding largely oxides of carbon and water, with small amounts of hydrocarbons. Is not the first class rather to be called the resinic bodies than the second? The first class predominates in the high grade Eastern coals of the United States and the second class in the Western lignitic coals. The Western coals absorb oxygen with much greater avidity than the Eastern, so is it not the cellulosic bodies which absorb oxygen rather than the resinic bodies?

F. SCHNIEWIND asked whether the investigations regarding the presence of resinous constituents of coal had been extended to the various components of a coal vein such as the lustrous coal, the dull coal, cannel-coal, mineral charcoal, bituminous shale, etc.

H. C. PORTER replied that no definite results had been obtained as yet.

S. W. PARR replying to the question by Mr. Porter said that the resins in coal contain oxygen and give at 400° C. distillation products high in oxygen which absorb oxygen vigorously. The oxygen absorption depends on the resinous substances present in the coal.

R. P. Perry. Tar Distillation in the United States. General Development and Recent Progress. (Vol. X, p. 233.)

۲

۲

٨

F. SCHNIEWIND, when asked by J. A. Holmes for an expression of opinion on the subject of his paper, stated that the question of the development of the tar industry in the United States along the line of the development of the same industry in Germany had been often discussed. The chief obstacles seemed to be the lack of American chemists trained in this field and also the patent situation as mentioned by Mr. Perry in his paper. The conditions are, however, changing in favor of a more rapid development of the tar chemical industry in the United States.

E. F. HICKS asks Mr. Weiss if he can tell us even approximately what quantity per annum of commercial crystallizable carbolic acid is being produced in this country at the present time.

J. M. WEISS: Accurate figures on crystal phenol produced in this country were not obtained but I may say at present that the amount is comparatively small.

Porter and Ovitz. The Spontaneous Combustion of Coal. (Vol. X, p. 251.)

FREDERICK H. FRANKLIN: One of our clients, who uses large amounts of steam coal, sent us for analysis a sample taken from the region at which a spontaneous combustion had occurred.

The specimen was very porous, high in carbon, and contained about 2% of ash.

E. J. BABCOCK: In our experience, hard dense coals ignite slower; open, soft and spongy coals are the worst, especially if moisture is present. The percentage of moisture in the coal is important; most Western coals are dangerous when containing 15 to 20% of moisture, with less than 5% or more than 20%they are less dangerous. The form in which sulphur occurs in the coal has much to do with its spontaneous combustion; as pyrites it is not so bad as organic sulphur. Spontaneous ignition is influenced by many factors: the physical structure, percent of moisture, form of the sulphur, fineness of the coal.

E. M. CHANCE: Another factor is the area of pyrites exposed to the air; if finely disseminated it oxidizes much faster and so causes quicker rise of temperature. The spontaneous combustion of coal in the mine is of greater importance than in coal piles outside; the oxidation of pyrites in the coal in place in a mine causes increase in the iron sulphate in the mine waters, and can thus be detected. Anthracite slack in piles causes trouble, but the moisture present is an important factor; non-dried coal will recombine with water. Coal with 2% of water, dried and moistened again gave out 14 calories per gram; sufficient to raise the temperature  $42^{\circ}$ .

81

E. H. HAMILTON: Copper smelters do not object to pyrites in their coal, as the iron is useful to them. In one instance, some shale on top of our coal pile took fire, and thus set fire to the coal.

W. S. AYRES: Coal dried in the air always shows air-cracks, and by these air enters into the interior of the lumps and oxidizes to the center. This increases the surface exposed to the air and causes heating in the center.

A. H. ELLIOTT. New York City has used Nova Scotia coal high in sulphur, in its gas works, also West Virginia coal high in sulphur, but never had so much trouble with spontaneous combustion from these as from some Welsh anthracite from Cardiff containing 6 to 7% volatile matter and very low sulphur, but which was very friable; it took fire often in spite of great precautions.

G. H. HULETT: The spontaneous combustion is a question of surface exposed, and also, so far as pyrite is concerned, whether the FeS<sup>2</sup> present is pyrites or marcasite. The latter is more friable and oxidizes faster.

W. S. AYRES: In Pennsylvania anthracite coals, those most liable to spontaneous combustion contain lime in the ash. This is a curious coincidence for which I, at present, can suggest no explanation.

HORACE C. PORTER: As to anthracite, the observations of the Bureau of Mines have been that anthracite screenings will heat spontaneously if the conditions are right. No laboratory work has been done, however, on anthracite. The oxidation of coal, probably even that of anthracite, is in the main an absorption and not an combustion forming  $CO_2$ , until the temperature has reached about 150°C or higher. The Bureau is now studying the question of spontaneous combustion in mines particularly. High moisture coals appear to be in general the most susceptible to spontaneous heating, but probably the heating does not result from the presence of moisture. The avidity of the coal substance for oxygen is greater in case of those types which have high moisture content and the heating takes place largely after the mois-

#### 82 Eighth International Congress of Applied Chemistry [VOL.

.

ture has evaporated. Dried ore, partially dried coal recombines chemically with water, developing heat. The effect of CaO in the ash on spontaneous heating has not been investigated by the Bureau.

۲

M. Taffanel. De l'Alteration des Poussieres de Houille Exposees a l'Air. (Vol. X, p. 277.)

J. A. HOLMES stated that in investigations of the Bureau of Mines it was found that the majority of explosions are caused by coal dust; especially in winter when the dust is dry.

F. SCHNIEWIND asked the author if any measurements had been made of the rise in temperature of coal during oxidation in the air.

M. TAFFANEL said that the rise in temperature was so slow that he had not determined it.

HORACE C. PORTER: The rate of oxidation varies between very wide limits for different coals. An apparatus so designed that oxygen may be continually supplied to the vessel containing the coal at such a rate that the pressure remains constant, gives much higher rates of oxidation than appears when the action takes place in sealed bottles. Answering Dr. Day's inquiry, the oxygen-absorbing action does develop heat. On exaggerating the conditions by admitting pure oxygen to a bottle of a certain coal kept at 40°C., the temperature of the coal itself rose 15° in four hours. High moisture coals often appear most dangerous for heating spontaneously but the heating begins probably after a large proportion of the moisture has evaporated.

The Bureau of Mines investigations along this line support the conclusions of M. Taffanel with gratifying agreement.

#### Burrell and Seibert. Composition of Natural Gas Gasoline. (Appendix, Vol. XXV, p. 637.)

E. S. MERRIAM: The gasoline producing capabilities of a specimen of natural gas depend primarily upon the amount of higher hydrocarbon vapors such as butane, pentane, etc., which are present. The precise analysis of a mixture of five or more gaseous hydrocarbons cannot be made from combustion data,

# XXVII] Discussions: Section Vc. Fuels and Asphalt

nor from any other data at present available. The following method has been used in the analysis of several hundred samples of gas and found to give results of value in estimating the probable amount of gasoline forming vapors; a small absorption bulb similar to a Liebig potash bulb is charged with five cc. of olive oil. This is saturated with natural gas and the whole weighed. A connection is made with a Hempel pipette and burette containing 100 cc. of the gas to be analyzed. The gas is passed back and forth until no further diminution in volume is noticed. The absorption vessel is again weighed. The increase in weight together with the volume of gas absorbed and the temperature and pressure readings give all the data needed to calculate the mean molecular weight of the vapor condensed in the oil. This has generally been found to be about 62, *i. e.*, between butane and pentane.

The condensation is, of course, incomplete; but from the figures thus obtained a fairly good idea of the probable yield of gasoline can be formed.

WALTER O. SNELLING: At the present time the liquid gas referred to is being shipped distances of several hundred miles by the company owning the patents covering its production, and while the freight charges for longer distances are considerable, they are not prohibitive. I cannot agree with the statement that the matter of freight will seriously limit the application of the new product. The gas is now being produced commercially in considerable quantities, and many new uses have been found for it.

I am pleased to be able to here make the first public announcement of an important property which has recently been found to be possessed by certain of the propane-butane fractions, produced by the new process of rectifying. Certain of these mixtures of propane and butane have been found to have remarkable anesthetic properties, and tests recently made indicate that a new and most valuable anesthetic is to be added to the small number of such substances that we know at present. Its very rapid anesthetic action, and the absence of unpleasant after-effects, shows its discovery to be most important.

Not enough tests have been made to determine its usefulness for major surgery, but for minor work, particularly in dentistry, it undoubtedly has a great future.

F. C. Phillips: The Determination of Soot in Mine Lamp Oils. (Appendix, Vol. XXV, p. 711.)

A MEMBER: I would like to ask Professor Phillips what the requirements are in the Pennsylvania law with regard to the flashing point of the miner's lamp. Is it a low oil or higher distillate?

F. C. PHILLIPS: It is a higher distillate; something less than 180.

P. H. CONRADSON: What would the flashing point be?

F. C. PHILLIPS: I think it must not get below 300°F.

A. H. ELLIOTT: What quantity of carbon do you get in the soot?

F. C. PHILLIPS: From a fraction of a milligram up to a number of centigrams. The method is not altogether satisfactory with higher percentages. The apparatus can take care of two or three tenths of a gram of soot. But the difficulty of the soot effect on the oil is so bad that it is hard to get the true height and the operator has to regulate the height of the flame. It takes one hour for the experiment.

A. H. ELLIOTT: How much carbon per cent would you get?

F. C. PHILLIPS: It has run up to several per cent in bad oils and  $\frac{1}{2}$ % makes a bad oil and the law requires 11/100ths of a per cent. But this percentage is bad. I think it should be brought considerably below that. I see no reason why the manufacturers should not produce oils that run considerably below 500/1,000ths of a per cent. Vegetable oils would easily run down to 1 to 2/100ths of a per cent.

Report of the Committee on Fuel Analysis. (Appendix, Vol. XXV, p. 41.)

E. J. BABCOCK: The suggested changes and improvements in the methods of coal analysis are very good but we need to go back of that to the methods of preparation of the sample before the regular determination of moisture. What we want in commercial work is an accurate and uniform method which will give the moisture as it is found in the car or pile or mine.

In the ordinary methods of preparation I am satisfied that there is a large loss of moisture. A variation of 2% or more is

### XXVII] Discussions: Section Vc. Fuels and Asphalt

not uncommon in wet coals. Our experience has led us to give special attention to the preparation of the sample before analysis begins. We reduce the car sample quickly from 50 to about 2 pounds placed in proper form of receiver and dried in hot air bath for twenty-four hours and then allowed to attain the atmospheric conditions and moisture determined. The whole sample is then ground to proper fineness and the regular chemical and moisture determination made. We thus get very uniform results and eliminate the moisture loss in preparation.

It would be well worth while for our committee to consider the adoption of uniform methods of preparation of samples of coal before methods of analysis are begun.

W. F. HILLEBRAND: With reference to the report of Mr. Holloway's committee the substance of which has just been printed by Dr. Lessing, I desire to call attention to one point which has not been sufficiently emphasized in the report. That is the absolute neccessity for the most rigid care on the part of all analysts to insure that the sample of coal undergoes no change in moisture-content in the process of transferring from the original container to the balance and during the process of weighing. The report tells us very little as to the way in which these operations were carried out by the different analysts. It is my firm conviction that the wide differences in the results of different analysts, which at first glance are very disheartening, are in many cases attributable to differences of procedure at this stage, whereby the samples lost or gained considerable moisture according as the atmosphere was drier or moister than it was at the time the samples were put into the cans. The figures on the board, taken from the paper by Mr. Badger and myself (Vol. VIII, p. 187) illustrate my point very clearly. They show that the coals (in equilibrium with the moisture content of the air in London) lost in all cases over 50%, and in some cases much more of the moisture when exposed to the winter air of Washington for comparatively that period of time; few chemists seem to be aware as yet of the magnitude and speed of the changes in the moisture content of coal that arise from changes in the humidity of the air.

W. A. Noves: The importance of the preliminary treatment of the coal emphasized by Dr. Hillebrand and others is very great

and must be the first point at which we should strike. It is useless to try to avoid errors of a tenth of a per cent in the laboratory determinations when errors of several per cent may be met in the preliminary treatment. The problem is much more difficult in the Dakotas with a moisture content sometimes reaching 30% or more than in Pennsylvania or West Virginia with a moisture content of 5% or less.

We should remember that coal is essentially a carbohydrate in its origin and that it is probably very difficult if not impossible to distinguish absolutely between real water and water which may result from the loss of hydroxyl groups and hydrogen of the coal. Also coal is a substance which has been kept for countless ages with exclusion of air and which has undergone profound chemical change which leaves it in a condition to be easily oxidized by exposure to the air. The loss at the end of one hour is simply a balance between loss of water and gain of oxygen, and the determination in that form must always be arbitrary and not absolute.

In the vacuum method the pressures must be below the vapor pressure of water and better down to 5mm. or less. Unless the pressures are checked by the use of a manometer and are kept very low, good results cannot be obtained. With that precaution the method is a promising one.

E. C. Uhlig. The Analysis of Water Gas Purification Materials. (Appendix, Vol. XXV, p. 765.)

۲

۲

۲

A. H. ELLIOTT: As I said on the previous occasion, the heterogeneous character of this material is the troublesome part of it. The method of oxidation by the Gerther method and also by the calorimeter bomb are probably the easiest to accomplish. The importance of the sulphur content to the gas engineer is quite evident. This material is put into the purifying boxes in large quantities and has to stay there many months. On some occasions I have known it to stay in the purifying boxes over a year. In large works where they are handling large quantities of gas, purifying houses are enormous structures and very often are one third of the entire buildings in the works. It is therefore very important that the material should be efficient and it should be constantly so. They have a way of opening the boxes

# XXVII] Discussions: Section Vc. Fuels and Asphalt

occasionally and taking samples to see how they are coming on. This has to be done in a very short time because they do not want to keep the box out of commission long and naturally a method which is rapid is one that has advantages. Mr. Uhlig tried a lot of these methods on a perfectly comparable scale. That is, the same material was very carefully sampled and he gave a very great deal of attention to it and worked it out properly. In my opinion the Gerther method was the best and the reason was because it was simple. We took a flask holding about 10 or 12 liters and suspended an old-fashioned deflagrating spoon that they use in elementary chemistry and to simplify the matter we had a fuse made of pure cotton, a cotton lamp wick. The fuse was started by a wire at the top of the flask. I modified that for the gas. The thing takes a very few moments, and 6 or 8 of these flasks can be used at once. Furthermore, the other method that he mentioned, the method of using barium chloride in the acid solution, we owe the use of to our friend Jackson and it has sustained its reputation very well. Some of these we had to do ten or a dozen times per day. We have lots of other things to do too. This simple method, the Gerther method, and also the method with nitric acid and the bomb method are the ones most practical and likely to give the best results.

E. C. Uhlig. The Determination of Tarry Matter in Water-Gas Purification Material. (Appendix, Vol. XXV, p. 769.)

٨

٨

ARTHUR H. ELLIOTT. This material which Mr. Uhlig has been working on is one of the bugaboos of the chemical laboratory of a gas works. It is made by taking planer chips, treating them sometimes with burned pyrites residue; a further method is by taking iron borings and gently oxidizing the mixture by exposure to air and water together with a little ammonia water the ammonia water of the works. It is very obvious that the method of manufacture complicates the question as to the character of the sulphur in it and yet it is important to know what sulphur is there and in a manner the amount of efficiency of

87

the material as a purifying material. Now Mr. Uhlig made it his business for a long time to try various methods of procedure and what he has told you has given you the results of his work. The simplicity of the carbon dissolving method is in its favor. But you must remember that we have also got there sulphate of iron, various sulphites and also some compounds of hydrocarbons. These are not so easy to determine and yet they are all derived from the sulphuretted hydrogen in the gas. He deserves a great deal of credit for the patience he has given to the work and it is to be hoped that others will work in the same direction. The material is produced in very large quantities in our large cities and unfortunately at the present time we have not been able to use it in chemical manufactures. It contains about 50 to 60% of sulphur and yet it is dumped into the marshes as good for nothing. The time is coming when we cannot afford to waste this material. I do not mean as gas manufacturers; I mean as chemical manufacturers. I believe in this city there are 4,000 to 5,000 tons of it thrown away every year. There ought to be a value attached to it in the conservation of chemical industry which ought to be utilized.

#### SECTION VD. FATS, FATTY OILS AND SOAPS

Arthur Lowenstein and Louis Boelio. Experimental Data on the "Cold Test" of Oil. (Vol. XI, p. 17.)

M. H. ITTNER: Dr. Lowenstein's paper emphasizes the importance of uniform physical conditions in carrying out empirical tests of this kind in order that the results which are apt to be greatly influenced by these conditions may not vary too widely. In the case of the coöperation work on titre test it was found that different operators frequently obtained very different results on the same samples due to a lack of uniformity of method, and a lack of uniformity in the cold test is also apt to give discordant results.

WILSON H. Low: The difficulties of getting up a cold test that will answer all purposes, and allow different operators to obtain fairly good checks on the same oil, are very great. This is owing largely to the fact that the ordinary animal and vegetable oils are not simple compounds, but are mixtures of various glycerides in more or less unstable equilibrium as regards their mutual solubilities. The stearine in particular appears to be held largely as a super-saturated solution, which of course is an unstable condition.

Various factors besides lowering of temperature will cause a deposition of the harder portions of oils. The size and shape of the vessel, and the material of which it is made all have their influence. Oils being very poor conductors of heat, the amount of oil taken for a test and the shape of the vessel it is put into has considerable influence on what will happen when this oil is subjected to a certain temperature for a certain time. All of these things have been spoken of and discussed many times, and I simply speak of them now that we may have all sides of the question fresh in our minds. It is very doubtful if it is desirable to have one general test for determining the congealing point of oil. One test, no matter how good, would probably not answer for all purposes. It is desirable though that whatever test or

tests are devised, they should be surrounded with such strict conditions that different operators could arrive at the same result without trouble. Probably two or three different forms of the test could be arranged to answer for the various uses to which oils are put. The whole subject is in a chaotic condition, and will remain so until those interested get together and make a serious effort to devise tests which will be satisfactory.

GEBHARDT BUMCKE: It will certainly be an improvement if the authors' efforts lead to uniformity in the method for which I have seen about half a dozen different prescriptions. But even with a uniform prescription for this method uniform results seem to me impossible on account of the many errors that adhere to this method. These are: the different condition of the "sample as delivered," the different thickness of the heavy glass of the 4 oz. bottle, the asbestoso r cardboard cover of undetermined dimensions, the temperature of the room, the varying temperature of the freezing mixture, the different character of the oils—some gelatinise, some crystallize, under vigorous stirring they sometimes form a foamy paste that will not flow at a temperature where the oil will be liquid if left alone—and last not least—the personal error.

This crude way of making the "cold test" has been abandoned in Germany some twenty or more years ago. A method which avoids all those errors as far as possible has been worked out and described by Professor Holde in his book "Untersuchungsmethoden der Schmiermittel, Fette u. fetten Oele."

I want to add that an oil that by the American method has a cold test of 20° F. will be solid at 20° F. if left alone, while an oil that shows 20° cold test by the German method remains liquid at 20° for one hour or more. It requires an oil of a cold test of between 12° and 15° F. by the American method to remain liquid at 20° F.

ARTHUR LOWENSTEIN: The paper under discussion merely represents some experimental data obtained, principally on one method during a general investigation of the subject of "cold tests." Heretofore there has been but little experimental data on the points developed in the paper. The authors do not feel that it will ever be possible to adopt one uniform method for the

# XXVII] Discussions: Section Vd. Fats, Fatty Oils and Soaps 91

"cold test," but three or even four methods may be necessary, depending upon the information desired, viz., at what temperature the oil will cease to flow, what temperature it will cloud, etc. A great deal depends on the definition of the term "cold test," and the object to be attained. In regard to the German methods we feel that the objections to them are just as valid as the objections made against the American methods. After additional data based on observation and experiment have been obtained coöperative work ought to be helpful in clarifying the situation.

Frank N. Smalley. Factory Method for the Determination of Total Fatty Acids in Cotton-Seed Foots. (Vol. XI, p. 31.)

۲

٨

۲

۲

M. H. ITTNER: Empirical methods of this kind are often helpful where the materials to be tested are of known origin and uniformly made, inasmuch as they give quick results and furnish a useful guide to further factory work.

J. Marcusson. Die Bestimmung des Seifengehalts Konsistenter Fette. (Appendix, Vol. XXV, p. 777.)

GEBHARDT BUMCKE: Everyone who has determined soap, especially lime-soap, in lubricating greases knows the difficulties which occur when the hot benzine-alcoholic solution of the grease is filtered to remove from it inorganic impurities. As the solution easily gelatinizes when getting cool, especially on the filter an addition of benzin-alcohol changes the proportion of oillimesoap-benzin and alcohol and the more benzin or the less oil is present the solubility for lime-soap is reduced, the latter being almost insoluble in the benzin-alcohol mixture. The consequence is, that part of the lime-soap is in the solution, another part in the precipitate on the filter and has to be determined in both. This is avoided in the new method of Professor Marcusson.

M. H. ITTNER: In the paper which Professor Marcusson presents, a direct method for the determination of soaps in mixtures of fats and oils is given, whereby the soap is isolated in a pure condition. Such methods when they lead to accurate results as this one seems to, are always to be preferred to indirect titration methods.

#### SECTION VE. PAINTS, DRYING OILS AND VARNISHES.

Godfrey L. Cabot. Carbon Black and Lamp Black. (Vol. XII, p. 13.)

G. W. THOMPSON: I would like to know what the composition is of carbon black. Mr. Cabot has given the composition of lamp black; I would also like to know if Mr. Cabot can give us any information as to the chemical reaction of carbon black; for instance, the action of nitric acid upon it.

R. E. Coleman asked Mr. Cabot if he could give any reason why some blacks would liven or thicken up in a paint, particularly with grinding japans.

H. A. Gardner. The Rarer Paint Oils. (Vol. XII, p. 33.)

٨

۲

۲

 $\langle \! \! \diamond \! \! \rangle$ 

H. WILLIAMS: I have heard Mr. Gardner's paper with much interest, as the Navy Department some time ago undertook rather extensive tests to determine the value of various oils for paint vehicles. These tests have lately been concluded and the results indicate that for exterior purposes on steel plates paints made with mixtures of certain oils show superior results to those made with linseed oil alone. One rather interesting fact is the very beneficial result small quantities of China wood oil appear to have on the wearing qualities of Soya Bean oil.

