

THE AMERICAN CHEMICAL
SOCIETY

(Continued)

SECTION OF CELLULOSE CHEMISTRY

Harold Hibbert, chairman

G. J. Esselen, Jr., secretary

*Report of the Standard Cellulose Committee.**Report of the Analytical Methods Committee.**Report of the Viscosity Measurement Committee.*

The effect of concentrated hydrochloric acid on different celluloses: E. C. SHERRARD and A. W. FROEHLKE. A preliminary report on an investigation to differentiate celluloses from various species of woods by observing the action of concentrated hydrochloric acid by means of the polariscope. Characteristic curves are given showing changes in specific rotation. Cotton and spruce cellulose give similar curves, although it has been shown that mannose is present in spruce cellulose and absent in cotton. For such a comparison a standard cellulose is required.

The effect of salts upon the acid hydrolysis of wood: E. C. SHERRARD and W. H. GAUGER. In a search for a material to act as a catalyst in the hydrolysis of wood a number of salts and acids have been tried. The effect of these added materials upon sugar and alcohol yields, as well as the effect produced by varying some of the conditions under which the hydrolysis was carried out, are given in the report.

Sugar formation in a sulfite digester: E. C. SHERRARD and C. F. SUHM. This paper contains charts showing the rate of formation of sugar during the conversion of white spruce into sulfite pulp by the Mitscherlich and Ritter-Kellner processes. Time and steam pressure appear to exert the greatest influence on sugar formation.

Ethyl alcohol from western larch: E. C. SHERRARD. This report describes the preparation of ethyl alcohol from the difficultly fermentable galactose obtained from western larch. Yields of sugar and alcohol are given for the hydrolysis of the water-soluble portion, the residue remaining after water extraction and the original larch wood. It is pointed out that western larch is the best source of ethyl alcohol of any wood yet studied.

Some of the products obtained in the hydrolysis of white spruce wood with dilute sulphuric acid under steam pressure: E. C. SHERRARD and G. W. BLANCO. A study of products formed in the hydrolysis of wood and wood cellulose has furnished valuable information concerning this reaction and the composition of these two substances.

Approximately 20 per cent. of the wood cellulose is hydrolyzed with the formation of mannose, glucose, galactose, xylose and arabinose. Mannose and glucose represent nearly two thirds of these sugars. Spruce cellulose prepared by the Cross and Bevan method yields mannose, glucose and pentoses on hydrolysis with dilute hydrochloric acid. This indicates a marked difference in the chemical constitution of wood cellulose and of cotton cellulose. The latter does not yield mannose or pentose sugars on hydrolysis.

The distribution of methoxyl in the products of wood distillation: L. F. HAWLEY and S. S. AIYAR. At the last meeting of the society it was reported that the methoxyl had been determined in the charcoal, settled tar, dissolved tar, pyroigneous acid and gas, from the distillation of maple wood both treated and untreated with sodium carbonate. This work has been continued to include oak and one softwood and also one other catalyzer, phosphoric acid. In the case of oak and the softwood the increase in methyl alcohol due to sodium carbonate is not balanced by the decrease of methoxyl in the charcoal and the dissolved tar alone (as was the case with maple) but also by a decrease in the methane in the gas. The increase in methyl alcohol due to phosphoric acid was accompanied by decreases in the methoxyl of all the other products.

The chemistry of wood. V: G. J. RITTER and L. C. FLECK. This article records the analysis of eight more species of wood in continuation of similar previous work. No very striking variations in composition were noted. In a study of the distribution of the pentosans it was found that both alpha and beta cellulose contained pentosans, the alpha cellulose containing the higher proportion. The distribution of the methoxyl groups was also studied, and it was found that in general the lignin of softwood contained a greater proportion of the total methoxyl of the wood than the lignin from hardwoods.

The chemistry of wood. IV. The analysis of western white pine and eucalyptus: S. A. MAHOOD and D. E. CABLE. This paper represents a continuation of the investigation of the chemistry of wood carried on by the U. S. Forest Products Laboratory. In addition to those constants determined by Schorger methods are given in this paper for the determination of alpha, beta and gamma cellulose and of lignin. The values obtained for western white pine are in the main similar to those obtained for other conifers, while the values for eucalyptus do not vary greatly from the values previously obtained on broad-leaved

trees. Since, according to the values obtained in this series, the woods fall into two groups of fairly uniform composition, depending upon whether they are from broad-leaved trees or from conifers, the suggestions are made that a more detailed study of the splitting products, particularly the cellulose and lignin, of the woods of these two groups be made.