# L. F. Hawley. Wood Turpentines. (Vol. XII, p. 41.)

M. TOCH: Can wood turpentine be had which is to be regarded as chemically and physically the equal of sap or gum turpentine?

L. F. HAWLEY: Yes. One of the samples refined by us did

have the same physical and chemical properties as gum turpentine. But material like that can be made with difficulty and in small quantities.

Difference in composition between gum and wood turpentine on technical scale is very slight and due to the presence of small amounts of dipentene. There is probably no difference in value for technical purposes.

C. A. LUNN: Mr. King of Savannah was given a sample of steam distilled wood turpentine and a sample of gum turpentine. He could not distinguish between the two. Ordinarily there are differences in the wood turpentine lots because fractions are collected directly into the barrels, with the result that one barrel will contain a lighter fraction, and another a heavier one. In the improved methods now in use at the Yan Yan stores the wood turpentine is very uniform in quality.

Sp. gr., .865 to .867.

Time of evaporation, 12 to 15 minutes.

Flash point, 110°-112° or 115°F.

Distillation test: Initial b. p. 153-156°F. with 95% distilling over below 170°F.

Residue on evaporation, 0.6 to 0.9%.

F. P. VEITCH: We ought to define wood turpentine. As a rule, with gum turpentine, when well prepared, 90-95% distils below 165° to 170°F. Those constituents which boil above 170°F. cannot therefore be considered as turpentine. Hence it must not include dipentene or high boiling oils. These must be removed. If wood turpentine is properly refined within the limits of distillation, it agrees almost exactly if not exactly in composition with gum spirits. Dipentene also occurs in gum spirits, but only in the last distillate as the temperature rises and in the presence of wood chips. The latter may account for the presence of dipentene. When the last runnings are mixed with the whole distillate, the dipentene is very difficult to detect. This work confirms the work in Bureau of Chemistry and published in Bulletin 144.

M. TOCH: The U.S. navy specifications call for turpentine that flashes at 105°F. When the majority of lots flash between 98° and 105°F. the navy has rejected (in the past) lots of perfectly pure turpentine which flashed below 105°F.

The prohibitive price of turpentine has forced manufacturers to use substitutes.

Manufacturers now find that a 14¢ material can be made to do the same work as gum turpentine.

F. P. VEITCH: In defence of the U.S. Navy Specifications, I should like to say that 105° F. is chosen as the minimum flash point for turpentine because of the possible danger in storing turpentine of lower flash point in the storage rooms which sometimes become quite warm.

E. C. HOLTON: I am inclined to disagree with the chairman. Samples of turpentine give an average flash point pretty close to 105°F. I consider a sample which flashes at 103° F. suspicious.

J. A. WEIR: I could not find any difference between wood and gum turpentine when the former is well distilled. As a result of investigations carried on for quite some time, I am led to the belief that turpentine is not an aid to the drying of varnishes.

M. TOCH: In regard to the previous question, there is not much difference in safety between turpentine which flashes at 98° F. and one at 105° F. provided accidents due to negligence are avoided.

G. BUMCKE: When such differences occur, why not use the same apparatus as is used for petroleum distillates, the Abel-Pensky closed cup with conditions of flashing perfectly regulated.

A. H. SABIN: The odor of ordinary turpentine comes from the oxidation of pitch and dirt on the tree. We allowed a man to redistil some wood turpentine in our laboratory. We examined the samples, and then sent some of them to experts asking for opinions. We obtained conflicting reports regarding the value of the distilled samples.

In general, heavier solvents are better than lighter ones of the same class. While benzol cannot be called worse than kerosene, still heavy benzine is a better solvent than light benzine. Gasoline is a very poor solvent. The heavier petroleum distillates are much better.

Turpentine substitutes are essentially thinners. Wood turpentine is as good if not better than gum turpentine. Wood

95

turpentine is bad when it is acid (acetic acid) and causes trouble in paints. Odors can be controlled by distillation methods.

L. F. HAWLEY: In regard to fractionation, we have examined a large number of samples and no difference was found between the different barrels even when put directly into the barrels. This is due (1) to the fact that one run will not average more than  $1\frac{1}{2}$  or 2 barrels and (2) to the methods of steam distillation used. This gives little or no variation among the different lots.

Presence of dipentene is readily indicated by decrease in specific gravity and rise in boiling point. There is not much dipentene in gum turpentine because pinene does not change to dipentene before 200° C. or in the presence of wood chips. In ordinary gum turpentine the dipentene is present in such minute amounts as to be in capable of detection. The dipentene in wood turpentine need not be separated because it has no bad influence; then again, such separation cannot be done commercially.

C. H. Herty. The Naval Stores Industry, its Past, Present and Future. (Vol. XII, p. 101.)

M. TOCH: Have there been any investigations as to coloring matter of rosin? and has anything been done in reference to tree surgery?

C. H. HERTY: I never did work on that line so I cannot say. As to tree surgery, it is impracticable now because of the expense. New trees are less expensive in the South than tree surgery.

H. A. GARDNER: Was cement used for the pots for collecting turpentine?

C. H. HERTY: Cups are made of any sort of material, galvanized iron and clay are chiefly used in the southern United States.

J. R. CHITTICK: Would stumps turpentine refined have the same constants as other turpentine?

C. H. HERTY: The quality of wood spirits is just as good as the usual turpentine.

T. R. BURTON: As a means of fire preventive, has a wide strip of clearing ever been tried?

C. H. HERTY: This has never been attempted.

XXVII] Discussions: Section Ve. Paints, Drying Oils and Varnishes

Edwin F. Hicks. Shellac Analysis and the Detection of Small Amounts of Colophony in Shellac. (Vol. XII, p. 115.) 97

MR. BOUGHTON: I have tried the test in Mr. Hicks' first paper. There is a question in the color tests in regard to shade. At times in the Halphin test it is difficult to distinguish between the adulterants. Boiled linseed oil containing rosin on long standing could not be detected by Lieberman starch test, yet it could by the Halphin.

J. R. M. KLOTZ: Does the solvent used on the mixed gum have any effect on the constant (acid and saponification) values?

MR. GILLON: Has Mr. Hicks' method been tried on gum resins?

MR. WILLIAMS: I have been informed by a person who was employed in India in the export trade of shellac that practically no unadulterated shellac is exported, but that all shellac received in this country contains more or less rosin. I am rather curious to know if this is true and whether Mr. Hicks' method can detect such adulteration when made in the course of manufacture.

John R. M. Klotz. Benzol and the Coal Tar Distillates and their Application in the Paint Trade. (Vol. XII, p. 123.)

G. BUMCKE: Would too much benzol have a bad effect, and is the lack of oxidizing power in coal tar naphthas a detriment?

J. R. M. KLOTZ: Lack of oxidizing power in coal tar naphthas is a good thing. Resinous material in turpentine gives it its drying power. Too much benzol is a detriment.

M. TOCH: Benzol as a priming coat is of great assistance as it carries the oil into the fibres of the wood.

J. R. M. KLOTZ: Benzol is not used much over 30%, therefore it does not affect the paint.

V. P. Krauss, Cobalt Driers. (Vol. XII, p. 127.)

M. TOCH: Cobalt driers which are blue or violet in color are not active; only the brown ones are useful.

P. H. WALKER: How are the cobaltous compounds oxidized to cobaltic state?

V. P. KRAUSS: By blowing into the liquefied drier, cold, ozonized or oxygenated air. Solid oxidizers can also be used, *e. g.*, potassium dichromate, potassium permanganate, and sometimes manganese dioxide.

E. LIEBREICH: Oxidation alone does not explain the difference between the action of the lead and manganese driers on the one hand, and the cobalt driers on the other. Dissociation of the paint film by light probably takes place when cobalt driers are used.

V. P. KRAUSS: In regard to the ultimate effect on the paint film, there is no real difference between cobalt and lead or manganese driers. Cobalt does not seem to be as progressive a drier. Very little can be used. If too much cobalt drier is used the film remains tacky.

R. E. COLEMAN: When cobalt driers are used in boiling oils, is the resulting oil of heavy consistency and different from a lead and manganese treated oil?

V. P. KRAUSS: The bodies produced with a cobalt drier can be made lighter in color than with lead or manganese. The speed of drying is a little faster in the case of cobalt than otherwise.

M. TOCH: It may be added that  $1\frac{1}{2}\%$  of a cobalt drier is equivalent to 5% of a lead or manganese drier.

MR. KENNEDDY: Can cobalt treated varnishes be obtained from the gum resins?

V. P. KRAUSS: Good results can be obtained by using cobalt driers in varnishes, and less drier need be added.

MR. KENNEDDY: I have found that a varnish in which the cobalt is incorporated directly with the resin and oil in the course of manufacture is better than one in which the drier is added after the varnish has been made.

B. GOLDBERG: By adding acetate of cobalt to oils at the rate of  $\frac{1}{2}$  oz. per gallon at 480°F. and blowing with air at that

temperature for a whole day, a drying oil is obtained. It has a tendency to wrinkle on drying. Cobalt does not give a bodied oil as well as lead or manganese. Whereas a film with lead drier alone dries well throughout, a cobalt treated oil gives a film which dries at the surface but remains unoxidized at the bottom.

G. W. THOMPSON: How can cobaltic oxide act as a drier if it is inactive in the cobaltous state?

V. P. KRAUSS: I do not see any argument against the existence of a cobaltous organic compound which is oxidizable to the cobaltic state. In my experiments, I assumed that the cobaltous compound was oxidized to cobaltic.

M. TOCH: All acetate driers give the same peculiar results as those which Mr. Goldberg mentioned. In regard to the action of cobaltic driers, we must remember that the cobaltic compounds are good catalytic agents while the cobaltous are not. The reason for this is not known.

G. W. THOMPSON: What is the rate of drying of cobalt driers as compared with manganese driers alone? We must not forget that lead and manganese driers are very different in their drying action, the latter being much more powerful.

E. C. HOLTON: Is cobalt used alone, or in combination with lead? Has it the same money value as a lead manganese drier?

V. P. KRAUSS: For soya bean oil, cobalt is more efficient drier than any others; it costs a little bit more.

MR. KEELER: Which of the cobalt salts is the most efficient? Does the speed of drying vary with the amount of cobalt used? Has nickel been tried as a drier?

V. P. KRAUSS: The resinate, tungate and resino-tungate are most effective. By means of these fish, soya, and corn and cotton seed oils can be dried. This cannot be done with the lead manganese driers.

Within small limits, the speed of drying is proportional to the amount of cobalt used.

Nickel has been tried as a drier but does not seem to be as good as cobalt.

J. W. Lawrie. Painting of Modern Steel Passenger Cars. (Vol. XII, p. 133.)

C. A. PETERSON: What is the proper temperature for baking?

J. W. LAWRIE: The temperature for baking depends entirely on the kind of a vehicle'used for the particular paint in question. Each separate kind or brand of baking paint has a particular temperature at which it should be baked to give the best life and protection. If baked at too high a temperature then the film becomes brittle and often burned. At too low a temperature then the good effects of baking are not completely realized. It is necessary to determine for each paint its own best baking conditions both for temperature and time. In general the lower the temperature necessary to produce the internal changes in the vehicle the better the paint film.

MR. WILLIAMS: Do you consider the results obtained with the pigment separated from oils and then given the razor blade test as giving results which are comparable with what actually takes place with the pigment in the vehicle in the form of a paint on a steel surface?

J. W. LAWRIE: The tests of the pigment in a comparative manner with over 250 pigments and mixtures of pigments in these vehicles and applied on steel panels with exposure tests indicate that the results are the same if the razor blade test is properly carried out. Every test we have made in this way when compared with the razor blade test has shown results in accordance with the exposure tests. From these confirmations lasting now several years I have absolute confidence that the razor blade test is truly indicative of the exposure test, and that the relative value of any pigment as shown by this test is a fair measure of its value as an inhibitor of corrosion.

R. E. COLEMAN: Do you get concordant results from different shipments of paints which are of the same nature and from the same manufacturers?

J. W. LAWRIE: We have not found many pigments that are always uniform in chemical composition. Those pigments which are uniform do give closely concordant results. Tests made at

long intervals on the same pigment from the same sample of paint and tested as we frequently do six to eight months after the first test have always given results duplicating with wonderful accuracy the first results. The test on the same pigment is therefore repeatable in a quantitative manner. In this connection also the test is delicate. We have done a great amount of work on sublimed white lead. It is possible to obtain on the market white lead made by this process, the basic sulphate, which has the lead oxide in combination varying from 0% to 22% and the lead sulphate (counting other ingredients with it) from 100% to 78%. In order to determine which of these percentage of lead oxide (combined) pigments was the best for inhibiting corrosion we obtained samples of the pigments ranging from 0 to 22% lead oxide and made the razor blade tests. The results were astonishing. The 0% was an extremely strong accelerator of corrosion, the 3% oxide slightly less, the 7% still less, the 11% a mild accelerator but the 15% was an almost perfect inhibitor. However, when we tested the 22%, instead of the pigment becoming a better inhibitor as we would naturally expect, it becomes gradually again an accelerator of corrosion so that with 22% oxide the acceleration is about as much as with a 7% oxide. I might state here, however, that you must not think that the basic carbonate of lead is for this reason a better inhibitor of corrosion because the results show that it is in about the same class as the 7% oxide and is an accelerator in the same manner as the basic lead sulphate other than the 15% which is These results brought up the very natural quesan inhibitor. tion, "Why?" Applying the theory which I have brought out in my paper I found that electrically the 100% lead sulphate was actually positive or of higher potential than the steel and for this reason it should be an inhibitor of corrosion. Chemically, however, by hydrolysis lead sulphate is strongly acid and its acceleration of corrosion due to its acid properties is much greater than the inhibition due to its electrical properties. Therefore lead sulphate is a strong accelerator. Passing up to the higher percentage oxides at 15% we find that the pigment is neutral or slightly alkaline in its chemical properties and at the same time it is almost neutral in its electrical properties still, however,

being slightly positive; and so from both the chemical and electrical properties is inhibitive. The higher percentage oxides-22%, etc., are negative electrically and also slightly alkaline; but the negativeness is a greater factor than the very slight alkalinity and therefore the pigment is again an accelerator or at least not as good an inhibitor as the 15% oxide. The question of whether a pigment is an accelerator or an inhibitor is a very delicate one and it would be better to say in general that there is a difference in the value as protectors of steel from corrosion. The only neutral point which we have been able to suggest is that where the corrosion is stronger, due to the pigment, than is found by the use of water alone, under the same conditions, then this pigment could be called an accelerator, and where the action is less than for water alone under the same conditions of test, then the pigment is an inhibitor. This is more in the way of a suggestion and in our own work has been of some value. The conditions of test must, however, be rather definite to get comparable results.

# Erik Liebreich. Können Anstriche Rostfördernd Wirken? (Vol. XII, p. 143.)

P. H. WALKER: A number of tests were carried out by the Bureau of Chemistry on a series of pigments. Steel plates were painted with 1, 2 and 3 coats of paint and then exposed. In some cases, it was observed that one coat showed the better protection from rusting.

M. TOCH: I obtained patents in 1903 and 1907 as a result of experiments in the laboratory to prevent corrosion in iron and steel by the use of small amounts of alkali. A Portland cement paint was made. This was made by heating 85% pure clay and 15% CaCO<sub>3</sub> to red heat to form tri-calcic silicate. This material when ground with oils continually forms small amounts of calcium hydroxide. Thousands of tons of steel have been protected in this way.

Small amounts of alkali in paint are the most valuable means of rust protection known.

# XXVII] Discussions: Section Ve. Paints, Drying Oils

Four smokestacks have been protected in this way for the last six years.

When such a paint is coated over a surface from which the rust has not been quite entirely removed, the calcium hydroxide combines with the rust and forms calcium ferrite. This is generally acceded.

A. H. SABIN: What was the method used for determining the potential difference between the linseed oil and pigment?

E. LIEBREICH: e. g., A glass vessel containing linseed oil in contact with a solution of potassium chloride with a calomel electrode. Both of these were connected to opposite quadrants of a quadrant electrometer and the potential difference measured.

۲

#### A. Lusskin. Herring Oil. (Vol. XII, p. 155.)

۲

MR. FREELAND: In the drying of the fish oils mentioned in the paper, just what driers were employed?

A. LUSSKIN: Tungate and cobalt driers were used. I would rather not enter into a discussion of their composition since they will be the subject-matter of a paper by Mr. V. P. Krauss on Thursday.

R. E. COLEMAN: Were analyses made after blowing the oils, to determine whether any change had taken place in the amount of either insoluble bromides which could be formed?

A. LUSSKIN: That subject was not investigated.

A. M. AGNEW: Can menhaden oil be changed to an elastic substance on heating? This can be done with linseed oil. Does fish oil give such a result?

A. LUSSKIN: When linseed oil is heated to about 580°F. and kept at that temperature for a long time, polymerization takes place, and an elastic, stringy substance is formed. With fish oil, however, this cannot be done. By blowing fish oil an extremely heavy bodied oil can be produced, but the consistency of the polymerized linseed oil cannot be attained.

G. BUMCKE: Had you any means to determine whether the samples, with which you worked, were authentic specimens of herring oil? Have you found any means to determine the pres-

103

ence of herring oil in other fish oils, or vice versa? Color tests have been used for this purpose.

A. LUSSKIN: The oils examined were obtained from reliable concerns. It was assumed that they were specimens of pure herring oil.

I do not know of any method by which the various fish oils can be identified or determined in mixtures of fish oils. The color tests which have been proposed from time to time have proved to be absolutely worthless.

J. A. WEIR: Is there any way by which the nationality of the blown fish oil can be denied? Will a sample of deodorized fish oil remain so for any length of time?

A. LUSSKIN: I have not investigated that subject to any great extent.

G. BUMCKE: About fifteen years ago, when the price of linseed oil was very high, we used (in Germany) fish oils with linseed oil, cottonseed oil and tallow for making potash soaps which are much more in use there than here. The fishy odor could hardly be detected in the soap, but came back when used in washing. Goods, washed with such soap, even after being well rinsed in water and then dried, had a strong fishy odor.

J. C. Olsen and A. E. Ratner. Decomposition of Linseed Oil during Drying. (Vol. XII, p. 165.)

۲

٨

MR. CABOT asked if the amount of nitrogen and argon were determined before and after drying linseed oil to learn what amount of either had been gained or lost by exposure to the air. J. C. OLSEN: No such determinations were made.

J. A. Schaeffer. The Manufacture and Properties of Sublimed White Lead. (Vol. XII, p. 175.)

G. W. THOMPSON: I wrote several articles on the analysis of white paint, determining lead oxide by dissolving out with acetic acid, but lately we have found zinc acetate will dissolve lead sulphate, and the amount dissolved is in proportion to the amount of zinc present.

In addition to Dr. Schaeffer's reference to Dr. Toch's statement, I am informed that a Mr. Tuttle has a patent for making basic lead sulphate by the wet process. That is, by lead sulphate and litharge in the presence of acetic acid. The product it is claimed has the opacity of the basic sulphate. I have partially proven this to be true.

J. A. SCHAEFFER replying to Mr. Thompson's remark regarding a patent by Tuttle on a wet process for the manufacture of basic sulphate of lead. I can say that I am very much interested in this process though I have not as yet gotten the patent.

W. PLATT asked the question regarding the possible combination of the zinc oxide present in the sublimed white lead with the lead. I am of the opinion that there is no such combination, the zinc sulphide present in the original lead ore is not in combinaton and the percentage present depends entirely upon the way in which the zinc sulphide has been separated from the galena. A large proportion of the zinc sulphide by the process of manufacture is converted into zinc oxide and passes over as a fume, where being in a finely divided condition is intimately mixed with the sublimed white lead.

R. W. LINDSAY asks regarding the variation of the content of zinc oxide in sublimed white lead. This content of zinc oxide in sublimed white lead is very definite though I have come across some basic sulphates of lead, which have been placed upon the market as sulphate of lead, which do not contain the same percentage of zinc oxide as that found in sublimed white lead. This content will average within small limits about 5.5%.

The question is asked regarding the proportion of lead which is recovered as sublimed white lead and that which is recovered as pig lead. In answer to this I can say that this proportion depends entirely upon the method of manufacture and can vary over all limits. The most deficient process of course is that which gives the maximum yield of sublimed white lead.

C. A. PETERSON asked regarding the uniformity and fineness of the product. The product, sublimed white lead, is very uniform in physical size and must necessarily be so on account of its

105

method of manufacture, it being a sublimation process, which is carried out in the same way from day to day.

J. A. WEIR desired to know why sublimed white lead has not been more uniformly used in the past. Sublimed white lead, since its discovery, has had the struggle which all new paint pigments have had when placed upon the market. It has had to combat the prejudice against a new compound as against one which has been universally used, namely corroded white lead. This prejudice has been slowly overcome and during the past six years the exposure tests which have been made have shown the great value of this pigment as compared with other pigments. Since those exposures have been made the use of sublimed white lead has increased rapidly and we look for a still more rapid increase in the years to come. The prejudice against the compound as compared with other paint pigments has been entirely overcome and all paint manufacturers are realizing its great value.

A. W. Schorger. The Examination of the Oleoresins from Several Species of Pine Native to the Western States. (Vol. XII, p. 181.)

R. E. COLEMAN asked if any examination had been made of Douglass fir in Oregon, as to the amount of turpentine yielded.

J. Cruikshank Smith and Gaston de Pierres. The Technology of Varnish Manufacture with Notes on an Improved Scientific Process. (Vol. XII, p. 185.)

E. C. HOLTON: I would like to ask a few questions: Is this varnish being made at the present time on a commerical scale in England or elsewhere? Is the varnish thus made as durable, lustrous, elastic and hard as varnish made by the usual process? Do 100 pounds of gum used in this way yield any more gallons of varnish than 100 pounds of gum used in the old way?

#### XXVII] Discussions: Section Ve. Paints, Drying Oils and Varnishes

٨

Henry Williams. Modern Painting Methods in the Navy. (Vol. XII, p. 203.)

107

T. R. BURTON asked whether the U. S. Navy has experienced any cases of explosion of volatile emanation from paints in confined or enclosed spaces.

Gaston de Pierres. The struggle between White Pigments in Europe. (Appendix, Vol. XXV, p. 783.)

۲

۲

۲

G. W. THOMPSON: This is an exceedingly interesting contribution to the subject of paints. It would appear from information received by us that a large part of the opposition to the use of white lead in Europe has been due to the unfriendliness which has existed between the manufacturers there. In this country there is now a very friendly attitude among manufacturers. They generally recognize that all the pigments used in the manufacture of paints have their proper basis.

An important commercial consideration that must be borne in mind is that if zinc oxide were by law compelled to take the place of white lead, the price of zinc oxide would probably jump to 25 cents a pound. The reference to Norway and Sweden is interesting but would be more so if more facts on the subject were available. All contributions to this subject must be viewed in the light of the connection of the contributor.

Gustave W. Thompson. The Coating and Hiding Power of Paints. (Appendix, Vol. XXV, p. 795.)

R. E. COLEMAN asked if in using the disc machine, would a different tone color be obtained by painting the disc with zinc oxide instead of white lead.

G. W. THOMPSON replying said that probably there would be a slight difference in tone—not sufficient, however, to prevent a satisfactory comparison.

C. A. PETERSON: I too have spent a considerable portion of

my time in endeavoring to use the sectored disc machine in determining the relative strength of pigments.

I would like to ask Dr. Thompson what degree of accuracy he obtained with the instrument for in my experience the results by obtained method of rubbing out weighed portions of pigment and standard white with equal amounts of oil and the same amount of rubbing to both the standard and the sample under test are far more accurate than the results obtained by the disc machine.

#### SECTION VI A. STARCH, CELLULOSE AND PAPER

A. P. Bryant. Composition of Commercial Glucose (Vol XIII, p. 47), and A. P. Bryant and C. S. Miner. A Study of the Unfermentable Residue in the Hydrolytic Products of Starch. (Vol. XIII, p. 57.)

C. E. G. PORST: Mr. Bryant has used the ordinary commercial press-yeast and brewer's yeast for his fermentations. In a strictly scientific bio-chemical separation of sugars only pure cultures of yeast should be used, and fermentation should be carried on, under such conditions that all danger from infection is eliminated. Furthermore, I see from the papers that fermentation was very slow. This is natural, as Mr. Bryant did not add any yeast food in the form of phosphates and ammonia compounds, but had to depend entirely for yeast food, on the dead yeast cells.

In his sugar determinations Mr. Bryant has used the volumetric determination. I wish to call attention to the splendid gravimetric method worked out by Kjeldahl. This method eliminates many sources of errors in the reduction and we are able to determine in the indirect way, quantitatively two copper reducing sugars together.

H. Buel. A Study of some of the Physical Properties of Starches. (Vol. XIII, p. 63.)

۲

۲

۲

MARTIN L. GRIFFIN: In connection with the use of a viscosimeter in testing starches and their products, I would like to inquire whether the author of the paper is able to connect the adhesive qualities of such products, when used in pastes, with these tests?

Speaking in this connection as a paper-making chemist, I to comment at this time, that rosin, commonly used in sizing paper, is becoming more expensive from year to year, and the time is not distant, when a substitute, in part at least, must be found.

I would like, therefore, to present this problem to you—to so heat starch as to make a colloid suitable for sizing paper; or, if you please, to so treat half-stuff in the paper making heaters, by special processes as to hydrolize cellulose, which will of itself effect its own sizing qualities when made into paper.

G. M. MACNIDER: In connection with Mr. Buel's paper, I wish to call attention to the viscosity or fluidity of starches when boiled with water.

In the textile industry starch is used for sizing and finishing the yarn and cloth. In preparing the starch for use it is boiled with water and other ingredients, such as tallow and oils. As a number of different starches are used in this industry it is very important to have some method of determining the values of the different starches which will give results that are comparable to the mill practice. In the June issue of the Journal of Industrial and Engineering Chemistry, I published a method for determining the viscosity of starches which depends upon boiling the starch with water for a definite period of time and measuring the viscosity of the solution in a Scott viscosimeter. This method gives very accurate results and affords a very satisfactory means of comparing the value of different starches for textile purposes. In studying the effect of different reagents on the viscosity by this method it was found that a very small amount of alkali reduced the viscosity while a slightly larger amount increased the viscosity. As the effect of alkali on the viscosity varies with the different kinds of starches it would hardly be possible to obtain results which would show the comparative values of the different starches when the viscosities are determined on an alkaline solution of the starch.

McGarvey Cline and J. H. Thickens: The Effect of Variable Grinding Conditions on the Quality and Production of Mechanical Pulp. (Vol. XIII, p. 83.)

ALFRED LUTZ: Ich habe mit grossem Interesse die Arbeit der Herren Cline und Thickens gelesen. Die Herren haben sich ein grosses Verdienst erworben, indem sie alle die Einfluesse, welche bei der Holzschleiferei in Frage kommen, planmaessig erforscht haben. Ich setze hier als bekannt voraus die Untersuchungen, welche von Professor Ernst Kirchner in Chemnitz auf diesem Gebiete gemacht worden sind. Professor Kirchner ist insbesondere seit Jahren in Deutschland dafuer eingetreten, dass man bei der Holzschleiferei das sogen. Heissschleifverfahren anwendet.

Ich moechte nun auf einige Einzelheiten aus der Arbeit kommen. Die Verfasser wundern sich ueber die hohen Werte fuer die Festigkeit des Papieres in Tafel 13, die fast doppelt so hoch sind als bei Zeitungsdruck. Der Grund hierfuer liegt offenbar in dem Umstand, dass den Proben kein Fuellstoff zugesetzt wurde. Die Art der Papiermaschine und das Glaetten haben auf die Festigkeit nur einen verhaeltnissmaessig geringen Einfluss.

Weiter ist aus Tafel 13 zu ersehen, dass die Festigkeit einmal als Reisslaenge, das andere Mal als "Strength Factor" bestimmt wurde. Ich moechte hier auf eine Arbeit, ich glaube aus dem Bureau of Standards in Washington hinweisen, die zeigt, dass fuer genauere Untersuchungen nur die Bestimmung der Reisslaenge nicht der Strength Factor in Frage kommen kann. Ich glaube daher, dass man auch in Amerika frueher oder spaeter, wenigstens fuer genaue Festigkeitsbestimmungen an Papier, die Reisslaenge, nicht den Strength Factor zu Grunde legen wird.

Die Verfasser ziehen aus dem Konvergieren der Linien in Tafel 2 und 4 den Schluss, dass man Holzschliff mit einem geringeren Kraftverbrauch als etwa 50 Tages-Pferdekraefte fuer die Tonne von 2000 englischen Pfund niemals werde herstellen koennen. Dies mag fuer den normalen Schleifer zutreffen. Dagegen kann ich mitteilen, dass in Deutschland Versuche mit einem neuen Holzschliffverfahren im Gange sind, bei dem man schon heute mit einem Kraftverbrauch von etwa 40 Tages'—P. S. fuer die Tonne auskommt. Die Kraftmessungen wurden an dem elektrisch angetriebenen Apparat wochenlang genau durchgefuehrt. Ein besonderer Vorteil des Verfahrens besteht in der Moeglichkeit, auch Abfallholz zu gutem Schliff zu verarbeiten. Ferner ergaben die Versuche mit harzigem Holz, dass der nach dem neuen Verfahren daraus hergestellte Schliff sich gut verarbeitet.

Groessere Apparate sind zur Zeit in Bau und duerften in einigen Monaten in Betrieb kommen.

A. L. Dean and C. R. Downs. Antiseptic Tests of Wood-Preserving Oils. (Vol. XIII, p. 103.)

J. M. WEISS: The authors have taken some exception to my method of petri dish testing of preservatives for comparison of the antiseptic action of preservatives, as outlined in my communications to the *Society of Chemical Industry Journal* of February 28, 1911, and December 15, 1911, and by a change, namely, that of emulsifying the oils, they have obtained results that on their face would seem to indicate that water gas tar distillates are but very slightly inferior to coal tar creosote as an antiseptic, and even superior to the latter with its acids and bases removed.

As the latter day work on the chemistry of colloids has shown, when a material is emulsified, that is, reduced to a condition of ultramicroscopic fineness, the properties and action may be radically changed. The authors using oil in an emulsion, then, introduce conditions never found in practice, as the writer considers their experiments to have been on oils in the colloid condition, and in no way comparable to the condition in wood, where certainly it is not in an emulsified state, else it would be washed out. In my work, the mixture of oil and media was poured into a chilled petri dish, and coagulating instantly, had no chance to settle. The drops at largest were not in any case over a micron in diameter, and the majority were smaller than ordinary micrococci, so that a very perfect mixture can be obtained without the intervention of an emulsifying agent.

Other conditions of the experiment were such as to lower the resistance of the organisms, as in a plugged test tube the air circulation is largely cut off. This is also aided by the methods of planting and covering with a cap of agar.

The authors, too, take an indefinite amount of culture for each plant, and this, I feel to be a very undesirable feature, and one likely to introduce variations.

Of course, it is impossible to compare the authors' results

directly to mine, as we used different organisms, but I may say that in a paper by Mr. Howard F. Weiss, in the Forest Service of the United States Department of Agriculture, figures are given on similar tests, using *fomes crunosus*, a true wood destroyer, which completely check and confirm my own results.

113

I feel that with the growing interest in determinations of this kind in the wood preserving industry, that some standard method and some standard organism should be adopted generally, somewhat along the lines of the Rideal-Walker method for standardization of disinfectants. With such a method, different workers would obtain comparative results, and ones that should be concordant.

S. R. CHURCH: As Dr. Dean is not present, and Mr. Downs is engaged in secretarial work at one of the other sections, I have been asked to call attention to a typographical error in this paper, as printed in Volume 13 of Original Communications. On page 109, in the table of results of the second series of tests, sample "A" inhibition point should be below .1%, instead of below .4%, and sample "B," .15%, instead of .4%. (Print was accurate to copy. B. C. H.)

My only criticism of this paper is that the authors' conclusions are hardly justifiable, when they state that the difference in antiseptic value between coal tar oils and water gas tar oils appears to be of no great significance, and that oils distilled from water gas tar have a distinct value as wood preservatives. The latter may be proven true, but it does not appear to me to be a sound conclusion from this comparatively slight evidence, particularly as the results obtained by the authors are not wholly in accord with results of other investigators along these lines.

In regard to the tar acids or phenoloid bodies in coal tar creosote, I would call attention to the fact that their solubility in water is very slight, and that while carbolic acid is quite volatile, the bulk of the tar acids occurring in creosote oil are of much higher boiling point, and not more volatile than the other hydrocarbons in which they are found. This has been shown by Samuel S. Cabot in two papers recently published in the *Journal of Industrial and Engineering Chemistry*. Cabot has also indicated that some of the higher boiling phenolic bodies undergo a chemical

8

change, possibly due to oxidation, so that they do not afterwards respond to the ordinary test for tar acids, and it is more than likely that the apparent absence of tar acids in oils extracted from wood after periods of service, is due to the fact that they no longer respond to the usual test of extraction by caustic soda.

Newton has also obtained similar indications, as he found that the high boiling residues in oils extracted from treated wood had increased to a greater extent than was theoretically possible from concentration by evaporation.

Geo. Defren. The Presence of Maltose in acid Hydrolyzed Starch Products. (Vol. XIII, p. 111.)

۲

C. E. G. PORST: I have read Dr. Defren's paper with the greatest interest. He has succeeded in separating maltose from glucose in a biochemical way using *saccharomyces apiculatus* to ferment the glucose, thus leaving the maltose intact.

A similar method was first tried by Karl Amthor, Z. F. Physiol. Chem., 88. He examined beerwort. Later A. Ban and Elion tried Amthor's method and got negative results. Amthor again published a paper-Chem. Ztg., 1891-in which he showed how slowly saccharomyces apiculatus fermented glucose and he was not even sure that all glucose was fermented after several months fermentation. Looking at the specific rotatory power of the various carbohydrates in commercial glucose running from achroödextrine 192 to D-glucose, 52.8 it seems to me that there may possibly be room for other intermediate products than maltose. When Dr. Defren has eliminated the glucose will he then get pure maltose extracted with alcohol or will he get a mixture of intermediate products of lower and higher specific rotatory power than maltose? In other words, is maltose the only product, crystallizable from alcohol that is formed by the acid hydrolysis of starch?

I am sorry that Dr. Defren gives very few details in his interesting paper. I would like especially to hear how he carried out the fermentation and to have further information as to the identification tests he made. XXVII]

#### William Raitt. Bamboo Cellulose. (Vol. XIII, p. 219.)

E. SUTERMEISTER: I have had no experience with bamboo itself but might say that when I was in the Forest Service we made some experimental cooks on canes from the Southern cane-brakes. These were found to reduce easily by the soda process and the nodes gave no trouble so it was not necessary to remove them. The yield, if I remember correctly, was about 40-42% based on the bone dry weights, and the fibre was soft and of excellent quality, somewhat resembling esparto in its characteristics. This fibre bleached readily and appeared to contain practically no material of a pithy nature. It is my opinion that this fibre would form a valuable addition to our paper-making materials provided the raw material could be economically collected and handled.

E. Sutermeister. The Consumption of Caustic Soda in Cooking Wood and the Influence of this Consumption on the Yield and Bleaching Properties of the Fibre Produced. (Vol. XIII, p. 265.)

٨

۲

۲

A. B. LARCHER: Offering a brief discussion of Mr. Sutermeister's valuable paper, I think we must agree that his arraignment of the methods employed in the soda fibre industry is probably justified by the facts, and it would be well for the industry if more work of the character recorded here were done. I assume that in all cases there was an excess of the alkali used; that is, more than enough to enter into combination with the products of the decomposition. If there was a deficiency different weights of resulting material might accompany the same consumption of soda if the time and the temperature were varied. Experiments carried on under my direction upon maple and birch as well as spruce and poplar confirm in a general way the results of Mr. Sutermeister. The use of other alkaline compounds as well as caustic soda develops the fact that the wood is attacked and certain resultant products removed by a treatment which failed almost entirely to act upon the more resistant

bodies associated with the cellulose in the wood. This suggests the possibility of so combining a mild with a drastic treatment as to utilize more fully the properties of the alkali. Mr. Sutermeister's suggestion that the chemical examination of the black liquor during the progress of the cook, might yield valuable information has occurred to me, but when stationary digesters are used it is doubtful if a sample accurately representative of the mass of liquor in the digester could be obtained. On page 268 Mr. Sutermeister expresses the conclusion that in the cooking of wood the important point is to use up a definite percentage of caustic. I would supplement this statement by saying that so far as cooking is done in stationary digesters, it is also important that enough liquid be present to produce a "clean blow" that is, it should be possible to completely empty the digester at the completion of the digestion period. Considering now the conditions in a commercial digester the moisture in the wood may vary from 17% to nearly 50% which would result in a difference of perhaps 10 or 15% of the volume of liquid in the digester. The weight of dry wood may vary several percent, due to the size of chips and method of packing, and the sodium hydrate present may vary considerably on account of difference in degree of causticity, the percentage of non-alkali compound and the accuracy of the specific gravity tests by the workman with his hydrometer. The quality of the wood as regards decay also exercises influence. Until the weight of reagent is accurately proportioned to the weight of dry wood present and the volume of liquid added so maintained that the total volume in the digester including all water from the wood and from condensation shall be constant, we cannot say that the cooking of wood by the soda process is scientifically controlled.

A. D. LITTLE: Not long ago we carried on in the laboratory a series of experiments in the endeavor to fix upon some method of standardizing a commercial wood pulp and one of the first things which occurred to us was to test the crop of the commercial pulp uniformly for a short time with a weak solution of 1 or 2%or even a half of 1% of caustic soda at the ordinary temperature Now it would seem as though a pulp which does withstand the drastic treatment of the soda process would not show any con-

xxv11] Discussion	S: Section VIa. Starch, Cellulose and Paper
-------------------	--

siderable loss in weight by such a mild treatment as that suggested and just the contrary is the fact. We found that commercial pulp does sometimes lose in the course of a two or three-hour cook or boil as much as 40% of its original weight and that sulphite pulp would vary through a series of tests from 7 or 8%up to 40 and 50%. These results are satisfying indeed, but they were later on confirmed by one of the workers, whose names I unfortunately forget, at the Bureau of Standards.

H. R. RAFSKY: In the discussion of the foregoing paper, Mr. Little has given some figures that were obtained in his laboratory on the boiling of soda poplar pulp with dilute caustic soda solutions. His statement that a loss of material of from 20 to 40% is caused by this treatment, leads me to mention some experiments which we have made along this line with considerably different results.

We boiled several grams of our regular mill unbleached soda poplar pulp (whose bone-dry weight at  $105^{\circ}$ -, had been determined from a similar sample), with 1% caustic soda solution in a flask with a reflux condenser with sufficient liquid to avoid bumping. The resultant material was thoroughly washed, dried at  $105^{\circ}$  and weighed. Check results showed that this treatment produced a 2% loss, or that 98% of the original pulp was unattacked. So that I can say, at least, that the soda poplar pulp which we regularly produce and use in our paper must differ very radically from the material examined by Mr. Little.

E. SUTERMEISTER: I have noticed in connection with work on corn-stalk papers that the pithy material when partially separated from the fibrous matter and made into air dried hand mould sheets gives a very hard horny product which is practically ink- and oil-proof. These sheets shrink enormously on drying, sometimes as much as 25% of their original width and length. If now, this same fibre is dried by pressing firmly against a heated cylinder, as would be done in paper making, the shrinkage is greatly reduced and the dried product is largely lacking in the ink and oil resisting properties of the air dried sheets.

117

### H. F. Weiss. Tests to Determine the Commercial Value of Wood Preservatives. (Vol. XIII, p. 279.)

J. M. WEISS: I would take exception to one of the methods for determining decay in wood from fungus pit tests, viz., by loss of weight, as in my opinion this figure would be vitiated by losses due to volatilization of preservative. The ball method I believe to be good, and is useful as eliminating possible personal equation and bias.

I was gratified that the petri dish toxicity tests checked in all comparable cases some figures presented by me recently in a paper before the Society of Chemical Industry, and published in their journal of December, 1911. My work, contrary to that of Mr. Howard F. Weiss, did not include actual wood destroyers, and it is of interest that the effect of various antiseptics is relatively the same on different organisms. The general work shows that from an antiseptic aspect, the amount of creosote used in practice is certainly more than sufficient to prevent fungus growth.

S. R. CHURCH: This paper is of the utmost importance to those interested in the art of wood preservation, and opens up so many new lines of investigation that it has been impossible to prepare a comprehensive discussion in the brief time at my disposal since the paper was printed. At this time I can only express my general appreciation of the scope of the author's undertaking, and take up one or two points as subjects for criticism.

I do not think the author intended to state, as definitely as he did, that as a result of the toxicity tests it might be concluded that fifty times as much coal tar creosote was being injected as was necessary to prevent decay. And I must object to the use of the term "factor of safety" in this connection. I think it is just as erroneous to conclude from these toxicity tests that the amount of preservative necessary to inhibit fungus growth under the conditions of the test is sufficient to preserve wood in practice, as it would be to undertake to demonstrate that the theoretical B. T. U. contained in a given quantity of fuel could all be transmitted in the form of heat units to do certain work. XXVII]

To justify this use of the term "factor of safety," it would be necessary to demonstrate:

1. That perfect distribution of the preservative can be obtained when using minimum amounts. This is manifestly necessary for maximum efficiency, as it is now known that a quantity of creosote oil greater than one-fifth pound per cubic foot, if applied on the surface by brush or superficial dipping, does not, under severe conditions of service, satisfactorily preserve wood. It is obvious that a perfect distribution throughout the timber is impossible by present methods of impregnation;

2. That the preservative is permanent in its toxic and physical properties;

3. That fungi are not susceptible to the toxic action of the preservative when growing on wood, as in the medium used in the petri dish experiments.

As the reverse of 1 and 2, and no affirmation of 3 is shown in Mr. Weiss's own experiments, it seems unwise to use the term "factor of safety" in this connection.

Regarding permanence of preservatives after injection into wood, in connection with the evaporative loss of coal tar creosote and fractions derived from it, it seems to me that from a commercial standpoint, comparative evaporation tests of original creosotes, having different distillation ranges, are of much more value than tests of the separate fractions. To illustrate: tests made in our laboratories indicate that the lighter fractions, boiling below 205-210° C., and which are volatile in character, tend to carry off portions of higher boiling fractions.

As Mr. Weiss intimates that his paper is in the nature of a progress report, and that the experiments are to be continued, I would suggest that in future reports the distillation tests of each preservative be given for purpose of comparison, and that evaporation tests along the lines I have indicated, be made, to enable us to specify the amount of lower boiling fractions permissible, a matter that has been largely guesswork in the past.

119

#### SECTION VIB. FERMENTATION

Alfred Fischer. The Analysis of Hops as Basis for their Valuation. (Vol. XIV, p. 77.)

GEORGE DEFREN regrets the omission of hop oil as a criterion for the valuation of hops and urges the more careful study of the hop oil and hop tannin.

W. WINDISCH lays great stress on the amount of those constituents which are *really soluble* in the finished product, and recommends the strict differentiation between those bodies imparting bouquet and those imparting bitter taste only.

#### SECTION VII. AGRICULTURAL CHEMISTRY

Gabriel Bertrand. Emploi du Manganese Comme Engrais Catalytique. (Vol. XV, p. 39.)

A. RINDELL: Le sujet de la communication de M. Bertrand étant très important, il me semble opportun de lui poser ici quelques questions provoquées par la forme très abrégée du rapport présenté.

1.—Qu'est-ce qu'un engrais catalytique?

Est-ce un composé chimique qui influence d'une manière catalytique les réactions nécessaires pour transformer les composants du sol dans une forme assimilable, ou est-ce bien un agent intervenant dans les actions physiologiques de la cellulle.

Quant à moi, je ne serais pas disposé à ranger les catalyseurs de la seconde catégorie parmi les engrais.

2.—Est-il bien démontré qu'il y a eu une action du sulfate, comme le prétend M. Bertrand?

La preuve définitive ne saurait être donnée autrement qu'en cultivant des plantes dans un sol ou un milieu de culture absolument déprivé de manganèse, et en comparant la récolte d'un groupe de parcelles sans manganèse avec celle d'un autre groupe où l'on a donné du manganèse.

Le manganèse étant très répandu dans les sols ce qui est la cause de la présence si générale de cet élément dans les produits du monde organique—il semble à—priori peu probable que l'addition d'une quantité infinitésimale du sulfate, très vite décomposé, pourrait cercer une action catalytique en dehors de celle des combinaisons manganiques du sol même.