Some observations on the determination of cellulose in woods. II: S. A. MAHOOD. In a previous communication the author showed that the yields of cellulose from woods obtained by Schorger's modification of the Cross and Bevan method of cellulose determination are higher than those obtained by Seiber and Walter's modification. It was suggested that this difference might be due (1) to a difference in concentration of the chlorine in contact with the sample or (2) to a difference in temperature at which the chlorinations are made. The present paper covers an investigation of these two points. It has been found that the yield of cellulose obtained by the Seiber and Walter method of chlorination can be made to accord with that obtained by the Schorger method by diluting the chlorine used with an equal volume of air. There appears to be no difference in the percentage of cellulose obtained by the Seiber and Walter method when chlorination takes place at zero and at room temperature. The Willard crucible* has been found to be more suitable than the Gooch crucible with the fiber pad, as proposed by Seiber and Walter, for making chlorinations of cellulosic materials. The results show that the lower yield of cellulose obtained by the Seiber and Walter method of chlorination is due only to too concentrated a stream of chlorine and not to too high a chlorination temperature.

Preparation of a "standard cellulose": W. O. MITSCHERLING.

Synthesis of derivatives relating to polysaccharides: HAROLD HIBBERT and HAROLD S. HILL. Bromoacetaldehyde has been condensed with mannitol, glycerin, glycerin brom-hydrin and various glycols. The bromine atom in the resulting cyclic derivatives may be replaced by hydroxyl by boiling with dilute alkali. In the case of glycerin a bicyclic derivative is apparently formed at the same time. The condensation products are being subjected to a careful examination in view of their relationship to the anhydro-sugars and polysaccharides.

Synthesis and properties of cyclic acetal derivatives: HAROLD HIBBERT and JOHN A. TIMM. Par-

tition experiments carried out on the condensation of a mixture of one mol. each of a 1:2 and a 1:3 glycol with one mol. of an aldehyde show that in the various cases investigated a much higher yield is obtained of the six- than of the five-membered ring compound. Also, the stability of the latter towards dilute acids is much less than that of the former. Similar experiments are being carried out using a mixture of one mol. each of two aldehydes with one mol. of a glycol. The nature of the products resulting from the condensation of various aldehydes (1 mol.) with glycerol (1 mol.) is also under investigation as well as the part played by the catalyst in bringing about such condensations.

Constitution of sedoheptose anhydride and its relation to cellulose: HAROLD HIBBERT. The constitution of this anhydro-sugar first prepared by Hudson and LaForge is probably represented by a 5:7 dilaetonyl-configuration for the following reasons: It is stable towards mineral acids so that the absence of an ethylene linking may be assumed. The product is a mono-molecular, stable, crystalline derivative showing no tendency towards polymerization, in this respect differing from the intra-molecular condensation product of a $\gamma\Delta$ di-hydroxy aldehyde-derivative, the outstanding feature of which, as found by the writer, is its rapid ease of conversion into a polymorphic form. The evidence for this view could be found in the oxidation of sedoheptose anhydride to the acid, from which, by elimination of carbon dioxide, levoglucosan should be formed. Experiments with this object in view are in progress. The properties of $\gamma\Delta$ dihydroxy-aldehyde derivatives are being examined, the first under review, viz., 2:keto-5:6 dihydroxyhexane, being found to yield a highly polymerized product when submitted to the intra-molecular condensing action of a small amount of a mineral acid.

Symposium. The action of alkali and acid on cellulose, wood and waste cellulosic material with special reference to the production of cheap cattle foods.

Joint symposium with division of organic chemistry on recent work on the constitution of starch and cellulose.

SECTION OF PETROLEUM CHEMISTRY

T. G. Delbridge, *chairman*

W. A. Gruse, *secretary*

Volume changes in petroleum products: A. P. BJERREGAARD. This paper will deal with some peculiarities exhibited by petroleum oils under

changes of atmospheric temperature conditions when the oil is in tank cars. A set of expansion coefficients that fit the observed phenomena will be included.

The surface tension of petroleum: C. K. FRANCIS and H. T. BENNETT. The surface tension of petroleum from different sections of the United States and of the products derived from the various crudes was determined in order to ascertain whether a relation existed between the surface tension and any other physical properties of the oils. The surface tension of petroleum varies almost directly with the specific gravity, but is influenced by the asphaltic content. The presence of high boiling fractions and high viscosity products tends to raise the surface tension of the lighter petroleum products, such as gasoline and naphtha. The small quantity of sulfur compounds, amorphous and crystalline wax, fatty acids and related substances commonly found in petroleum products do not appear to appreciably influence the surface tension. The surface tension at 85° F. of the substances examined varies as follows:

Crude	28.8	31.2
Gasoline	24.4	25.8
Naphtha	26.3	29.2
Kerosene	30.7	31.2
Gas oil	33.1	
Lubricating oil.....	36.0	37.5
Wax distillate	33.6	36.2

The change in viscosity of oils with the temperature: WINSLOW H. HERSCHEL. It is often necessary to estimate the viscosity of an oil at one temperature from an observation made at another. While it is not convenient to do this by equations, because no two petroleum oils are alike, and the relation between viscosity and temperature is complex, a graphical method has been developed which it is believed is accurate enough for commercial purposes. The method depends upon the observed fact that the graphs of a logarithmic viscosity-temperature diagram will, under certain conditions, meet at a point.