3.—Comment pouvons-nous savoir que l'action du sulfate de manganèse, si elle est réelle, est dûe à l'élément métallique du sel et non à l'acide sulphurique qui, lui aussi, assez souvent, se trouve présent en quantité très minime.

4.—Comment a-t-on prouvé que l'action du sulfate de manganèse ait une action catalytique? Cette assertion me semble être une hypothèse gratuite. En terminant, je voudrais faire remarquer qu'il y a un nombre d'expériences dont les résultats sont négatifs. Je voudrais spécialement rapporter ici ceux de M. Von Feilitzen, membre de ce congrès. Comment expliquer de tels résultats!

M. BERTRAND: 1. En principe un engrais catalytique apporte à la plante un élément qui est nécessaire à son fonctionnement chimique. Son action est donc directe; mais il peut agir aussi sur les constituants: bactéries moisissures, etc. contenus dans le sol.

2. Les expériences sur la sensibilité extraordinaire de l'aspergillus niger au manganèse suffisent à prouver que c'est le metal introduit sous forme de sulfate et non le soufre qui est actif.

3. Quand on obtient dans ces conditions rigoureuses, en élevant la plante dans une solution, il y a toujours effet positif du manganèse. Lorsque, au contraire, le substratum nutritif —par exemple la terre arable—renferme déjà du manganèse, les résultats sont irréguliers, tantôt positifs, tantôt nuls, selon la proportion et la forme du manganèse contenu dans le substratum.

4. Pour le reste, voir ma conférence sur le rôle des infiniment petits chimiques en agriculture.

۲

 $\langle \diamond \rangle$ 

P. E. Browning. The Conservation of Phosphates in the Urine. (Vol. XV, p. 41.)

F. K. CAMERON: In view of the fact that recent investigations by the Federal Government show that the country possesses enough phosphate rock to supply three times the present consumption for at least twelve centuries Professor Browning's suggestion is not so important from the conservation viewpoint. Nevertheless, it may have a considerable importance for production of a cheap phosphate.

I am led to wonder if it would not be well to follow with experiments using sulphate or other salts of lime, and with a view to conserving not only the phosphorus, but to stop the very important wastage of nitrogen compounds in the urine.

P. E. BROWNING: I did have in mind the great importance

the conservation of some of the other constituents present, but have not in mind any definite work along these lines.

H. A. HUSTON: The disposition of urine and such products is essentially a sanitary problem, and the conservation of phosphoric acid and nitrogen is a secondary one.

The chairman has shown that phosphoric acid is abundant enough to last twelve centuries, and every farm has enough nitrogen above it to permit a supply to be gathered by means of legumes.

The composition of the phosphate of lime recovered is not such as to make it suitable for use in the fertilizer industry for the manufacture of acid phosphate.

# F. K. Cameron. Concentration of the Soil Solution. (Vol. XV, p. 43.)

٨

۲

۲

A. RINDELL said he could fully accept the views of Dr. Cameron, and he wished to direct the attention of his colleagues to an especially interesting point in the paper read before the section. This point is the hydrolysis, which cannot increase the concentration to the degree demanded by the law of mass action. This concentration must be corresponding to the point of saturation of the absorbing compounds in the soil. But at present time we do not know anything about these compounds and their saturation. Here is a large and important field for future research, which should not be neglected.

## B. E. Curry and T. O. Smith. A Study of Soil Potassium. (Vol. XV, p. 51.)

 $\langle \! \! \! \rangle$ 

H. A. HUSTON: The facts presented in this paper are exceedingly interesting, but the conclusions seem to call for some comments. If the table relating to the hay plots be somewhat extended, we may discover that the field work reported is not a study of potassium in these soils but a record of the effects of nitrogen, since that element seems to have been the limiting one

in these soils. The nitrate of soda and the acid phosphate used have such a marked effect in releasing soil potash, as shown by the authors,—tables IX and XII, pp. 64—65,—that they might totally mask the effect of the muriate of potash. The nitrogen was nearly, if not quite all, recovered in the increased crop. The phosphoric acid supplied was in moderate amount while enough soluble potash was used to provide for more than double the maximum crop produced and to provide for about four times the increased crop over that on the check plat.

The potash releasing power of the nitrate used per acre was 155 pounds  $K_2O$ , and the gypsum in the acid phosphate used could release 63 pounds  $K_2O$  per acre, not to mention the releasing power of the acid calcium phosphate. In the extended table I have endeavored to show how the fertilization appears when translated into terms of 1,000 pounds per acre of a fertilizer formula,—the first figure meaning percent ammonia,—the second percent available phosphoric acid, and the third figure the percent of potash. The first set of formulas show what the mixtures of the fertilizer ingredients would analyze, while the second set of figures show the formulas after the possible released potash has been included. It will be seen that when this is included all the plots had vastly more potash than they could use and that there was really no plot without some potash.

Table IX, p. 64, shows that from the soils in question sodium nitrate in about forty days could release from 80 to 138 pounds  $K_2O$  from the top eight inches, while the amount of actual potash in the highest increase per acre, 2.03 tons on the light clay soil, was only 70 pounds, reckoning that this hay contained 1.72 %  $K_2O$  which is the average of all the hays reported on page 68.

The amount of nitrogen supplied was too small to permit the phosphorus or the potash to be fully utilized.

Notwithstanding these conditions, on the first four soils the potash was used at a profit. At \$40 per ton for muriate the potash used cost \$4.80 per acre and the increases due to it, reckoning the hay at only \$20 per ton, are \$11.90, \$18.20, \$6.35, \$6.76 and \$1.22.

The field tests certainly show that four out of five of these soils

Column No.	1	2	3	4	5	6	7	8	9
Nitrate Soda lbs	None		264	264		264			
Acid Phos. lbs	None		350		350	350			
Mur. Potash. lbs	None	240		240	240	240	1.52110		
Equivalent to 1,000 lbs. pre acre of		0-0-12	5-5-0	5-0-12	0-5-12	5-5-12		THE STORE	
Fertilizer could release Potash lbs Including this Potash formula be-			218	155	63	218	Apparent increase from		
comes 1,000 lbs. per acre		0-0-12	5-5-22	5-0-27	0-5-18	5-8-34	1		
							Nitro- gen	Phos- phorus	Potas
Yields tons.		20-0	Store 1	of the second			6-5	6-4	6-3
Sandy Soil	1.155	1.155	1.575	1.330	1.120	2.170	1.050	.840	.59
Light Sandy Loam	.945	.875	1.715	1.890	1.085	2.625	1.540	.735	.91
Light Clay Loam	.931	.805	2.660	2.415	.945	2,975	2.030	.560	.31
Heavy Clay Loam	1.505	1.330	2.537	3.110	1.910	2.905	.995	.205	.36
Heavy Boulder Clay	1.702	1.616	2.079	2.089	1.819	2.140	.321	.051	.06

are potash hungry. We fail to find any facts in the paper to justify paragraphs 12 and 15 of the summary on page 71.

Experiments conducted as these field tests were cannot be expected to give any reliable results until the expiration of at least ten years and probably not for twenty or thirty years.

In this paper conclusions seem to have been announced from five years' work and these conclusions are not in accord with the field results on which they appear to be based.

The suggestions in the summary for the fertilization of hay might be profitable for a short-time tenant but could hardly fail to prove disastrous to the landowner.

(See, also, Field Tests with Fertilizers, Original Communications, vol. XV, pp. 139-147.)

B. E. CURRY: In this paper the released potash has not been considered in the discussion of the results, when the practical application was considered. When the necessary amount of potash can be obtained without the addition of expensive potash salts it has not been considered profitable to buy them.

G. S. FRAPS: In the practical application of fertilizer experiments the matter of fixation of potash is not a consideration. The matter to decide is whether the soil responds to applications of fertilizer or does not respond. The farmer should make use of his soil potash, and if the acid phosphate aids in this it is so

much aid to the farmer. If the soil supplies sufficient potash, then the purchase of additional potash is a needless expense. The experimenter will make a mistake to select intentionally substances which will prevent the soil potash from coming into action.

## R. O. E. Davis. Comparison of Rock Grinding with Balls and Cylinders. (Vol. XV, p. 73.)

C. VON GRÜBER: With reference to Mr. Davis' paper on comparison of rock grinding with balls and cylinders respectively, I cannot quite agree with his conclusion as to the relative value of balls and cylinders and his arguments entirely depending on the amount of material adhering to the surface of the grinding parts, as there are many other factors to be considered in this question.

Principally, however, I want to discuss this paper in the hope of obtaining some statements of American manufacturers as to what fineness is required or regarded as necessary in this country in the grinding of phosphates.

Some years ago there was a considerable difference in this respect between the opinions of American and European manufacturers and while in Europe fine grinding was advocated, American manufacturers were employing considerably coarser grinding, which, as it seems to me now, was partly due to the roll-grinding principle so largely employed in this country.

Since then, however, roll or cylinder grinding has been introduced in Europe as well by the importation from the United States of what is commercially known as the Kent grinding principle. But there is still a considerable divergency of opinion as to what fineness actually should be employed for acidification purposes, and it would be very welcome to obtain some definite figures as to what residue on say 100 mesh is preferably employed here.

From my experiences there is no doubt whatsoever that the grinding by cylinders or rolls results in a much better product than the grinding by balls, disregarding what diameter these

balls may have, although it is a fact that for phosphate grinding the roll or cylinder mills are generally adjusted in such manner as not to give a very large amount of so-called impalpable powder, but rather a larger amount of finely ground but gritty material passing, for instance, 100 mesh with a small percentage of very fine and uniform residue on this screen. Many experiments by manufacturing chemists, particularly in Germany, seem to have proved beyond doubt that for the conversion of the insoluble  $P_2$  O<sub>5</sub> or in fact for any chemical reaction, finely ground materials with not too large a percentage of impalpable powder are best adapted, and it is probably this reason why in some instances, particularly in British manure works, we are still finding old millstone plants for fine grinding, with so-called edge runners, for the preliminary crushing as the product resulting from these machines comes very near to that produced by roll or cylinder grinding.

The question as to how much material is probably adhering to the grinding parts, in my opinion, has no particular effect in phosphate grinding excepting when the material contains an unusual degree of humidity; and in this case the roll grinding principle and the so-called bulk grinding seems to be even more advantageous as compared with ball grinding, because the coarser particles always contained in the mass of material passing between the grinding parts, assist in scraping off and cleaning the rolls or cylinders.

I regret very much the absence of Mr. Davis and I would have liked much better to discuss his paper in his presence, so as to obtain his view on my own opinion, yet I could not pass this subject entirely without stating my experiences in the hope of obtaining some data and facts on the grinding question of manufacturers in this country.

F. K. CAMERON: I should say that Dr. Davis undertook this work largely because of the growing use in this country of finely ground rock phosphate for direct application to the soil. It is generally agreed that machines of this kind should be sufficiently fine for the major part to pass a 200-mesh sieve.  $\hat{A}$  priori, we assumed that balls should be preferred to cylinders in the mills for passing this material. Our conclusions were contradicted

by some of the operators with practical experience which could not be disregarded. Hence, the experiments described in the paper just presented.

Mr. KITT asked, if the rock used by Mr. Davis was burned or raw.

ANSWER: Raw.

C. VON GRÜBER: I understand from Mr. Cameron's remarks that in this particular instance, the grinding of phosphates was not meant for the mixing with sulphuric acid to produce superphosphate, but for applying the finely ground rock phosphate direct to the soil and for this application the material must be ground finer and I suppose that a large percentage of so-called impalpable powder is very beneficent.

However, my previous remarks related only to the grinding of phosphates for the manufacture of superphosphate and as far as European countries are concerned hardly any other process can be considered.

R. O. E. Davis. Sponge Spicules in Certain Soils. (Vol. XV, p. 77.)

H. von FEILITZEN: In regard to the sponge spicules I can tell you that we have at the Experiment Station of the Swedish Association for cultivation of peatsoils in a great many samples of the soil and also in bogwater, found microscopic plants formed chiefly of silica (diatomes). Our botanist, who made the microscopic work, thought to have found that the diatomes are more frequent in bogs poor in lime than in those, which contained enough of this base.

H. von Feilitzen. The Fertilizing Effect of Palmaer-Phosphate on Peat Soils. (Vol. XV, p. 85.)

۲

A. RINDELL: I would like to tell you that I have made a field experiment on peat soil with a fertilizer very similar to the Palmaer-phosphate. This phosphate was a precipitated one made

from bones, containing three-fourths of its phosphoric acid in the form of bicalcic phosphate and one-fourth as tricalcic phosphate. I used it for timothy and clover, comparing it with basic slag and giving 50 or 100 kg.  $P_2O_5$  per hectar. The total effect was on an average for three years 25% in favor of the precipitate. In the first year this phosphate showed a much better effect than the basic slag, the difference being at least 40%; in the following year this difference decreased so that basic slag gave a somewhat better yield in the third year, but taking the effect of the first year, and the residual effect of the following years I had a difference of 25% in favor of the precipitated phosphate. These results are published in a German paper: "Mitteilungen des Vereins zur Foerderung der Moorkultur im deutschen Reich."

H. J. WHEELER: I should like to ask Professors Rindell and von Feilitzen if they experimented with "Hochmoor" or with "Niederungsmoor" soil, for the former is usually deficient in carbonate of lime and consequently acid; whereas the latter is usually not acid and is well supplied with lime.

If Professor von Feilitzen did not add an extra series of boxes with additional calcium carbonate as a check to show that lime was present in sufficient amounts it would seem possible, in case his peat soil was acid, that the better residual effect of basic slag meal as compared with superphosphate and with Palmearphosphate may have been due to the large amount of free and combined lime. On the contrary, if Professor Rindell used a soil well provided with lime or a "Niederungsmoor" of typical character, one would not be surprised at the quite different residual effects.

H. von FEILITZEN: As I said, the soil was very rich in nitrogen and also contained enough lime for the plants; it is also a "Niederungsmoor."

I don't think that the lime content of the basic slag has any influence, because the soil contained a sufficient amount of lime.

MR. STODDART asked: In what form was the 3% of lime in the peat soil; total CaO or was some of it CaCO<sub>3</sub>?

H. von FEILITZEN: Calcium Humate.

F. K. CAMERON: What is calcium humate?

<sup>9</sup> 

H. VON FEILITZEN: I do not know.

۲

MR. BROWN: This matter has interest for certain parts of the United States, in that in certain regions of crystalline rocks, notably northern New York, there are extensive deposits of apatite of low grade, and considerable production of apatite as byproducts of certain iron-mines. It also happens that these parts of the country are farthest from the large phosphate-rock deposits and are rich in water powers, thus tending to promote manufacture of this material in such sections.

The matter is of subsidiary interest in the regions tributary to the great rock-deposits, since there, the commercial availability of such a material would be determined by the relative cost of available  $P_2O_5$  in Palmear's phosphate and in raw ground phosphate rock.

G. S. Fraps. Relation of Active Phosphoric Acid and Potash of the Soil to Pot and Field Experiments. (Vol. XV, p. 99.)

MR. PATRICK: With soils containing calcium carbonate do you use more or stronger acid, in order to neutralize the alkalinity and still have  $\frac{N}{5}$  acid to act upon the remainder of the soil?

G. S. FRAPS: We do not correct for the acidity in our work. It is not necessary to make such correction.

A. RINDELL: (1.) May I ask, what is phosphoric-acid, soluble in one-fifth normal nitric acid?

(2.) The content of phosphoric acid obtained in this manner cannot have any general significance and can especially not give us any record of the solubility of the phosphoric acid in the soil. We can get out the solubility only when different quantities of soil are treated with an equal amount of solvent. When we proceed in this manner the concentration of the solution (f. i. in the  $\frac{1}{5}$  normal nitric acid) is increasing with a certain point, from which there is no more increase. This point makes the concentration of the saturated solution, and only this concentration gives the measure of a solubility. In a paper "Ueber

Loeslichleitsbestimmungen in der Agrikulturchemie" (printed in Helsingfors, 1911) I have developed this idea, and I refer to this publication.

G. S. FRAPS: In answer to Professor Rindell I will say:

The work is based entirely upon experimental results, and not on theory. It is true that carbonate of lime complicates matters. When carbonate of lime is dissolved, it is impossible to tell whether the phosphates are outside or inside the soil particles. The fixing power of the soil effects results, since the extract represents the difference between solution and fixing power. Some soils may contain 200 parts per million of soluble phosphates, and yet give up only ten parts per million to the solvent. These and other factors have been discussed fully in bulletins of the Texas Experiment Station.

G. S. Fraps and J. B. Rather. Composition and Digestibility of Ether Extract of Hays and Fodders. (Vol. XV, p. 105.)

L. W. FETZER: Q. 1. Whether tests microscopical, chemical, etc., were made for phytosterol or cholesterol in the ether extract?

Q. 2. Whether lecithin or organic phosphorus were determined?

G. S. FRAPS: In answer to the question of Dr. Fetzer we will say that the total phosphorus in the ether extract was determined and calculated to lecithin. This paper is only an abstract of the work, which will be published in a bulletin of the Texas Agricultural Experiment Station in a few weeks.

The possibility of the presence of cholesterol and phytosterol was considered, but as the products had melting points much below that of these compounds, it is thought improbable that they were present except in traces.

P. F. TROWBRIDGE enquired if in the digestion experiments the various grasses were fed alone, and pointed out that in many cases the single grasses are far from a balanced ration and in practice are never fed singly.

Further, the digestibility of such single unbalanced feeds is

not normal and the results therefore are of but little practical value to the feeder.

G. S. FRAPS: The digestibility of single hays and grasses is no doubt affected by the other feeds, when fed in a balanced ration. This is a subject for other investigations. The digestion coefficients, however, are of great value to the feeder, and are used extensively in the calculation of balanced rations.

F. T. SHUTT: We have all realized the unsatisfactory character of the "ether extract," and especially is our information vague and uncertain with regard to that extract as obtained from course forage material. The work that has been presented in this paper is valuable, not merely in giving us the proportion of non-fatty bodies in this extract as obtained from certain grasses but in pointing out the depressing effect of the substances on the digestibility of the associated fats.

The research is one well worthy of continued attention.

B. L. Hartwell and P. H. Wessels. The Effect of Sodium Manures on the Percentage of Sugar in Certain Plants. (Vol. XV, p. 129.)

P. F. TROWBRIDGE asked if the purity of the juice was considered and then attention was called to the fact that a liberal addition of sodium salts tends to decrease the purity of the juice in sugar beets.

H. A. Huston. Field Tests with Fertilizers. (Vol. XV, p. 139.)

G. S. FRAPS: In my opinion, the fertilizing materials used in a plot experiment should be such as are ordinarily used by the farmer, such as acid phosphate, nitrate of soda, etc. If these materials liberate potash, so that the soil does not respond to potash fertilizers, the result is in accord with farm practice. If, however, the experiments are made with materials which do not liberate potash, as advocated in the preceding paper, so that

the soil appears to be deficient in potash, then the results are not in accord with farm practice. The farmer uses the materials which liberate potash, and does not need to buy potash, but the experiments indicate that his soil needs potash. Hence, the results are not correct. The experiment indicates a need for potash which does not exist. It is no justification for such a method of experiment to say that the soil will need potash at some time in the future. When that time comes, the need should be supplied, but in the meantime, the farmer should not be advised to purchase potash which he does not need. It is out of question to use in a fertilizer experiment materials which may indicate the soil to be deficient in potash, when it is quite possible that other materials, ordinarily used by the farmer, will show that it is really not deficient. The soil potash should be utilized as fully as possible, and then only supplemented with fertilizer potash, if needed.

H. A. HUSTON stated that the experiment station men should lead rather than follow agricultural practice, and that in a scientific experiment care should be taken to exclude confusing factors, and that it was the business of the investigator to not only obtain results but to put a reasonable interpretation upon them.

There is a marked distinction between a scientific experiment and a demonstration of the effect of this or that substance or group of substances.

G. S. FRAPS: The paper as read refers to practical fertilizer experiments rather than to purely scientific experiments. Any investigator knows that it is his duty to lead, but it is also his duty not to mislead, and he should not use materials which show the soil to need potash, while the farmer actually does not need potash. A scientific experiment may use any material available, which may appear suitable to the end in view.

H. A. HUSTON stated that since the mention of potash seemed to cause some irritation it might be well to discuss the form of nitrogen used and that it must be obvious, even from the standpoint of the men who advocate the use of the materials that the farmer uses, that in those sections where cottonseed is almost the only form of nitrogen used, nitrate of soda would not be the correct thing to use in soil-testing, notwithstanding its high value in agricultural practice.

B. L. HARTWELL: There seems to be an idea expressed in the paper of the last speaker that the use of nitrate of soda and acid phosphate in connection with soil tests is unwarranted, and yet these are not only the materials actually used by the farmer, but at present prices they are as cheap sources as exist in available form.

It is not denied that the effect of these materials is not limited to that of the nitrogen and phosphorus which they respectively contain, nor is it the object of such field tests to ascertain other than the requirements of soils for commercial manures regardless of whether their effect is direct or indirect.

H. A. HUSTON stated that the matter was discussed at the VII International Congress of Applied Chemistry and it was agreed that were Rothamsted to inaugurate new experiments such confusing factors could be avoided.

H. von FEILITZEN: In all parts of Sweden we have carried out field experiments to show the farmer if the soils need N,  $P_2O_5$ and  $K_2O$  and we do that in the following way:

We have six checkplots fertilized and then three control plots of each of the following:

Nitrogen Phosphoric acid Potash Nitrogen+phosphoric acid Nitrogen+potash

Phosphoric acid+potash

Nitrogen+phosphoric acid+potash

The experiments have shown that most all soils need nitrogen, most of them phosphoric acid, and about 30-40% of the soils (all peat soils and part of the light upland soils) potash.

F. T. SHUTT: Unfortunately I was not present when Dr. Huston's paper was presented and therefore I cannot offer any criticism thereon, but from the discussion on that paper this morning I am led to say that the practical use of fertilizing materials is primarily for the profitable increase in the yield of crops.

It is of course quite possible that certain nitrogenous and phosphatic fertilizers liberate potash from their inert stores in soils that is, in certain classes of soils—but such liberation may be so slight that the application of potash may still be beneficial and profitable.

### F. W. Morse. Some Effects of Fertilizers on the Growth and Composition of Asparagus Roots. (Vol. XV, p. 191.)

٨

J. J. MACHATSKE: What is the effect of the nitrogen of other ammoniates, such as ammonium sulphate and calcium cyanamid on the composition of the asparagus plant, as compared with the effect of nitrogen of sodium nitrate?

F. W. MORSE: The experiment as planned, included no nitrogenous chemical in comparison with nitrate of soda, therefore, I cannot say anything about the effect of ammonia salts.

A. Rindell. Remarks on the Theory Concerning the Action of Fertilizers. (Vol. XV, p. 209.)

F. K. CAMERON: I would suggest that to Professor Rindells proposition should be added the statement that in fact every factor of the soil affecting crop production is dependent on every other, and that no one changes without corresponding changes in all others; furthermore, all these factors are continually changing. Consequently the relation of crop production to the soil is a dynamic function of dependent variables only.

A. RINDELL: I can accept the remarks of Dr. Cameron and concede that the factors of soil fertility are not independent ones. But if we wish to progress we must, for a first approximation, treat some of these as independent ones, else the problem becomes so complicated, that it is impossible to solve it.

W. O. Robinson and W. H. Fry. The Use of Ground Rocks and Ground Minerals as Fertilizers. (Vol. XV, p. 215.)

A. S. CUSHMAN: I have taken great interest in this line of experimentation, and have published a number of papers on it from time to time; notably, a bulletin which I published in cooperation with the Bureau of Plant Industry, U.S. Department of Agriculture. My investigations were carried on over a period of about four years, and to me they were of great interest. I wish to say very emphatically that I am not recommending the purchase by anyone of fine ground rocks or minerals as fertilizers except for experimental purposes. I am, however, free to confess that in some isolated cases when ground rock was used as fertilizer very extraordinary results were obtained. All finely ground rock contains a great deal of material which one could only best describe as ultimate fines. Of course, it should be remembered that material in passing through the 200-mesh sieve still has a wide range of different sizing in the particles. The range is between that size of grain that one might adopt the name ultimate particle for, up to those which just manage to squeeze through the meshes of the 200-mesh sieve.

Now, let us suppose that one of our 200-mesh powders consisted entirely of particles which just manage to squeeze through the meshes of the 200-mesh sieve, whereas another product consisted of particles all of which could be described as having arrived at that degree of fineness beyond which it is not possible to go by any mechanical means. Any unit weights of two such powders although they might both be described as "200-mesh material" would vary enormously in surface area. And as decomposition and, *ipso facto*, fertilizing value depends on surface area this is an important point which is often overlooked.

Different powders when experimented with in regard to their fertilizing value, must be considered very particularly from this point of view, and not from the general point of view that they are either 100-mesh or 200-mesh material. Working along this line I have concluded that as a scientific proposition, without application to commercial fertilizers it is possible to produce

some surprising results, with no other source of potash food present except that which comes from ordinary so-called insoluble potash in finely ground orthoclase. Some of my experiments were made on land which was newly stumped. That is to say, it was land on which scrub oak had grown for many years. The land was divided into three plots of one-half acre each. One was given all potash in the pure carbonate salt form, another one was given ground feldspar to an equivalent amount of potash, and the third field was left blank. For two years we cut the crops from these experimental plots. For both first and second year the crop from the manure salt was strictly in the lead of the feldspar field but the crop from the blank field was stunted and I believe unsalable.

Unfortunately some one made a mistake the third year and scattered potassium carbonate on all the fields, thus ruining the experiment.

In conclusion, I wish to repeat that I am not in favor of the commercial exploitation of ground rock as fertilizer but I am interested in control experimentation along this line.

H. L. WHEELER: I wish to ask Dr. Cushman in what manner the feldspar was prepared? Whether it was prepared with a tube mill, or by some other method.

A. L. CUSHMAN: The feldspar was bought in Trenton, N. J., for about \$12 a ton, and was an extremely white, fine product such as is prepared in Trenton for the ceramic industry of this country. The material is usually hand picked, and then ground with the utmost care. The first grinding is done through burr stones, and the material then goes to a silex-lined tube mill, which is screened to about 180, I believe. The Trenton feldspar grinders do not claim that the material is 200-mesh, but they usually sell it as 180-mesh. Anyone who has ever handled it in the laboratory knows that it is much finer even than the manufacturers give it credit for being.

F. P. DUNNINGTON: In the use of the ground feldspar mentioned in this paper, the authors have no record of the exact variety of this mineral which was employed.

It is noted that some well-crystallized varieties of feldspar, as presented in certain granites are exceedingly permanent, resisting the action of the weather for ages; whereas other varieties of similar composition and (by fresh fracture) apparently as well crystallized, are soon hydrated and disintegrate upon exposure, even when in larger pieces.

H. von FEILITZEN: An der Moorversuchstation in Jönköping in Schweden sind jährlich seit dem Jahre 1886 bis zum heutigen Jahre Düngungsversuche mit feingemahlenen Feldspath (Ortholelas) auf saurem Hoch moorboden als Vegetationsversuche in Küsten und auch als Feldversuche zu den verschiedensten Pflanzen ausgeführt, und obgleich der Boden durch seine saure Beschaffenheit als besonders gut geeignet angesehen werden muss, war das Resultat fast ganz negativ. Die Versuche wurden bis zum Jahre 1900 von meinem Vater geleitet, und habe ich dann dieselben fortgesetzt.

In der letzten Versuchsreihe, die 11 Jahre verlief und wo auf denselben Parzellen jedes Jahr dieselbe Menge an Kali in Feldspath resp. Stassfurterkali (ausser Phosphorsäure) gegeben wurde, war die Wirkung des löslichen Kalis sehr hoch, diejenige des Feldspathes aber fast nicht bemerkbar. Die durchschnittliche Wirkung war im Mittel von 11 Jahren mit Feldspath nur rund 8% des löslichen Kalis.

William H. Ross. The Extraction of Potash from Silicate Rocks. (Vol. XV, p. 217.)

A. S. CUSHMAN: As I read it, Ross's paper is to be taken as a review of laboratory work that has been done by various experimentors during a number of years in the effort to find some economical way to attack the silicates, so as to make the potash content available for agricultural purposes. Most of the reactions reviewed by Mr. Ross were made a subject of special study in the laboratories under my charge during the years that I was employed in the Department of Agriculture. My various publications on the subject have also reviewed the efforts which have been made to apply the various modifications of the Lawrence Smith analytical process to the general problem of making silicate potash water-soluble. Although it does not seem to me that Mr. Ross's paper brings out anything new, it is unquestionably of some value to have this interesting subject reviewed and from time to time brought up-to-date. It is my belief that no effort should be spared by American chemists to make the country independent of every other country in the world with respect to the necessary supply of potash which is necessary to support our large and growing agricultural industry. No one realizes the importance of accurate laboratory data more than I. But I would point out that the greatest difficulties which attend the solution of this problem are found on that middle ground on which the chemical engineer is endeavoring to make laboratory data available on the mill scale of operation.

H. A. HUSTON: Much of what I may have to say applies to several of the preceding papers. It is a dull day when we do not have offered to us some process or deposit which is to supply the United States with potash. These are filed under the heading "Important if True."

Potash is potash wherever found and the only question is the cost of producing and marketing a unit of water soluble  $K_2O$ .

Many processes not mentioned in the above papers, but based on much the same ideas have been offered to manufacturers but found unprofitable on a commercial scale. The Pacific kelps were investigated from the same standpoint several years ago.

Replying to Dr. Cameron's question as to value of the  $4\frac{1}{2}\%$  potash product of the Cushman process. Such a product is not worth anything in the fertilizer trade because such a low grade is unsuited for mixing and will not bear transportation charges.

So far as the conservation question is concerned the United States proposes to prohibit the exportation of phosphates while Germany is quite willing to supply the world with potash at prices not less than the German buyer pays and has passed laws to effect this. While the United States talks conservation Germany really puts it into effect.

A. S. CUSHMAN: If I understand, the point raised by Mr. Huston, it is that he states that no matter how interesting our process may be, from a technical standpoint, the product which we have arrived at is quite valueless in any commercial sense. If Mr. Huston is right we have reason to be much disappointed

at the failure of our long and arduous labors. I would remind you, however, that in many cases things are being done at the very time that people are saving that they are impossible of accomplishment. I beg to take issue with Mr. Huston in regard to the value of our product. I cannot deny that based upon the unit market value of potash manure salts, that our product will hardly compete in price. I wish to point out, however, that the commercial aspects of the rock potash situation are hardly debatable before a gathering of this kind. I can, however, remind you that many of the manure salts which are at present available as potash fertilizers are very rich in salts of magnesia, and many growers have discontinued their use on that account. Canadian wood ashes is still in considerable demand as a potash fertilizer, in spite of the fact that it commands a much higher price in the market than the unit potash value would appear to justify; which only goes to show that the price is controlled by the demand. In justification of our material up to the present time I can only state that it has not as yet been offered for sale, but a number of hundred tons have been distributed by us, free of charge, to a number of the leading experiment stations and to individual growers. I might also add that we have paid the freight, so that if Mr. Huston is correct in stating that the material is valueless, it is at least a comfort to reflect that we will be the only losers. We hope, however, that at the next International Congress we will still be alive and in a position to report progress.

## Oswald Schreiner. Organic Soil Constituents in their Relation to Soil Fertility. (Vol. XV, p. 231.)

۲

H. J. WHEELER: It may be of interest to state that it has been found at the Rhode Island Station that barley will not attain a height of more than a few inches on soil which has received no fertilizer nor farmyard manures for nearly thirty years, whereas oats thrive very well under the same acid conditions.

In regard to wheat it seems to be slightly less sensitive than barley and barley is even less so than sorghum; rye is far less sensitive than oats and will give splendid crops with "complete" fertilizer where the acidity of the soil and the consequent need of calcium carbonate is very great, and yet barley will fail utterly under the same conditions.

Attention should also be directed to the fact that substances toxic or even helpful in solution may not act the same in the soil.

M. X. SULLIVAN: It is true as suggested by Dr. Wheeler that the toxic or beneficial action of substances are shown more easily in water culture than in soil. It takes a much larger quantity of material to show toxicity in soil than in water as has been found by the Bureau of Soils in the case of dihydroxystearic acid and other substances. By testing the beneficial or toxic action of a substance in the solution it strikes me that we get at its physiological effect directly without the intervention of the many factors that are present in soil culture.

If a soil is found to be poor in productivity and contains material which on extraction is toxic to the plants which do poorly it seems to me to denote that the substance or substances in question had something to do with the infertility of the soil. The lack of material as a rule excludes the possibility of making extensive tests of the physiological action of the substance when added to soils, but enough work has been carried on along this line to allow us to feel that we are interpreting properly.

H. von FEILITZEN: (1.) I would ask Dr. Sullivan, if the experiments with the different poisonous substances were carried out only during a short period of 20 days, or if the plants have not been allowed to ripen, because it seems to me, that the plants could recover, if they had been allowed to become mature.

(2.) I would also ask, if the poisonous substances are found in soils, where the plants grew well.

M. X. SULLIVAN: The physiological action of the various substances have been tested on the young seedling for about twenty days as a rule. As to the recovery of the plant I may say that the toxic material has been found in the field where the crop had matured but with a much lessened growth than in neighboring fields where the substance in question, that is dihydroxystearic acid was not found.

In answer to Dr. von Feilitzen's second question I may say that dihydroxystearic acid and other injurious substances have been found in a few cases in good soils. However, these soils also contain beneficial substances and after all the question of fertility as regards the rôle of the organic matter may be a question of balance between beneficial and harmful substances. With a large excess of beneficial substance it would be quite probable that a small amount of harmful substance would have no effect. Example of such relationship I could give quite readily from the field of human physiology, but time forbids.

J. J. Skinner. Effect of Histidine and Arginine as Constituents. (Vol. XV, p. 253.)

S. L. JODIDI: The classification of organic soil constituents into useful constituents and such that are detrimental to plant life can be based on the chemical constitution of the compounds, in addition to direct experiments, while the latter (pot experiments) furnish us with data enabling us to judge whether or not an organic compound is useful, the chemical constitution of the compound enables us to judge why it is the case.

A. Stutzer. Die Steigerung der Wirkung des Cyanamids auf den Ertrag landwirthschaftlisher Kulturpflanzen unter dem Einfluss von Eisenoxyd. (Vol. XV, p. 301.)

 $\langle \! \! \circ \! \! \rangle$ 

A. RINDELL asked if Professor Stutzer had determined the content of  $Fe_2O_3$  in his soil. There are very great variations in iron contents in different soils, and it seems to be possible, that the action observed by Professor Stutzer would not appear in soils rich in ferric oxyde, but only in cases where the content of iron oxyde is very small.

A. STUTZER: Den Gehalt des Bodens an Eisen habe ich festgestellt. Die Trockenmasse hatte ungefachr 2% Fe<sub>2</sub>O<sub>3</sub>. Durch Beimengung von Eisenoxyd (1 Teil Fe<sub>2</sub>O<sub>3</sub>; 1 Teil N. in Cyanamid) ist die katalytische Wirkung des Eisens viel besser, als bei der als bei der starken Verduennung des Eisens im natuerlichen Boden.

J. J. MACHATSKE: (1.) What was the composition of the commercial calcium cyanamid; in what form was the total nitrogen.

(2.) Have you tried other catalyzers besides the ferric oxid?

A. STUTZER: (1.) Ich habe nur Calcium-Cyanamid mit 18-19% N. angewendet, und kein Cyanid. Cyanid ist im Calcium Cyanamid des Handels nicht enthalten.

(2.) Mit Mangan habe ich Versuche in Toepfen (nicht auf dem Felde) gemacht. Mangan scheint ungefacht dieselbe Wirking zu haben, es ist in der Praxis deshalb nicht anwendbar, weil  $Fe_2O_3$  viel billiger ist.

P. F. TROWBRIDGE: How much  $Fe_2O_3$  should be added to the cyanamid.

A. STUTZER: 1 part N. to 1 part ferric oxide.

M. X. Sullivan. Biochemical Factors in Soils. (Vol. XV, p. 305.)

۲

H. J. WHEELER: It seems desirable to bring out the fact at this point that in our experiments at the Agricultural Experiment Station of the Rhode Island State College it has been found that on a soil made so toxic by long continued use of sulphate of ammonia that most agricultural plants fail to thrive and where many of them die almost outright, certain other plants among which are the cranberry, certain lupines, the Norway spruce, common white birch and watermelon thrive well; and the common sorrel (*Rumex acetosella*) and *Silene orientalis*, for example, thrive better than elsewhere. It must therefore be evident that in all discussions of toxic effects upon plants it it important to state what kinds of plants are referred to, since conditions toxic to one may be ideal for another and vice versa.

M. X. SULLIVAN: In answer to Dr. Wheeler's remarks I should say that the plant used to test the physiological action of the various substances extracted from soil has been wheat in the main, though other plants as cowpea, corn and rye have been often employed. In the various publications of the Bureau of

Soils it has been pointed out that the substances, which are injurious to wheat may be non-injurious to other plants and *vice versa* and that, as was brought out by Mr. Wheeler, the soil condition which is intolerable for one kind of plant may be very suitable for other plants.

J. W. Turrentine. The Composition of Kelps. (Vol. XV, p. 313.)

۲

۲

F. P. DUNNINGTON: While mention is being made of the potash in the sea-weeds of the Pacific Coast and of the coasts of Europe, it seems well to mention the occurrence of potash in the sea-weeds of the Atlantic.

In a recent examination, by a student at the University of Virginia, of several kinds of weeds collected at Kennebunkport, Me., two or three varieties afforded much potash and considerable iodine, while in other varieties no iodine was detected and little potash was present.

A. Vivier. Recherches su la Fumure Minerale de la Betterave a Sucre. (Vol. XV, p. 343.)

M. SAILLARD: Les résultats qu'a obtenus M. Vivier ne suffisent pas pour justifièr sa conclusion quand on fait des essais sur un même champ ensemeneé avec la même grain, on peut trouver des ecarts dans la composition minérale des racines. La vérté apparait même on fait les essaies dans plusieurs champs avec les variétés du richesse diffèrents. On voit alors, par le moyenne que les betteraves les plus riches, contiennents, dans leurs autres, moins des sonde que les betteraves de moindre rucgesse saccharine. Cependant, la loi n'est pas mathématiques.

Depuis que nous avons fait nos essais (1901 et 1902) j'ai cherché, dans la bibliographie Lucrière s'il y a des essais ou des résultats qui conduisent à la même conclusion que les nôtres etje puis dire que les publications faites par Dubrunfaut Lucrerie Indigènè (1867) sur la composition des mélasses par G. Ville et Pagnoul ((1874) par Wolf (1870 et 1880); par Pagrorul (1882)

par Pétermann (1885-1886); par Urban (1905-1906) in Bohème; par Andrlik et Urban (1902 à 1908) par Graftiare (1908) sur la composition de la betteraves à Lucre touts dans un cas. C'est touts à que je veuz rappeler pour le moment.

L. D. Haigh. A Study of the Variations in Chemical Composition of the Timothy and Wheat Plants during Growth and Ripening. (Appendix, Vol. XXVI, p. 115.)

۲

۲

٨

I. J. MACHATSKE: Is the amount of plant food removed from the soil by timothy, a constant for all kinds of soils, or is it a variable one?

J. H. WHEELER: In soil of the same type, on plots of land in close proximity to one another, the per cent of potassium oxide in the dry matter of the plants just past the blooming period, ranges from about 1% to more than 2.5%, according to the manurial treatment employed.

P. F. TROWBRIDGE: Our comparative analyses have been only upon commercial samples, where we find a fairly uniform composition.

In the samples reported in this paper, cut at different stages of growth we find a variation of more than 100% in the amount of potash taken from the soil.

S. L. Jodidi. Amino-acids in Soils. (Appendix, Vol. XXVI, p. 119.)

۲

DR. RINDELL mentioned that one of his assistants, Mr. Valmari, obtained similar results working with moor and soils. In the paper of Valmari is also shown a new method for the determination of small quantities of nitric acid in the presence of ammonia and organic nitrogen compounds.

This paper is published in "Verhandlungen der Agrikulturwissenschaftlichen Gesellschaft," Helsingfors, 1912. J. N. Le Clerc and J. F. Breazeale. The Effect of Lime upon the Alkali Tolerance of Wheat-Seedlings. (Appendix, Vol. XXVI, p. 135.)

F. W. MORSE asked if the authors obtained results similar to those of Osterout.

In reply Mr. Le Clerc said that Osterout claimed that such substances as lime acted as a dam in preventing the absorption of toxic substances by the protoplasm. The author had not determined microscopically whether NaCl was in the protoplasm or not but had simply analyzed the plants and found that these plants had absorbed as much (if not more) NaCl when lime was present as when lime was absent.

J. A. Le Clerc and P. A. Yoder. Soil Exchange Experiments with Wheat. (Appendix, Vol. XXVI, p. 137.)

 $\langle \diamond \rangle$ 

F. T. SHUTT: This inquiry as to the influence of environment (soil and climatic conditions) on the composition of wheat is one that has received attention at our hands in Canada for some years. Our results (which are to be found *in extenso* in the reports of the Dominion Experimental Farms) are in the main in accord with those which have just been presented.

We find that the protein content of wheat, and also of barley, is profoundly affected by the moisture content of the soil in conjunction with atmospheric temperatures during the filling out and early ripening stages of the kernel. Conditions which lead to a rapid development and speedy ripening of the grain (a comperatively dry soil and high temperature) tend to produce a hard grain with a high protein content, and on the other hand, an abundance of soil moisture accompanied by low temperatures during this period—conditions which lengthened the vegetative period resulted in a more or less starchy grain. Undoubtedly heredity is much less potent than environmental conditions during the filling out of the grain, in determining the protein content of the kernel.

J. A. LE CLERC: We have found in growing wheat on irrigated and non-irrigated soils in the same locality that the

protein content of the wheat on the irrigated soil was 12%, while that on the non-irrigated was 18%.

Likewise experiments in the greenhouse with pot culture, where the crops were treated with varying amounts of water, we obtained wheat with a far lower protein content where the soil was kept saturated than was obtained in the other pots which had been watered normally, thus showing that of the climatic conditions the amount of water seems to be the one which affects the crop to the greatest extent.

M. X. SULLIVAN: I should like to suggest that the general metabolism of the Kansas soil would be different in California than in Kansas, and vice versa; in other words, the microflora of the soil might be different, the organic constituents might be different and other bio-chemical factors influencing the cropproducing power, and general individuality of the soil would be different with wide variation in the climatic environment. Since variation in the organic soil-constituents would most certainly affect the growth and composition of the crop, it would seem that the soil plays some part in the question of the composition of the wheat, even though it may be secondary to the climatic environment.

It seems a truism to me to say that the potentiality of a New Yorker in New York is quite different from that of a New Yorker in Egypt. So it seems to me that the Kansas soil in Kansas would be different from the Kansas soil in California.

P. A. YODER: The question raised by Dr. Sullivan is a very pertinent one, and is a question which was also raised in our minds by the data in these experiments. We clearly have evidence before us that climate is the major factor in influencing the composition of the grain, and that the soil has only a minor influence. But whether the climate, in producing these differences, operates indirectly through the soil, *i.e.*, by changing materially the physical, chemical and biological properties of the soil, or operates more directly upon the crops, we prefer not to discuss upon the basis of the data before us. That during the first year there may be a difference. in the composition of the crops, assignable to the soil, which is equalized by the time the second year's crop or the third year's crop is being produced, was suggested by the data, but with only the data of a single series of years before us, we prefer not to attempt to draw a general conclusion on this question.

H. von FEILITZEN: I should like to ask Dr. Le Clerc the same question I did in London three years ago: what kind of soil he used from the different places. I only ask, because it is well known, that small grains harvested on soils rich in nitrogen such as peat soils are much richer in protein than from soils with a low percentage of nitrogen.

J. A. LE CLERC: In reply to Professor von Feilitzen I may say that the question of soil in these experiments played a very small part in influencing the composition of the grain, for example, Kansas soil in Kansas yields wheat with 22% of protein, while the same soil in Maryland and in California yield a crop containing only 10% or 11%. This was true likewise of the crops produced on the Maryland and California soils in Kansas, that is, crops grown in Kansas on these soils contained in the neighborhood of 22 to 23% of protein, while on the same soils in the other localities the percentage of protein was only about half as much.

P. F. TROWBRIDGE: In connection with the influence of climate upon the character of wheat it is of interest to note that in Huron County, Michigan, a wheat is grown that is used in the manufacture of wheat starch (a low protein wheat). In an adjoining county to the south within a distance of less than twenty-five miles the same wheat is grown not at all suitable for the starch manufacture.