Some notes on the determination of the absolute viscosity of petroleum oils: W. H. FULWEILER and C. W. JORDAN. In connection with the determination of absolute viscosity, of certain samples of petroleum products, it was noted that the viscosities decreased when the sample had been left in the viscosimeter for 24 hours. In other samples, the viscosity increased on standing. Some data is given showing the effect on viscosity of various samples of petroleum, vegetable and animal oils. Some suggestions are made as to the cause of this phenomenon.

Detonation characteristics of blends of aromatic and paraffin hydrocarbons: THOMAS MIDDLEY, JR., and T. A. BOYD. The compressions to which aromatic hydrocarbons can be subjected in internal-combustion engines without detonation are very high as compared to the initial compressions that can be employed when paraffin hydrocarbons are used as fuel. Accurate measurements have been made through a wide range of relative composition of the tendency of blends of these hydrocarbons to detonate in engines. Values are given for the limiting compression ratio at which the various blends will give combustion that is free from detonation. The new instrumentation used for the accurate measurement of the degree of detonation occurring during the combustion of the fuel mixture in the engine is described.

The catalytic oxidation of insulating oils: C. J. ROMAN. Many oils used in electrical apparatus for insulating purposes tend to slowly form "deposits" known to the trade as oil sludge. Experiments have been carried out in both open and closed systems to substantiate the view that numerous substances may act continuously in small quantities to materially assist in the formation of the undesirable sludge. Such substances found somewhere in the transformer or circuit breaker construction are: copper, brass, lead, iron, tin, organic resins, oxidized asphaltic "varnishes" and some loading materials such as magnesia, calcia and a small proportion of certain driers found in the protective paints. Properly protected materials of electrical apparatus construction are discussed as well as the desirability of protecting the oil from oxygen contact.

Corrosion of petroleum refining equipment: R. R. MATTHEWS and P. A. CROSBY. The authors have shown in earlier papers that in refining Mid-Continent petroleum in a so-called pipe still hydrochloric acid was formed, due to hydrolysis of the magnesium chloride in the brine associated with the petroleum. Ammonia has been used in the fractionating system to reduce the corrosion caused by the acid. The cost has been small and results gratifying. This paper shows that hydrochloric acid is also produced when Mid-Continent crude is refined in shall stills arranged in series for continuous operation. The action was especially noted in stills where the oil temperatures were 175° C. to 250° C., and where bottom steam was used. The acid corrosion was also noted in a heat exchanger where the outgoing crude oil was not over 110° C. Evidently the acid formation was small there, however, as the ex-

changer was in use one and one half years before a tube was corroded badly enough to give away.

Recent developments in the methods for the extraction of gasoline from natural gas: FRED E. HOSMER and F. M. SEIBERT. The commercial importance of the natural gas gasoline industry is reviewed. The chemistry of natural gas is briefly discussed. Two new methods of gasoline extraction are described. The first is known as the low pressure evaporation method, in which the crude product is utilized to furnish refrigeration for cooling the gas after being subjected to pressure. The second method is known as the crude oil absorption method. This method consists in subjecting the gas to about fifty pounds pressure, at ordinary temperatures, and absorbing the gasoline in crude oil, carrying the saturation to about 25 per cent.

Petroleum education: EDWIN DE BARR and FRED W. PADGETT. A survey of petroleum education from the standpoint of pedagogy and practical application throughout the course of several years. The paper is outlined as follows: I, Relation of the various branches of engineering to the petroleum industry; II, Theoretical discussion of petroleum education; III, Petroleum education at the University of Oklahoma; IV, The future of petroleum education. The writers realize that the subject of petroleum education, especially from the standpoint of chemistry, is in a formative stage and it is hoped that the present paper will stimulate discussion and that outlines of courses in other institutions will be presented.

Sulfur compounds and the oxidation of petroleum oils: C. E. WATERS. In general, mineral lubricating oils which contain large percentages of sulfur compounds are more easily oxidized than those in which there is less sulfur. This is true whether the oils are heated to 250° C., as in the oxidation method for determining the "carbonization values" of oils, or when the oils are exposed to sunlight. The precipitates formed on diluting the oxidized oils with petroleum ether contain higher percentages of sulfur than the original oils. The residues left behind on cracking and partially distilling off oils, as in the Conradson carbon residue test, tend to retain the sulfur in the oil. The bearing of these facts upon the formation of sludge in transformer and turbine oils and of carbon in internal combustion engines is pointed out.