L. E. Morgan. The composition of Beef fat as Influenced by the Age and Condition of the Animal and Location in the Body. (Appendix, Vol. XXVI, p. 155.)

۲

F. T. SHUTT: Some years ago in an investigation to learn the influence of the food on the character of the fat of pigs, we we found at the outset of the research, it was of the greatest importance that the fat analyzed, if the results were to be comparative, should in all cases be taken from exactly the same place in the animal.

C. R. Moulton. A Study of the Cost of Maintenance and Growth of the Changes in the Composition of the Mature Beef Animal during the Fattening Period. (Appendix, Vol. XXVI, p. 157.)

G. S. FRAPS: Do the figures in the maintenance ration represent protein as stated on the blackboard, and are they proteids? If they represent "protein," they should not be compared with Armsby's standard, which represents proteids.

P. F. TROWBRIDGE: The term "protein" used is the broad term including all nitrogenous bodies.

### SECTION VIIIA. HYGIENE

## S. Rideal. International Standards for Disinfectants. (Appendix, Vol. XXVI, p. 261.)

JOHN M. WEISS: I have had considerable connection in the past with standardizing methods of a similar nature to the Rideal-Walker test in connection with my work on coal tar and creosote oils, pitch, etc. In all these cases a merely approximate method is used and one which depends for its accuracy on the care given to the details by the operator. The standardization of disinfectants lies somewhat along the same lines and in considering the test we would care to adopt, it seems that we should select the one which, other things being equal, will be the easiest for the operator to manipulate.

I have had considerable experience with both the Rideal-Walker test as originally proposed and with the Anderson modification, and I feel that this latter is no improvement but is, in fact, a retrograde step. In the first place, it is very complicated and hard to handle and in the second place, under ordinary conditions such as obtain in the regular analytical laboratories, it is very hard to avoid contamination. Not everyone can have a laboratory ten or twelve stories from the ground or far out in the fields away from the dust of the city streets and stables. With open seeding tubes it is almost impossible to prevent contamination by bacillus subtilis. Of course, as Dr. Anderson suggests, you can in cases of doubt apply the typhoid immune sera as a confirmation, but this is hardly practical for the ordinary bacteriological chemist, moreover, adds unnecessary trouble to the test which is entirely avoided in the Rideal-Walker modification.

Some time ago the speaker, in collaboration with Mr. Walker, published an article in the *Journal of the Franklin Institute* on the Purity of the Phenol Control, and we showed there that in the ordinary commercial phenols sold as pure crystal carbolic acid there is sufficient cresol contamination to lower a disin-

#### XXVII] Discussions: Section VIIIa. Hygiene

fectant actually having a value of twenty to an apparent 15 or 16. This feature seems to me to be of a great deal more importance than a number of the minor objections Mr. Anderson makes to the Rideal determination, as the error from this source can be greater than any other.

Another point which I would like to bring forward as an objection against both the Rideal-Walker test and the Anderson modification, is the use of "typhosus."

In adding the culture to the disinfectant there is, in haste to do this at stated time intervals, danger of splattering and possible infection, I would suggest that this feature be obviated by reversing the order; in other words, measure out the amount of culture in the seeding tubes at your leisure, and then at stated intervals add the disinfectant.

Of course it does not make any difference if a drop of the disinfectant should splatter into the room, and some experiments I have made have shown that this does not affect the test otherwise.

It certainly is necessary that we have some such test for the standardization of disinfectants and the sooner workers all over the world get together and decide upon some test by which they can with certainty check each other's results the better for all concerned. We do not care whether this test accurately measures what the material will do, or how it acts practically in disinfection. No test would give us that information; but as a method of contrasting two disinfectants and determining their *relative* value, the test is of inestimable value.

In my opinion the Anderson modifications are mostly unnecessary and that the Rideal-Walker test in its original form, and as modified later by the authors, is all that is required. The suggestions I myself have made also should be given consideration, not as a change, but as additional precautions.

#### SECTION VIIIB. PHARMACEUTICAL CHEMISTRY

Miller and Baker. The Potency of First Year Cultivated Digitalis Leaves as Indicated by Physiological Assay. (Vol. XVII, p. 51.)

T. SOLLMANN: The necessity of a bio-assay for digitalis, etc., is self-evident and I believe that simple physiologic assays can be executed by the pharmacist the same way as chemical assays.

The cultivation of medicinal plants undoubtedly offers prospects of more uniform and perhaps stronger drugs and greater uniformity is very desirable.

JOSEPH KAHN: I agree with Dr. Sollmann that the standardization of drugs is of the utmost importance. It is, however, very difficult to elaborate the tests so as to make them practicable in operation, and obtain satisfactory results. The assay processes must be simple and rapid in operation to meet the requirements of the pharmacist who is to use them.

In cases where chemical assay processes are impossible of application, the use of physiological tests become imperative, especially in the case of potent drugs, such, for example, as strophanthus and digitalis.

I agree with what has been said by Mr. Raubenheimer.

Ditigalis is a glucosidal drug. The nature of the glucosides, forming the active cogstituents of digitalis, has been but scantily investigated. As glucosides are easily hydrolyzed by acids or enzymes, being resolved with the addition of the elements of water into simpler compounds, digitalis leaves should be kept away from moisture as much as possible, in order to prevent decomposition. XXVII]

Discussions: Section VIIIb. Pharmaceutical Chemistry

Ransom and Henderson. Belladonna. The effect of Cultivation and Fertilization on the Growth of the Plant and on the Alkaloidal Content of the Leaves. (Vol. XVII, p. 63.)

JOSEPH KAHN: The cultivation of medicinal plants is a problem of great interest, fully deserving the attention which it is beginning to receive.

Alkaloidal drugs usually contain several alkaloids exerting varying physiological effects. These constituents vary in amount according to conditions under which the plant may produce them. Climate, soil and other conditions produce variations in the constituents of plants. Besides the alkaloidal constituents there are other important constituents present which exert a therapeutic action.

With any increase in the alkaloidal content there is, probably, a corresponding change in the proportion of other constituents.

To determine the therapeutic value of a drug the quantitative determination of all important constituents is necessary. Man, with all his knowledge and skill, can hardly work so carefully as Mother Nature. Further investigations regarding the cultivation of plants are, therefore, necessary.

G. L. Shaefer. Quinine Alkaloid and Some of its Compounds. (Vol. XVII, p. 75.)

۲

۲

H. V. ARNY: The variations in the physical properties of quinine, as set forth in the paper, because of different amounts of water in the crystallized chemical, have counterparts in many other experiences of laboratory work.

One experimenter does a piece of work and gets a certain result; another equally skilled experimenter repeats the work and gets entirely different results and the frequent cause of discrepancy is the fact that the chemicals used by the two are not identical.

I was particularly interested in Mr. Schaefer's study of the inclusion of solvents other than water and alcohol in the crys-

153

tals of quinine. We are all, of course, familiar with water of crystallization and alcohol of crystallization but that other solvents combine with quinine in molecular proportions is indeed noteworthy and still more so are the facts deduced by the author that such crystallization blends as quinine, water and a hydrocarbon are indeed remarkable; while it is to be hoped that we will later have details of the crystalline compounds of quinine with the volatile oils he mentions.

#### SECTION VIIIC. BROMATOLOGY.

H. A. Baker. Special Adaptation of Iodine Titration Methods for the Estimation of Tin, Especially in Connection With Determination of Salts of Tin in Canned Goods. (Vol. XVIII, p. 35.)

W. S. ALLEN: May I ask what form of starch was used in the preparation of the starch indicator solution and what precautions were taken to keep these solutions constant?

H. A. BAKER: Water soluble starch from Eimer and Amend was used. Some of the solutions were kept constant by the use of preservatives; in general, however, the solutions were prepared every two days in order that they might be fresh.

H. A. Baker. "Springers" in Canned Foods, Their Causes and Prevention. (Vol. XVIII, p. 39.)

 $\langle \diamond \rangle$ 

۲

 $\langle \diamond \rangle$ 

L. P. BROWN: I would like to ask Mr. Baker a question, perhaps not directly bearing on the chemical matter of this paper, but one directly concerning the examination of food products in tin containers, and that is whether or not it is possible to distinguish a springer from an ordinary swelled or spoiled can by external examination.

H. A. BAKER: Yes, it is practically always easy to determine whether a bulged can is a springer or a swell. The gas pressure in a springer is usually very low, only amounting to two or three pounds per square inch; whereas, the gas pressure in a spoiled or swelled can is very high, fifteen to twenty-five pounds, except where the spoilage is in the incipient stages.

In that instance, it is necessary to incubate the cans for a few days. The springer, after cooling, will not show increase in gas pressure, but the spoiled cans will greatly increase in gas pressure. If the springers are immersed in ice water, the ends of the cans will practically always draw in and become flat. This is not true with swelled or spoiled cans, particularly after they have been incubated. It is, of course, always dsirable to cut a number of cans in any suspected case and examine them as to freshness and sterility, and also as to the fill of the can.

It is desirable and possible to so pack food that springers will be practically eliminated and this will very probably be the case in the near future.

L. R. FERGUSON: It is your opinion, is it not, that the difference in gas pressure between a springer and a swelled can is a practical guide as to whether the contents of the can are sterile or not, and may not these two varieties be differentiated by noting the different behavior of the two under temperature change?

H. A. BAKER: Yes, that is the idea when external examination only is considered, but this examination must be safeguarded by incubating sample cans and afterwards chilling them down to the original temperature or chilling them previously in ice water, and then chilling them again in ice water after incubation.

We have gas pressure gauges which will show the gas pressure in a tin container, or we can judge by the drawn in ends of the cans after they have been chilled in ice water.

## H. A. Baker. The Disappearance of Oxygen in Canned Food Containers. (Vol. XVIII, p. 45.)

۲

BRADLEY DEWEY: I should like to ask Mr. Baker if, from his experiments, proving that oxygen and hydrogen are never found together in canned food containers, we could not deduce that oygyen is used up by what is commonly known as depolarization of electrolytic couples. Hydrogen is, in this action, also used up and corrosion facilitated. Should not these results and experiments be taken to heart by the canners as showing them that they should have present the very minimum of oxygen, in order that this depolarization may be minimized and hydrogen may plate out, thereby protecting the tin plate from further corrosion?

H. A. BAKER: Yes, the statement is true that the minimum

٨

of oxygen or air should be left in the head space in a container. We have followed that through by packing food products in tin containers, exhausting in one instance, and sealing cold, or not exhausting in another instance, and we have always found that the salts of tin formed in the food product was more extensive in those containers in which the air had not been removed. Approximately twice as much salts of tin as is necessary will be found in the tin container in which a proper exhaust has not been used.

J. M. Bartlett. Eggs Preserved With Silicate of Soda. Vol. XVIII, p. 51.)

۲

F. T. SHUTT: In Ottawa we have been experimenting with preserving eggs, both in silicate solutions and in lime water over a period of eleven or twelve years. We have found lime water gave better results than sodium silicate solution. Probably this may have been due in part to not having had silicates of the proper composition. Those used by us were purchased in the open market. In some trials, better results were obtained than in others. No attention was paid to the composition of the silicates employed. We found that the whites of the eggs, preserved in sodium silicate, became yellowish and thin.

In the use of lime water we have obtained very fair, though not perfect results; a preserved egg is never as good as a fresh egg. We used the process of poaching in testing. Our results have always been strongly in favor of lime water as a preservative; in the appearance of the freshly broken egg and in the flavor of the poached egg, it always proved the superior preservative.

J. M. BARTLETT: Preserving eggs in lime is one of the oldest methods in use and was practiced in Maine quite extensively twenty-five or thirty years ago. A lime preserved egg has an entirely different flavor from one preserved with silicate of soda of the proper kind. My friend's trouble with his silicate preserved eggs was probably due, as he suggests, to the use of silicate of the wrong composition.

A silicate preserved egg, which has been kept but two or three months, is so good that it is difficult to distinguish it from a fresh egg. If kept much longer, the white becomes more limpid. We have no difficulty in obtaining a satisfactory silicate of soda from the General Chemical Company, when ordered under specification, as described in the paper. It must contain no free alkali, which is liable to go through the shell and affect the color and condition of the white. It is very essential that the pores of the eggshell be closed as soon as possible, and to do this, a silicate of the right kind must be used. When a fresh egg is boiled, air bubbles may be seen coming through the shell in many places, but silicate preserved eggs show nothing of the kind, unless holes are pricked in the shell with some sharp instrument. In the right kind of a silicate solution, the pores of the shell become closed in about four days, and to test this, an egg was taken which was in the solution but one day, and on boiling, bubbles of air could be seen coming from only two or three pores. On the second and third days, some eggs would show a few bubbles, but on the fourth day, all appeared to be closed.

William Frear. Food Standards—Their Functions, History and Forms. (Vol. XVIII, p. 129.)

٨

E. H. S. BAILEY: In some countries, more accurate work is not done and useful results are not obtained because of lack of the proper food standards. Some of us are familiar with the standards used in England, Germany and France, and with their results, and where the latter are not satisfactory, it is because they have no good accurate standards.

We cannot adopt foreign standards because they do not fit our conditions. An attempt to follow those standards would be extremely difficult if we tried to make them fit into our conditions. If given a chance, however, to bring out and report special standards, I believe we would grow up to those standards. It is not possible, with our limited knowledge at present, to make standards that will be positively permanent. It may be well then to make standards that might be called tentative standards which may serve until we more definitely solve the problem and arrive at more satisfactory and positive conclusions, after which our standardizing may be more perfect.

In our own case in Kansas, we might cite the effect of the standard on oysters which, while perhaps not a perfect standard, has at least raised the quality of oysters on the market very perceptibly from the beginning.

A. McGILL: I think there would be some difficulty in securing convictions under any tentative food standards in Canada. Our food law required that food standards shall be fixed; and if any cases were brought into court, under a tentative food standard, the court would be very apt to decline to pronounce judgment until those whose business it was to do so, had defined the particular food in a final and positive manner.

We also recognize a tendency to work down to our standards. For instance, country butter usually contains only 8 to 9% of water, whereas creamery butter always contains approximately 16% of water, the legal limit. This, of course, is due to the fact that water is cheaper than butter fat in Canada. We must take care lest, in legalizing standards for foods, we actually bring about the lowering of quality.

H. H. Hanson. The Packing of American Sardines. (Vol. XVIII, p. 131.)

 $\langle \diamond \rangle$ 

W. D. BIGELOW: Mr. Hanson's paper on the packing of American sardines deals with some points that are very interesting and pertinent to those engaged in food inspection work. The question of the bursting or breaking of the fish is rather complicated. If the fish are canned within a few hours of catching, and still show bursting, as they may from many causes, it would of course, be unjustifiable to consider them decomposed, even if their appearance was not inviting. On the other hand, when they are often held over a long period of time and transported one hundred or one hundred and fifty miles and decomposition accompanies breaking the packer often wishes afterwards that he had sent them to the fertilizer factory. In the

southern part of Maine it is possible to build weirs or pounds where they can be kept for some time and where they may purge themselves of "red feed." In some parts, however, it is stated that the tide is so deep that pounds would be very expensive and practically impossible. This industry is very important both to the consumer and the manufacturer, because it is very large and furnishes a large amount of food at a very low cost to a great many consumers although it does not compete with the French sardine industry whose product is roughly three times as expensive to the consumer. Last year the pack of sardines was very large, and large stocks were carried over. This year there does not appear to be much "red feed," and not so many are being packed, so the "red feed" fish are not used, and we shall have to wait over another year before we can get more data on this very important subject.

The placing of this industry on a more satisfactory basis is a question of great interest to the Food and Drugs Board, and of great importance to consumers and packers. There has been an attempt lately to pack American sardines in a more attractive manner and make them conform more to the French standards. This can be done very nicely and still the product will cost only about one half the amount that is demanded for the French sardines. These American sardines prepared in this manner are probably not inferior in any way to the French article. This class of trade is increasing rapidly.

H. H. HANSON: In regard to pounds for the sardines, I would say that there are a few in use in the southern part of Maine, and the fish are kept in them until the "red feed" is digested. In Passamaquoddy Bay and the whole northern coast, I do not think there are any pounds. The tide is too strong and the water too deep, and the bottoms, in many cases, would not permit the building of pounds. The pounds would need to be 50 or 60 feet deep and would be too expensive and impracticable.

#### XXVII] Discussions: Section VIIIc. Bromatology

Yuzaru Okuda. Quantitative Determination of Creatine Creatinine and Mono Amino Acids in the Flesh of Some Fishes, Mollusca and Crustacea. (Vol. XVIII, p. 275.)

P. F. TROWBRIDGE: In looking over this paper on the quantitative determinations of creatine, creatinine, and mono amino acids in fishes mollusca and crustacea, some points have occurred to me that might be well to mention. In regard to the water extraction of creatine it is stated in this paper that only three water extractions were made. We have found that at least eight are necessary for complete extraction. Also the paper speaks of concentrating the solutions previous to determination of the creatine. We have found that the concentration of the solution has a very important bearing on the results obtained and if the same concentrations are not reached duplicate results are impossible. It has, therefore, been our practice to evaporate to dryness. It is interesting to note that whereas creatine and creatinine are present in large amounts in fish generally, there are at most only traces in the mollusca and crustacea.

In regard to the distribution of the different forms of nitrogen, we do not think the record is clear. On page 278 the author states that the "flesh was extracted with water, alcohol, NaCl and KOH respectively." The results are tabulated in the order  $H_2O$ , KOH,  $C_2H_5OH$ , and NaCl and show that these are not successive extractions of the same sample. Yet in this same table he sums up these results and calculates the relative distribution of the nitrogen on the basis of these results. The discrepancy is still more apparent when we study his results for total nitrogen in the table on page 281. To illustrate, we find 2.655% total nitrogen in the Prussian carp and for his distribution of the total nitrogen in his table on page 279, he uses the sum of the results of his various methods of extraction or 4.347%.

F. C. COOK. This paper shows the presence of creatinine in large amounts in fresh fish, mollusca, crustacea, and in this respect these products differ from beef and chickens, which contain no creatinine but considerable creatine. In determining

the creatinine, the author has heated the solution in the presence of added acid and removed the coagulum. Here there is danger of any creatine that may be present being changed to creatinine, and consequently the creatinine results may be too high with a corresponding error in the creatine results. Our work with meat and chickens has led us to make many creatinine determinations and it is interesting to note that no creatinine is found in freshly killed chickens, while chickens held at low temperature for a period of fifteen months, show the presence of creatinine. In our work, we do not evaporate the solution to dryness, but apply the autoclave method as outlined by Benedict and Myers, which converts all creatine to creatinine in twenty minutes.

K. G. Bitting: Method of Determining Antiseptic Properties. (Appendix, Vol. XXVI, p. 353.)

WILLIAM FREAR: This interesting paper presents a method which may have high value for the classification of commercial antiseptics, inasmuch as it appears to present means of distinguishing biological conditions more delicate than those dependent upon other classes of organisms.

It remains, however, to be established that there is a parity of reaction between other organisms, for example, the bacteria and the penicillium used in this work. Since a large fraction of the organisms against which antiseptics are employed belong to divisions of organic life other than that of the fungi, it will be necessary to establish a parity of action in order that this method may be valid for all classes of antiseptics.

## SECTION VIIID. BIOCHEMISTRY, INCLUDING PHARMACOLOGY

Jowett, Pyman and Remfry. The Relation between Chemical Constitution and Physiological Action as Exemplified by the Glyoxalines, Iso-quinolines and Acid Amides. (Vol. XIX, p. 153.)

H. VIETH: Einfluss der Stellung der Substituenten auf die pharmakologische Wirkung wurde in letzten Zeit bei den Arsenderivaten studirt, die mit dem dioxydiamino-arseno-benzol isomer sind.

Durch ein neues Verfahren der Einführung von Arsen in organische Reste wurde eine grosse Anzahl neuer Isomerer dargestellt bei denen die Gruppen OH und NH<sub>2</sub> an anderen Stellen stehen als beim Salvarsan Ehrlich's. Es zeigte sich jedoch dass die meisten dieser Verbindungen stärker toxisch sind als das Salvarsan obgleich sie zum Teil stark parasiticid sind, so dass der Quotient  $\frac{c}{T}$  meist nicht besser ist als beim Salvarsan.

#### SECTION XA. ELECTROCHEMISTRY

Richard Amberg. The Function of Slag in Electric Steel Refining (Vol. 21, p. 7), and Albert E. Greene. Electric Heating and the Removal of Phosphorus from Iron. (Appendix, Vol. XXV, p. 191.)

JOSEPH W. RICHARDS referred to the valuable and extended discussion which had been held the day before at the International Congress for Testing Materials on slag inclusions in steel and emphasized that engineers are just beginning to recognize the great influence on the qualities of fine steel of the intermingled slag particles. Dr. Amberg's paper is an important contribution to this subject. This quality of the slag-its ability to clean out the small particles of slag-forming material from the metal, its unifying action, the scouring action—is something which is not properly appreciated in metallurgy. At the present time there are only three ways of meeting this problem; one is by regulating the composition of the slag as completely as possible. The other is to hold the metal in the furnace. The speaker had seen in Germany a 25-ton Bessemer converter charge blown for about twenty-five minutes, and then the converter turned, and the metal held in the converter another twenty minutes, as long as it could be held there before casting, in order to give a chance for the emulsion of slag and metal to separate, just like an emulsion of oil and water will separate after it has been stirred up. Now, the output of that great Bessemer converter and of the machinery was cut down, at least fifty %, in order to allow this rest of the metal in the converter simply to clean out the intermingled slag, and the cost of doing that was, therefore, exceedingly high. These reflections had led the speaker to a third solution of the problemnamely to hold the finished metal in an electric furnace melted for half an hour or an hour without any other treatment than letting it rest, and letting it stand and allowing the slag impurities to settle, comparable to the clarifying of muddy water, where the mud settles down, and gives these particles of slag and the aluminium oxide and silicon oxide, which are disseminated through

the whole body of the metal by the deoxidizing reactions, a chance to rise up into the slag and thus purify the metal. This leads close to the last point of purification of the steel. Removing nitrogen might be another one. This seems a very practical solution of the problem of removing the slag.

A. SINDING-LARSEN discussed the removal of sulphur during the first oxidizing period in the electric furnace.

MR. ROGERS referred to some experiments made by the American Steel and Wire Company on the inclusion of slag. They had held the metal in the bath for a short period of time, and also in the ladle as long a time as the temperature and conditions would permit. Then, in taking different sections from the ingots top, middle and bottom, and making microscopic examinations, it was fround that the period of time has a marked influence on the degree of inclusions of slag. However, they have not been able to determine exactly how much better steel with a very slight inclusion of slag would be as compared with steel of more inclusions of slag. The comparative differences were scarcely discernible in any process of test in the final article manufactured out of the two grades of steel. There is one difficulty in holding the bath for any great length of time, and that is the added expense. It is an enormous expense when it is taken into consideration that every minute counts in the production of steel on the final cost.

JOSEPH W. RICHARDS agreed that the additional cost of holding the steel melted for a time would be great if it was held in the refining furnace (converter, etc.). But the holding of the steel in an electric "holding" furnace requires only from 30 minutes to an hour at the most, and it can be a very simple furnace, simply for holding a dead melt of metal. The cost of holding the metal without any treatment, simply keeping it melted, without any labor put on it, will be from twenty-five to fifty cents a ton, according to the cost of power at the works. With thus added twenty-five or fifty cents a ton, the steel can be given that added freedom from intermingled slag which will show in steel used for high speed purposes. The tests of the engineers have shown a decided difference in the quality of the steel when great stress is put upon it, or when the requirements are very severe.

EDWARD R. TAYLOR referred to the practice of supplying the output of blast furnaces into a large mixer, primarily to equalize the differences in the pig iron produced from hour to hour in the blast furnaces. In an analogous way the steel finished in Bessemer converters could be run into a large tank and permitted to settle. As the first chemist of the Cleveland Rolling Mill Company (which was one of the predecessors of the American Steel & Wire Co.) he had met this question of slag inclusions in Bessemer steel very early in the day.

FRANK N. SPELLER agreed with Dr. Richards that the problem of cleaning the steel was a serious one, but the time of settling is not everything. There are one or two other factors which may be considered with a view to shortening the time required to clean the steel. First, the circulation of the metal in the ladle, and second, the nature of the slag on the furnace of the metal. It is part of the practice of his company to let a thorough circulation go on while the steel is being ladled. This circulation causes the scattered slag particles to gather together and remain permanently in the cinder and not become mixed up again with the steel. The nature of the slag has an important bearing on the result. Thev have made experiments in which they put some basic or acid cinder of a low melting point on the steel on the mold. The steel as a rule has considerable chemical circulation. In a few minutes that cinder will be saturated with the products of the oxidation of the impurities in the steel which would otherwise have been carried back into the steel if there had not been a proper cinder on the surface to absorb them.

MR. ROGERS agreed with Mr. Speller that the slag inclusions are very largely dependent on the condition of the slag when the steel is taken from the furnace, as well as on the rate of pouring. The viscosity and the physical condition of the slag have a great deal to do with the amount of slag inclusion. The question of time and the subsequent circulation are additional items of importance.

RICHARD AMBERG thought that the fact that Mr. Rogers' experience was chiefly based on wire production and on materials where the ingot had been stretched in its length direction, might explain some of his results. In that case, of course, the effect of ٨

slag in the finished product is not quite as harmful as in forgings or castings where transverse tests are to be made. In these cases the slag enclosures are much more serious with regard to quality of product. Finally, there is another important point. No matter how the steel is treated in the furnace and in the ladle, the question of pouring is at least equally important for good results.

W. D. Bancroft, L. V. Walker, and C. F. Miller. The Study of a Small Carborundum Furnace. (Vol. 21, p. 19.)

L. E. SAUNDERS doubted whether the paper contained much that was new. For instance, as to the first result of the authors (p. 32), that "a furnace has been devised in which it is possible to duplicate results with a satisfactory degree of accuracy," that had been done on a commercial scale very satisfactorily for the past twenty-five years or so. It would have been interesting to calculate in every experiment the watts per square inch of core area.

F. A. J. FitzGerald. Heat Losses in Furnaces. (Vol. XXI, p. 37.)

JOSEPH W. RICHARDS said that the problem brought forward in Mr. FitzGerald's paper was exceedingly important for all chemical and metallurgical industries. For the utilization of the energy in a furnace the rate at which the energy can be pumped into the furnace is very important. As the energy lost by radiation is practically constant with the time, the amount which is utilized in the furnace is increased by increasing the supply of energy to the furnace in the same time. In comparisons of the operation of two furnaces care must be taken to take the chemical reaction heats of the processes in both furnaces into consideration. If in one of them the reaction is strongly endothermic, it makes a considerable difference in the amount of energy which can be pumped into the furnace, on account of the energy which disappears as chemical energy absorbed. A fair comparison of the heat insulation of two furnaces working different processes

should therefore begin by first subtracting the heat absorbed as chemical reaction energy from the total heat supplied to the furnace. A point of considerable practical importance is the loss of heat from the walls of a furnace by convection of air currents. It is highly important that a furnace should never be placed where there is a strong draft. While in his calculations the speaker has usually taken the loss of heat by convection as proportional to the square root of the velocity of the air passing along the furnace, yet recent experience seems to indicate that it may be directly proportional to the velocity of the air current, so that the heat loss by convection may run up very rapidly if the furnace is exposed to a strong draft. As to insulating bricks, the speaker had seen a new material this summer in Europe, namely, aluminium nitride bricks which at temperatures of 1600° to 1800° are good electric insulators and good heat insulators.

Hugo H. Hanson and Warren K. Lewis. A Method for Testing the Mutual Corrosive Effect of Metals. (Vol. XXI, p. 43.)

٨

FRANK N. SPELLER asked as to the condition of the surfaces.

W. H. WALKER said they were emery-cleaned. The entire surface was cleaned and a portion painted over with bees-wax so as to leave a definite area exposed.

FRANK N. SPELLER referred to paragraph 3 on page 44: "In the atmospheric corrosion of most electropositive metals," and said that some copper-steels with a very low rate of solution are an exception to that rule.

C. H. Vom Bauer. Electric Induction and Resistance Furnaces (Appendix, Vol. XXV, p. 205), and Paul Heroult. Recent Developments in the Electric Steel Furnace. (Vol. XXI, p. 59.) Both papers were discussed together.

MR. ROGERS spoke of the experience of the American Steel & Wire Co. with electric steel for many different kinds of wires. While electric steel seems to have greater density than openhearth steel, yet the difference in the wire products is not so great as to justify the expense of the electric furnace refining treatment. According to their investigations the greatest usefulness of electric steel is in the manufacture of steel rails rather than wire products. As a general proposition they do not feel justified in introducing electric refining for wire products, for two reasons of which one is the increased cost and the other an apparent greater difficulty of mechanically working the electric steel for wire products. But as the speaker explained, this difficulty may be really due to their lack of experience with the properties of electric steel.

WILLIAM BRADY said that at the Illinois Steel Company they use the electric furnace for refining molten metal coming from the Beessemer converter, the product being put mainly into rails and castings and other things. All he could state definitely was that so far their results have given them very great encouragement in regard to the properties of electric steel.

FRANK N. SPELLER spoke of the experience of the National Tube Company with electric steel. They make both seamless and welded tubes. The electric steel is much better adapted to the seamless than the welded tube. It behaves very differently from the regular run of open-hearth and Bessemer steels in welding as all very pure steels do. For welding a steel should be, so to speak, self-fluxing. The greater density and greater purity of electric steel probably accounts for some difficulty in welding. Of course, for seamless tubes the advantages of uniformity and purity in electric steel are very apparent.

C. H. VOM BAUER said that electric steel rails have also been in use in the Prussian State Railings for the past four years, without breakages occurring. In that case the steel was refined in the electric induction furnace. In reply to several questions the speaker repeated what he had said in his paper concerning the alleged new recalescence point.

J. W. RICHARDS said that the difficulty in welding of electric steel, referred to by Mr. Speller, was undoubtedly due to the almost total absence of included slag. The more included slag there is in iron, the easier the welding operation is made. As is

well known, wrought iron which contains the most intermingled slag, welds the easiest. The speaker then referred to an interesting application of the electric furnace in the steel industry, which he saw in operation last summer near Stavanger, Norway. Many thousand tons of steel scrap are there available from the breaking down of old ships, and although electric power costs them only eight dollars a horse-power-year, yet it was found more economical to get coal from England and melt the scrap in an open-hearth furnace by means of producer gas, and then treat the melted metal put in an induction electric furnace for refining. They had found it more economical to use coal at \$4 a ton as fuel for the lower temperature range, but for the higher temperature range and for refining electric heat at a rate of \$8 per horsepower-year was cheaper and far more efficient.

E. P. Schoch and D. J. Brown. The Electroanalysis of Copper, Antimony, Bismuth and Tin with Acidified Chloride Electrolysis. (Vol. XXI, p. 81.)

W. F. HILLEBRAND expresses his interest in the work, in connection with similar work done at the University of Pennsylvania and by himself. The future developments in this field seem very promising.

William H. Walker and Ralph E. Gegenheimer. Some Factors in the Cost of Sodium Hypochlorite Production. (Vol. XXI, p. 127.)

٨

CHARLES E. BURGESS asked as to the practical conditions under which it would be preferable to make a hypochlorite solution directly by electrolysis instead of making it from bleaching powder.

WILLIAM H. WALKER replied that he would not commit himself as to which method is more economical. But some users of bleaching liquor are not accustomed to chemical operations and consider making the liquor from bleaching powder too troublesome; for such people the direct electrolytic process is simpler as it requires nothing but connecting the cell to the lighting circuit.

M. L. GRIFFIN said he knew a few bleachers, laundries, and white goods concerns that have employed this electrolytic cell, and while they do not claim that as far as the money is concerned they save anything at all, yet they find the cell a great convenience. They usually make what little bleaching liquor they need with their lighting current so that the power cost does not appear in their expenses anywhere.

W. LASH MILLER said one use would surely be made of Dr. Walker's paper. In more and more colleges there is coming to be a course in electrochemistry given to engineering students, and the lecturer in charge is compelled to refer to the cost side, because that is what settles it, whether an electrochemical or other process will be used. Of all the processes which lecturers have hunted up for that purpose there is none like that which Professor Walker has given in his paper which may be expected to become a regular classic in the teaching of the schools.

H. B. BISHOP asked whether it is possible to get free chlorine on the solution.

W. H. WALKER replied that he did not think so. Theoretically it is not possible because at the cathode just the right amount of alkali is produced to combine with the chlorine at the anode, and as the electrodes are quite close together, not more than half an inch apart, and as the hydrogen which is evolved at the cathode causes a very good mixing, the two products are brought into intimate contact immediately. In reply to a question by M. L. Griffin, W. H. Walker discussed briefly the conditions of chlorate formation.

L. D. VORCE thought that laundry people would not use the direct electrolytic process, as any electrolytic apparatus, however simple, requires expert attention. It is cheaper and simpler to make the bleaching solution from chemicals.

William H. Walker and Walter A. Patrick. The Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace. (Vol. XXI, p. 139.)

A. SINDING-LARSEN said he had found that phosphoric acid is not completely dehydrating in its action. If he wishes to prepare an absolutely dry gas, he makes an alloy of sodium and potassium in equivalent molecular weight proportions, and uses this alloy in a wash bottle to draw the gas through, which is thereby obtained in an absolutely dry condition.

WILLIAM BRADY asked as to the amount of time required to make a determination of oxygen.

WILLIAM H. WALKER said that when the apparatus is all set up, it takes about half an hour to get the furnace ready and ten minutes to take the melt, and perhaps half an hour to finish it, possibly in the whole two hours.

RICHARD AMBERG suggested that the smaller amount of oxygen found by the Ledebur method might perhaps be due to the fact that this oxygen is in a different combination with the metal than the balance of the oxygen, possibly dissolved in the metal.

JOSEPH W. RICHARDS thought that the Ledebur method gives the oxygen which is present as CO and as dissolved FeO, but not the oxygen present as alumina or manganese oxide or calcium oxide. Mr. Sinding-Larsen's drying method is excellent, but a little expensive, and it would be best to first dry the air as thoroughly as possible by a cheaper reagent, and then finish the drying by means of the liquid alloy. In that connection there is a reagent which is probably much cheaper than phosphorus pentoxides and that is alumina which, when thoroughly calcined, absorbs moisture up to 18% of its weight.

George C. Whipple and Melville C. Whipple. Mill Scale as a Cause of the Pitting of Steel Pipe. (Vol. XXI, p. 155.)

۲

A. S. CUSHMAN said that unquestionable mill scale is one of the important factors that is to be considered in every effort to

### XXVII] Discussions: Section Xa. Electrochemistry

reduce corrosion effects to a minimum. But all those who have been studying this intricate problem for a number of years have arrived at the conclusion that the mechanism of the corrosion reactions, under a given set of conditions, presents a very complex problem. The speaker went so far, several years ago, as to make a definite recommendation to some of the engineers of the United States Navy that boiler tubes that are put under intensive service in the Navy should be polished inside just the same as gun barrels are and with the same care. In spite of the fact that the recommendation has been made by several investigators of this problem over and over again, no work seems to have been done by engineers until this time to put into practice the suggestions made by those like the speaker who were unfortunately limited in the main at that time to laboratory investigation. The speaker was very glad to hear that now engineers are taking this matter up and are going to support the efforts that are being made by a number of progressive manufacturers to do everything in their power to make the most anticorrosive metal possible.

There is one great difficulty that is encountered in corrosive investigation. This is, that a certain condition under which observations are being made may lead on to results which may not be checked up by another investigator, equally earnest and equally careful, working under another given set of conditions. There are too many modifying factors to enable one to draw sweeping conclusions from any one set of investigations made in any one place, however ably they may have been carried out and however earnestly the investigator may have been seeking the truth. Experiments made under total immersion conditions may vary entirely from results arrived in experiments of atmospheric exposure. The concentration of oxygen, the condition of the surface stresses and strains, the general homogeneity of the material are all variables, and unfortunately not only variables between different types or kinds of metals presented to test, but variables as between materials made in different mills by the same processes. And furthermore, and still more unfortunately, variables between materials made in successive heats in the same mill: and still more unfortunately, variables as concern mate-

rials made in the same mill in different ingots from the same heat. So that with all these variables to take into consideration in the study of the corrosion problem, once more the danger is evident of arriving at conclusions from any one given set of investigations carried on under more or less artificial conditions.

He particularly pointed out the danger of arriving at the conclusion that wrought iron occupies one end of a scale of corrosion resistance under total immersion, such as pipe line conditions, that steel occupies the other end, and that the material called American ingot iron occupies an immediate position. He said he must differ from any opinion which is based upon one set of investigations that arrived at such a conclusion as that. He had been carrying on for years exposure tests under all different conditions, under total immersion in fresh and salt water and in the atmosphere, between all the different kinds of materials which are under discussion in the paper, and which have been mentioned by name, and he should hesitate, after the results of all his investigations, to draw any very definite conclusions.

However, he had no reason to recede from the position that he has always taken with respect to resistance to corrosion. that if freedom from pitting and therefore longevity is under consideration, then other conditions being the same, homogeneity in the metal is a most desirable quality. For in spite of the fact that the mill scale may be removed from a given sample of steel, and that it may not pit under the conditions of the test, yet the speaker ventured to doubt whether that would be found with respect to all steels, for many steels are badly segregated in their manufacture. It does not follow that steel must be badly segregated in the making, and there has been great improvement in the last five or six years in the quality of steels turned out to meet the increased demand for resistance to corrosion, and steels are more homogenous now than they used to be. But there are steels and steels, and there are irons and irons, and the speaker maintained that homogeneity is a desirable quality. For if manganese sulphide is contained in the body of the metal in segregated particles, there will be quite as great a difference of potential between the manganese sulphide inclusions and the body of the metal in the surrounding area, as may be found between the

### XXVII] Discussions: Section Xa. Electrochemistry

mill scale underlying the metal. It does not follow that the steel because it contains manganese and sulphur has suffered from segregation. Steel manufacturers are making very excellent steel, some of them. There are, however, steels in the market which are not so excellent. The same may be said of irons, irons that are offered for sale as such. But this is true that any manufacturer, be he a steel manufacturer or an iron manufacturer, who is earnestly endeavoring by all means in his power and through the services of his expert metallurgists to reduce lack of homogeneity in his material, to get away from segregation effects is improving his material.

In conclusion, he said that it would not be in order to express an individual opinion as to whether to recommend a certain steel at a certain price or a certain pure open-hearth iron at a certain price. There is still room for difference of opinion and for generosity to admit that all are trying as well as they can to improve their product with reference to resistance to pit-holing. Although the speaker is ranged on the iron side of the controversy he wished for his part to pay his respects to the steel manufacturers because they have improved so much their products in the last few years with respect to homogeneity.

R. H. GAINES asked whether the author recommended any special method for removing mill scale on a commercial scale with large plates.

MR. WHIPPLE said that they were going to continue their investigations. At the present time it is his general impression that the best way to get rid of the scale is some form of pickling.

BRADLEY DEWEY thought that the tests which had been brought forward had showed up differences in the character of the scale of the materials under test rather than the differences in the metals as such; because it has been noted in the paper that some of the iron under consideration had a reddish brown scale rather than the black scale of the steels. Further the author also noted that the red oxide shows very little difference in potential between it and the underlying material. Those who have had experience with the rolling of plates in a mill know that the color of the scale is largely dependent upon the amount of water which happens to be running over the rolls at the time of rolling.

If such is the case it is very conceivable that there was a slight excess of water during the rolling of the samples with red scale, or not enough during the samples of steel which were rolled, and that this may have been accidental and not at all characteristic of the material, that is, not characteristic of the ingot iron or of the steel. For that reason these tests have only shown the difference in the scale, not of the material underneath. This, of course, is emphasized by the fact that when the scales were removed none of the materials were found to pit.

FRANK N. SPELLER said that Messrs. Whipple had rendered a distinct service in pointing out again this important influence of mill scale. It is something that many have felt was a dominating influence, and it was so stated in papers and reports and researches that have been made. That was brought out as the result of some tests made in 1905, but engineers as a class have been very slow to appreciate the significance of this important point. Personally the speaker has been a little diffident in emphasizing it for fear that it should be taken that they were trying to shirk their duty in respect to uniformity of the metal; because that is not the case, as they are all striving to get the utmost uniformity. Nevertheless it is a fact that the predominating influence in corrosion and pitting of iron and steel is due to the surface such as scale or accidental patches of rust and other things. Professor Heyn had pointed that out in the recent Congress for Testing Materials. In discussing this very point he stated that as a result of his investigations he believed that the effects of the purity of the metal itself had been greatly overestimated as far as corrosion is concerned. So far as that point is concerned the speaker believes that a distinct advance has been made during these congresses in this question of corrosion. There has been a more general disposition to accept the fact that the surface influences have more to do with the question of pitting than any other one factor, but that does not mean by any means that uniformity in the metal itself is not also an important point.

Mr. Speller thought that in view of the small number of samples which the authors had of the materials and the small areas used, their conclusions are rather sweeping. The nature of the mill scale depends very much on the temperature at which the steel or iron is rolled, the amount of water used, the nature of the mill on which it is rolled, and how the metal is cooled afterwards, and a number of other points; for instance, the use of a little salt, so that unless the two classes of material were rolled in the same mill and under the same conditions of heat, rolling, and cooling, the results are hardly comparable.

177

Mr. Speller then took up Mr. Whipple's conclusion as to the difference between wrought iron and steel in their tendency to pitting. The speaker had made an investigation of this point during several years. The principle was to search through pipe lines in the country for cases where wrought iron and steel pipes had been coupled together by accident and used in the same line. In the past ten years both these materials have been generally used and both kinds of pipes have been accidently mixed up together when putting lines together. There is a distinct value in such a comparison, as it is as ideal as can be thought of. The speaker found 150 odd cases where both wrought iron and steel have been put together in the same line under these same conditions, and the extent of the corrosion was measured by the depth of the pitting. By averaging up the results he found that the depth of the pitting in the case of the wrought iron was slightly greater than in the case of the steel, although not enough so to be of any importance. But it is significant to note that under such conditions, such uniform conditions of manufacture and use, that the iron pitting, to say the least of it, just as much as the steel did. The speaker did not say that the area of pitting was the same, because that was not mentioned, since the vital point was the depth of the pitting which determined when the first hole punctured the metal.

Mr. Speller said that it was necessary to be very cautious in drawing conclusions from isolated tests, especially as the results of the tests which they are carrying out in service do not at all agree with the conclusions of Mr. Whipple. The speaker thought it necessary to put that pretty strongly for fear that someone might be misled on that particular point.

WILLIAM CAMPBELL called attention to the fact that in a line made up of both wrought iron and steel pipes in contact an electrical potential difference would be set up at the point of contact.

This would not be the case if the line was made up completely of wrought iron or completely of steel pipe. This fact might have something to do with the pitting.

F. N. SPELLER replied that this point was fully investigated. There is an influence one way or the other, sometimes in favor of one and sometimes of the other, between wrought iron and steel, when in contact; but this effect does not extend more than a quarter of an inch or so away from the point of contact, and in making all of these measurements of the depth of the pit, care was taken to keep well away from the contact. As the length of pipe was about twenty feet, there was plenty of material to work on while neglecting the points near the direct contact.

MR. JOHNSON asked Mr. Speller how he knew that some of the pipes were pure wrought iron pipes and not a mixture of steel and wrought iron. It is probable that when wrought iron gets into a line accidentally it is not then wrought iron, because evidently no pains have been taken to select pure wrought iron for this purpose.

F. N. SPELLER said that analyses were usually made, the sample etched and the manganese determined, and as a rule the pipes were pretty fairly pure wrought iron, but the conclusions drawn represent the general run of pipes sold as wrought iron ten years ago. That is the average length of life that they found.

MR. JOHNSON thought that in that case the conclusions do not apply in any way to pure wrought iron.

F. N. SPELLER begged to differ there because the samples that showed the most impurities were just as badly pitted as those showing only slight traces of steel scrap.

MR. WHIPPLE said, in reply to a question by the chairman, that the number of samples they experimented with was very small. But oftentimes one has to draw conclusions from a small number of experiments. He had contributed his paper as an engineer and not as a metallurgical chemist or an electrical engineer, and he was glad that the paper had aroused so much interest.

R. H. GAINES referred to some examinations by him of a wrought-iron conduit and a steel conduit, the latter being one of the oldest steel conduits in the country, having been laid in 1892 to 1894. After an examination he reported in 1907 that there had been 165 rust holes in that steel conduit. There had been previously, twenty years before, laid a wrought-iron conduit in which there had been at that time about six rust holes. Since 1907, he had learned recently, that there has been no further trouble with the iron conduit, whereas about 450 additional rust holes have been found in the steel conduit. That is one of the oldest steel conduits in this country as the use of steel for large conduits is comparatively recent.

M. Wilderman. Recent Progress in the Electrolysis of Alkaline Salts. (Vol. XXI, p. 185.)

H. CLEMM who has the Wilderman cell in operation in his plant in Germany said that he had nothing to add to the statements in the papers.

J. WHITING asked the author how he decomposes the amalgam in his oxidizing chamber, whether he depends on local action or not.

M. WILDERMAN replied that he depended on local action, with the aid of carbon in contact with the amalgam, and that he invented this method before Mr. Whiting.

J. WHITING replied that as he was rather in the position of host to his visiting friend, Dr. Wilderman, he was not in a position to answer his insinuations.

M. L. GRIFFIN said that Dr. Wilderman's paper had been very interesting indeed, and especially his statement that the cell may be closed up tightly without any further consideration for some months. That is an extremely important matter. What the author had said about the mechanical construction and endurance of it are the most valuable features, provided they are so, and as we have the testimony of two men that they are, the speaker had no means or disposition to doubt it. So far as the speaker knew of covering materials for iron, it is a pretty hard matter to find anything to stand two such drastic chemicals, which are opposed to each other as chlorine gas and caustic soda. It certainly is very remarkable if we have in the author's special

ebonite a material which will withstand the action, with no deterioration, as long as claimed for it. In any operation, no matter whether it is chemical or mechanical, in any manufacturing process, Americans endeavor to discover simplicity. The author of the paper on "commercial development" of a process said the child of the parent in a little time begins to look quite unlike its parent, and it is no exception in this case. The commercial development will shortly do its very best to simplify everything. Whether or not this cell is as simple as it will be one of these days, the speaker did not know. But it is evidently good enough to make money with, with power at rather a high cost, and probably like other developments commercially, it probably will not look like this at the next Congress in America.

A. H. HOOKER criticised the curve drawn by the author for the Townsend cell.

MR. WILDERMAN protested against the use of statements in the discussion beginning with "if this is so and so," as this implied doubts in the accuracy of his statements.

Jasper Whiting. The Commercial Development of Chemical Processes. (Vol. XXI, p. 203.)

۲

E. WILDERMAN said that the first and most important thing for any inventor is to study the literature of the subject so completely as to know what has already been done by others. This saves rediscoveries and useless expense.

W. H. WALKER expressed his appreciation to Mr. Whiting for having written the paper and for the educational value which it is going to have to the young men. When they start out they think that invention is one of the easy roads to success, that invention is an iridescent dream. He would give each young man a copy of Mr. Whiting's paper and of the pamphlet, "Carrying the Message to Garcia," as additions to his family Bible. Charles F. Burgess and James Aston. The Influence of Various Elements on the Corrodibility of Iron. (Appendix, Vol. XXVI, p. 479.) James Aston and Charles F. Burgess. The Rate of Rusting of Iron and Steel. Appendix, (Vol. XXVI, p. 453.)

WILLIAM H. WALKER said that these are two very important papers representing an enormous amount of work and deserving most careful consideration.

K. WILH. PALMAER said he would like to discuss from a theoretical point of view the general question of the attack of metals by solutions. Eleven years ago he, together with Dr. Auren. published a paper in which the modern theories of electrical conductivity of solutions and of electromotive forces were applied for the first time to an allied problem, the solution of zinc in acids. this paper and two following ones on the same subject being published in the Zeitschrift für Physikalische Chemie 1901-1906. Before this an attempt had been made to apply the law of mass action in the ordinary way, but without success. The speaker and his collaborator had taken up the old theory of De la Rive that the solution of metals is the result of local electric currents. which theory could not be subjected before to quantitative tests. He believed he had proved that this theory could explain the solution of zinc in all practical cases. A later attempt to explain the solution of metals as depending only on the rate of diffusion of the acid seemed to be established not to have been satisfactory. This seems obvious, for instance, in view of the fact that iron is more readily attacked by saltwater than by ordinary water as this difference cannot depend on any difference of velocity of diffusion, but merely on the difference of electrical conductivity.

The speaker and his collaborator had been able to make quantitative calculations only for zinc as in the corrosion of iron the reaction becomes more complicated, chiefly, because iron can give more than one oxide, the higher oxides being able to act as depolarizers. They had pointed out, however, that the theory of local electric currents seemed to be apt to explain the solution and corrosion of metals generally and had cited the well-known facts that iron in boilers could be protected through pieces of

zinc attached to it and that iron is not appreciably attacked by concentrated sulphuric acid, etc. The speaker was glad to hear that the theory of local electric currents seemed to prevail among American chemists who in the last years had done such important work on the corrosion of iron. He pointed out that his researches about the solution of zinc confirmed this theory. He thought the most useful way, in all cases of practical importance, to trace the question of solution or corrosion of metal would be to suppose that the phenomena depend upon local electric currents and then to examine which factors in every case can influence the strength of the local currents, *i. e.*, the rate of solution or corrosion.

A. S. CUSHMAN said that all these laboratory studies are very valuable and bring out new points which perhaps have not been considered sufficiently before. With respect to the first paper he said that unquestionably when we enter the alloy field there is an opportunity to find combinations which are far more resistant to corrosion in every sense of the word than when we are considering even the purest iron that can be made. Electrolytic iron is very interesting because, of course, it is very pure with respect to other metallic impurities. It is, however, usually saturated with hydrogen and a material that is saturated with hydrogen from electrolysis is entirely different from an iron that is saturated with hydrogen from being annealed in hydrogen. The hydrogen is unquestionably in a different form in the metal in these two cases.

Dr. Cushman then discussed the question of corrosion exposure tests which, he thought, are likely to lead to conclusions that are not altogether warranted by the evidence. If two sheets of metal are exposed to corrosive influences either in the air or in water, as the case may be, every once in a while our assistants take them in, boil them and scrub them off with a brush, then they weigh them and put those weights down in the note book; then they take them out of doors again for another attack; then they bring them in again at another period and use the same bath and weigh again, and it is finally said that the one that lost the most weight under that treatment is the one that is the real bad boy of the group, the other one is better. But that is far from being the case. On the contrary, the speaker ventured to state that nearly always the one that is losing the most is the best. Every pit hole means that there is an electro-positive point and that point has thrown the surrounding area into an electro-negative condition. Therefore, this is analogous to the method described in Dr. Clement's paper, as by electrolytic means a good portion of the surface (the electronegative area) is now protected and will rust more slowly than if there was a homogeneous metal.

Dr. Cushman then proposed the following simple analogy. Suppose one has two pieces of metal, very precious, of exactly the same size and thickness, and wishes to take off a sample of each for analysis, and distributes them to two laboratories for analysis. If they are cautioned to do as little damage as possible to the specimens, suppose in one of the laboratories they take the sample off with a planer by simply planing a very thin chip off the surface and then return the original specimen, whereas in the other laboratory they have not any planer and they take it off with a drill. To be sure they drill as small holes as possible, but they have to get a given weight of material for analysis. Unquestionably for museum purposes the one sample that is attacked with a drill is damaged to a greater extent, although the same weight of material may have come off both, and even it may have been possible to take much more off with the planer or shaver and do less damage than was done in the other case. Therefore, anybody who draws conclusions from a set of weights taken as a measure of corrosion losses and who, on the basis of those weights, states that one material is more anticorrosive than another arrives in many cases, though not necessarily in all cases, at conclusions diametrically opposite to what is really indicated by the test. There is really no accelerated test that the speaker knows of that is satisfactory. He quite agrees with the authors about an acid test. As a test by itself it is valuable. It gives some valuable indications to persons who know how to interpret them; but it is of no use in a general way. Neither does the speaker consider the immersion test in water or brine of any use. He has, unfortunately, never been able to evolve any test which he thought was of use except the use in service, and as Professor Burgess has very truly remarked the results of service tests may vary in different parts of the world, owing to climatic conditions, to the prevailing winds which blow with reference to the face of exposure of the test pieces, etc.

Dr. Cushman concluded that he would welcome it if all would get together and agree to put their materials in four different test fences in different parts of the country and in salt water and in fresh water immersion tests. He would welcome such a competitive test. Yet it would be necessary to be very careful to see that everybody's material should get a perfectly even, fair face of exposure to the elements and it would be found not to be an easy problem to work out if such a thing was projected.

W. H. WALKER said that he was very much interested to hear Professor Burgess say that he found that manganese was not deleterious to iron, which was an opinion he always had held, inasmuch as manganese should protect iron. But manganese oxide unquestionably is deleterious. Hence from tests of specimens which very rapidly corrode, and which are very often found to contain high manganese, we should not conclude that the corrosion is due to the manganese itself, but to the fact that the iron was highly oxidized before the manganese was put in, and manganese oxide was then formed. In Boston the frogs and crossings of the street car lines are made of a high manganese steel. After a rain it is easy to observe that the rails on either side of the switch will show rust before the switches themselves do.

MR. DEWEY referred to some tests recently made by Mr. Buck which are of interest in connection with Dr. Cushman's criticisms of Professor Burgess' weight tests. A test roof was put up with large sized sheets, some half dozen or so, of various metals. Then at the same point there were small test pieces, in insulated racks. Now at the end of some months there were very marked differences in the condition of the various steels, those high in copper being in very good shape, while those Bessemer steels, which are without copper had started to entirely break down, and recently, with the roof in this condition, and after a close examination and marking by several observers who all checked up reasonably well, the test pieces were taken down and the loss in weight determined. Now this loss in weight varied over very wide limits, and it was interesting to note that in almost every case the order of corrosion was the same in those different pieces as it was in the markings by the various observers of the roof itself.

C. F. BURGESS, in reply to Dr. Cushman's suggestion that electrolytic iron on account of its hydrogen content may not be as good as other forms of iron, said that if electrolytic is put through a melting process, heating it up to about 1600°, in all probability the hydrogen is driven off. Now the electrolytic iron which they make, after driving off the hydrogen, does not prove to be as durable a material.

W. H. WALKER said he had been interested to hear Professor Burgess state that he did not regard heterogeneity in the metal as the controlling factor in corrosion, but rather of secondary importance. Professor Burgess thus appeared to agree with the opinion expressed by Dr. Heyn of Berlin at the Congress for Testing Materials.

F. N. SPELLER confirmed that Dr. Heyn's remarks before the Congress for Testing Materials had been to the effect stated, namely that the influence of ordinary rust on the surface would predominate over that of the ordinary impurities in steel.

J. WEIR suggested that as there is a call now from steel manufacturers and users for some kind of paint that will prevent corrosion, it would be a good thing and of infinite value to all parties concerned, if the paint makers and steel makers would come together and consider what can be done.

W. H. WALKER called attention to the proceedings of the American Society of Testing Materials where a good deal of cooperative work between the steel manufacturers and paint manufacturers has been done.

MR. RICHARDSON referred to the controversy on the relative importance of lack of homogeneity in iron and steel and of rust and surface conditions. He had himself discussed this problem in a paper before the American Chemical Society some years ago, though it had never been published. The gist of it was that the surface conditions, especially rust, overbalance all the effects, or all the influences within the metal itself, after corrosion is

once started; that the composition of the metal influences, however, the commencement of corrosion. But after an adherent layer of rust is once formed, that rust is the contaminating influence, so that metals of quite different compositions, the one may be of pure iron and the other not so pure, will, if adherent rust is present, follow nearly the same time curve of corrosion, provided only that adherent rust is present. To produce the adherent rust it is necessary to have oxygen present, also to have alternate wet and dry, which are the conditions prevailing in ordinary atmospheric corrosion. The experiments which he carried out bore out these ideas in general. He also advanced the theory, as part of this general proposition, that it is only when the metal has a clean surface and when it is continuously maintained clean that the composition of the metal shows itself in influencing the corrosion. Such a clean surface is provided only in corrosion tests in acids. The difference between the results of early experiments with acid tests on one hand and service tests (or tests simulating service tests) on the other hand were due to the fact that in one case a clean surface was maintained and in the other there was a coating of rust.

W. H. WALKER referred to the ability of iron and steel to protect itself against corrosion under certain conditions. The old bridge at Newburyport has stood a hundred years where it is exposed to the salt sea air of the Atlantic. That iron has stood successfully for a hundred years, and yet a piece of iron removed from that bridge for testing was found to corrode more rapidly than any piece of iron he had ever seen. There are facts not yet understood which constitute the ability of iron to protect itself.

MR. WEST referred to the observation made with water pipes which rust internally, that the quality of the water has a great influence on the rate of corrosion. Ordinarily, after the rust has once started, due to imperfect coating of the pipe, that rust will go along very rapidly, provided the inside rust formed is taken away by the water. But if conditions are so that organic matter in the water causes the rust to form into a cake or lining, corrosion will come to a standstill after a few months or years. Most water works engineers with which the speaker is acquainted are very much in favor of what they call old-fashioned wrought iron. The speaker's experience is that wrought-iron pipe can be good and can be bad. He has been unable himself sometimes to tell by any microscopic test or by the ordinary tool test whether a pipe is iron or steel.

C. F. BURGESS referred to an investigation by him of a standpipe failure last winter where some portions were found to be very badly pitted. He picked out one of the deepest pits and cut through it and found that it was a deep pit with a flat bottom, with a nice cleanly defined layer of slag coming up to it. This, as the speaker said, does not mean anything or prove anything. But if he examined a lot of other pits in the same sheet and found the same conditions, it might prove that the slag had stopped further pitting. There are various elements in the mechanism of corrosion not yet understood and still under investigation by the speaker. There is an accelerating action of rust. That is, after one gets rust started once on the surface, that spot of rust is going to exert greater influence than the particles of impurities which were in the iron to start the rust. There is a quite considerable electromotive force set up between the part covered by rust and the surrounding iron. But there are possibilities to counteract the accelerating action of the rust. The speaker is continuing these researches on corrosion.

J. K. Clement and L. V. Walker. An Electrolytic Method for the Prevention of the Corrosion of Iron and Steel. (Appendix, Vol. XXVI, p. 491.)

J. O. HANDY asked as to the cost of the electric current and the cost of the method in commercial practice.

J. K. CLEMENT replied that he could not yet answer this question, for the reason that they are making larger-scale experiments on the Monongahela River at Braddock, and want to await the results of these experiments. As far as their experiments go, the current density is not so high as to make it out of the question to protect the plates in the Monongahela River in that way.

C. G. Fink. On Ductile Tungsten. (Appendix, Vol. XXVI, p. 503.)

RICHARD AMBERG asked whether the alloys of tungsten could also be made ductile just like metallic tungsten, as this might be of great commercial importance.

C. G. FINK replied that they had studied various tungsten alloys and had found that what was true of tungsten was in a general way also true of tungsten alloys. But they had not studied the particular alloy in which Dr. Amberg was most interested, namely ferrotungsten.

Walter B. Schulte. The Influence of Cinders on the Corrosion of Iron Embedded in Clay. (Appendix, Vol. XXVI, p. 555.)

٨

J. O. HANDY asked whether the composition of the cinder had any influence, especially the greater or smaller amount of sulphur in the cinder.

C. F. BURGESS said that different cinders have different electric conductivities and this has, of course, an effect, but the sulphur content does not seem to play any part.

J. O. HANDY called attention to the rapidity of the pitting action. He had made some comparative corrosion experiments, having samples of different kinds of steel embedded in coke of maximum size of a quarter of an inch and kept moist for a period of about three weeks, and the pitting during that time was very marked. He also called attention to another point of importance in connection with electrolysis in underground structures. If a wire is laid on the surface of the earth and another wire several feet below, there will be a difference of potential between those two wires; the one on the surface of the earth being the cathode; which may be explained by the fact that oxygen gets at it very readily. A piece of iron on the surface of a concrete structure is cathode toward a piece of iron in the interior of it by reason of the more ready access of the air to the outside piece. If air can get to the cinder bed, it has an effect.

# SECTION XIA. LAW AND LEGISLATION AFFECTING CHEMICAL INDUSTRY

### Edward J. McDermott. "The Expert Witness." (Vol. XXIII, p. 67.)

WILLIAM L. DUDLEY. We are under many obligations to Governor McDermott for his excellent paper, which places the subject so clearly before us.

It should be the aim and purpose of the expert witness to give the court the benefit of his knowledge, for the sake of equity and justice. When an expert is employed by either of the litigants, it is difficult for him to refrain from being partial. Some perfectly honest and thoroughly competent men are, by nature, partisans. The court needs facts and should have the power to call in experts on its own account; but, of course, the litigants should not be debarred from having their own experts though the court should have the right to know in what manner, and how much these experts are paid. Contingent fees should not be permitted.

The court expert should aid the court in getting the facts out of the expert witnesses of the litigants, and should himself be put on the witness-stand at the pleasure of the court.

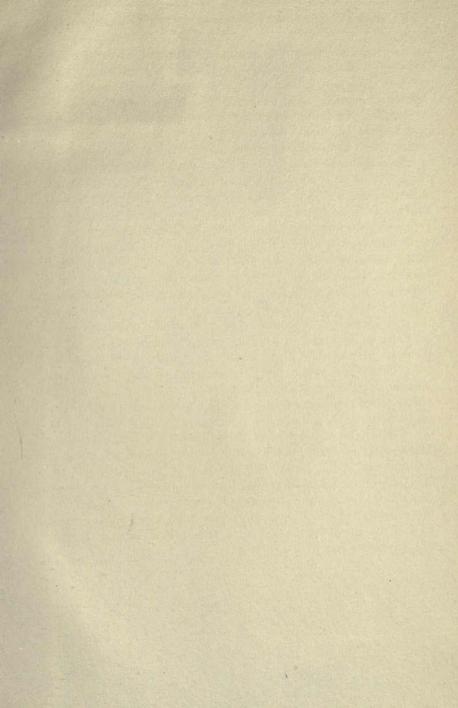
All expert witnesses should be examined and cross-examined only on relevant matter and the court should consider as irrelevant, everything which does not bear directly on the point of issue, or on the integrity of the expert. The expert should be at liberty to bring out any point that he considers to have a bearing on the case, even though it was not brought out in the direct examination. The court should have the right to call in an expert to aid in deciding purely scientific questions. Abstruse scientific questions are becoming more and more involved in important industrial litigation.

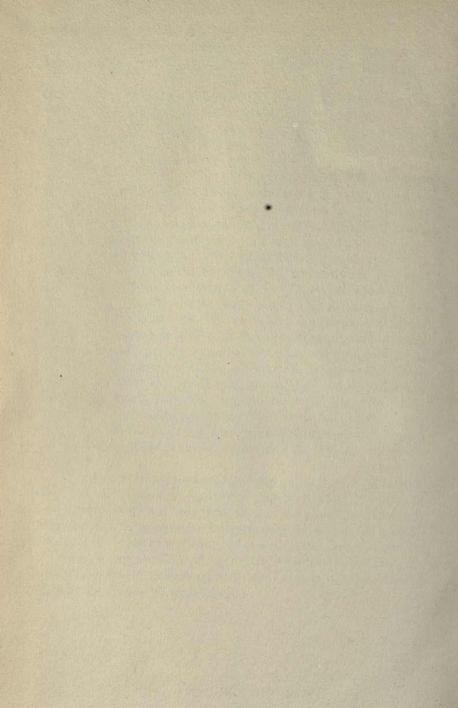
JOHN C. PENNIE: The careful and scholarly exposition of the present state of the law and practice prevailing in this country as affecting the status of the expert witness in his relation

to the court and jury well deserves the appreciative attention with which the paper has been received by the section.

That there are, in many cases, grave defects in the administration of justice, due to the methods of taking the testimony of experts, the failure of the courts and of juries to properly weigh their qualifications, and the almost inevitable bias with which their testimony is given (amounting in many cases to a suppression of facts and opinions unfavorable to the side for which they are summoned, or favorable to the opponent) must be regarded as established. In fact, in so far as the legal profession is concerned, the disposition of cross-examining counsel is, in most instances, not to ask direct questions whose legal import would be appreciated by the expert witness, but to approach him by indirection, so that in eliciting his real opinions, the witness may not so clearly appreciate their legal bearing. It need hardly be said, however, that the skill of many expert witnesses is fully equal on the witness-stand, to that of the most experienced counsel, so that their depositions often amount, in fact and substance, to partisan presentations of the case in hand, from the standpoint of the party in whose behalf they are summoned. In fact, in a well-known case, famous in patent litigation, the Supreme Court of the United States referred to them as often occupying the position of "sworn counsel."

The defects of our system, carefully pointed out in Governor McDermott's paper, undoubtedly justify serious attempts at reformation, and it is encouraging to note that the paper not only points out the defects, but proposes remedies. The remedies proposed are, in my view, in line with the best thought on the subject, and should lead to further consideration of a subject so fundamentally concerned with the welfare of the interest of individuals and of the state.







# GENERAL INDEX REPORT OF EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

### ORIGINAL COMMUNICATIONS

Volume	Section
1	I Analytical Chemistry.
2	II Inorganic Chemistry.
3	IIIa Metallurgy and Mining.
4	IIIb Explosives.
5	IIIc Silicate Industries.
6	IV Organic Chemistry.
7	IVa Coal Tar Colors and Dyestuffs.
8	Va Industry and Chemistry of Sugar.
9	Vb India Rubber and other Plastics.
10	Vc Fuels and Asphalt.
11	Vd Fats, Fatty Oils and Soaps.
12	Ve Paints, Drying Oils and Varnishes.
13	VIa Starch, Cellulose and Paper.
14	VIb Fermentation.
15	VII Agricultural Chemistry.
16	VIIIa Hygiene.
17	VIIIb Pharmaceutical Chemistry.
18	VIIIc Bromatology.
19	VIIId Biochemistry including Pharmacology.
20	IX Photochemistry.
21	Xa Electrochemistry.
22	Xb Physical Chemistry.
23	XIa Law and Legislation Affecting Chemical
	Industry.
24	XIb Political Economy and Conservation of
	Natural Resources.
25	Appendix, Original Communications, Sections I
00	to Ve.
26	Appendix, Original Communications, Sections VIa to XIb.
	10 AID.
27	Discussions.
28	Transactions and Organization.
29	Typographical and Authors' Changes; Index.