DIVISION OF WATER, SEWAGE AND SANITATION

A. M. Buswell, *chairman*

W. W. Skinner, *secretary*

The effect of temperature on the rate of reac-

tion in water softening by the lime-soda ash method: EDWARD BARTOW, M. E. FLENTJE and W. U. GALLAHER.

Observations on the mechanism of iron removal: A. M. BUSWELL.

Specific gravity of mineral waters by calculation: J. W. SALE.

Bottled mineral waters of unusual composition: W. W. SKINNER, C. H. BADGER and J. W. SALE. The composition of the domestic and foreign bottled mineral waters examined in the water and beverage laboratory of the Bureau of Chemistry during the last fifteen years is discussed with particular reference to the presence of unusual constituents or of ordinary constituents present in unusual amounts. The majority of these waters belong to one or another of the three following types: First, those in which the dissolved mineral constituents consist chiefly of dissolved limestone or of dolomitic limestone; second, of sodium bicarbonate and sodium chloride; third, of either or both sodium sulfate and magnesium sulfate. Usually a determination of the acid radicals, namely, nitrate, chloride, sulfate, carbonate and bicarbonate, and of the basic radicals, iron, aluminum, calcium and magnesium, together with a calculation of the sodium by difference, will furnish sufficient knowledge as to the composition of a water, provided qualitative tests are made for the more unusual constituents. Ordinarily, constituents other than those mentioned and silica are present only in traces. There have been some exceptions to the above, and instead of traces only substantial amounts of certain constituents enumerated below were found. The following maximum amounts of constituents expressed in milligrams per liter are reported: nitrate, 5700.; nitrite, 10.; hydrogen sulfide, 496.; bromide, 1510.; iodide, 30.; fluoride, 0.4; phosphate, 32950.; borate, 2000.; saline ammonia, 69.; lithium, artificial water, 288.; natural water, 32.; strontium, 200.; barium, 18.; manganese, 50.; and arsenic, 15. The composition of the so-called iron and alum waters is discussed briefly.

Two instances in which acute troubles were explained by means of the p_H determination: W. F. MONFORT.

Hydrogen ion concentration and coagulation: W. D. HATFIELD. For the majority of water works laboratories Gillespie's method for determination of p_H values, without buffer solutions, is most applicable. The amount of alum required for coagulation of a water is dependent on the buffer value of the water or the methyl orange alkalinity. Turbidity has very little effect. Coagulation begins at a p_H of 7.6-7.8 and the

flock settles readily until a p_H of 6.6 is reached. The Highland Park filtration plant operated most efficiently at a p_H of 7.3 but most economically at 7.5-7.6.

Formulation of equilibria in the coagulating basin: A. M. BUSWELL.

Report of committee on standard methods of analysis: A. M. BUSWELL.

CHARLES L. PARSONS,
Secretary

THE KENTUCKY ACADEMY OF SCIENCE

THE ninth annual meeting of the Kentucky Academy of Science convened in the physics lecture room of the University of Kentucky on May 20, with President G. D. Smith in the chair.

Twenty-three new members were elected. Officers elected are: Lucien Beckner, Winchester, *president*; John A. Gunton, Transylvania College, Lexington, *vice-president*; A. M. Peter, University of Kentucky, Lexington, *secretary*, and W. S. Anderson, University of Kentucky, Lexington, *Treasurer*. A. M. Peter holds over as representative in the council of the American Association for the Advancement of Science.

The following are abstracts of the communications:

The Boleti of Kentucky: G. D. SMITH, Eastern Kentucky State Normal School (President's address). Colored lantern slides and stereoscopic photographs of 37 species of boleti observed in the vicinity of Richmond were presented and explained.

Factors affecting the germination of the sclerotia of Claviceps (Ergot of rye): FRANK T. MCFARLAND, University of Kentucky. Most mycologists are fairly well acquainted with the method of germination of sclerotia of *Claviceps*, but there still remain several factors which are poorly understood. During the past two years, the writer has been engaged in a study of the sclerotia of ergot from various countries. In the course of these investigations it has been found that sclerotia more than one year old failed to germinate. Sclerotia sown out of doors, on the surface of the soil, without any covering showed good germination of the sclerotia with many well-formed stromata but the stalks usually are short. Some mycologists seem to have the idea that these sclerotia may have the power to retain their germination ability for more than one year. It is

quite unlikely that any sclerotia under out-of-door conditions should remain dormant during the first spring after their maturity and germinate the second season. Sclerotia of *Claviceps* must go through a period of rest. The shortest period of rest so far found is about eight weeks. During this time when the sclerotia are at rest, they must be kept stratified in moist sand. Removal of the cuticle of sclerotia with a scalpel does not prevent the germination, but the stromata are nearly always deformed, and all seem to rise from a stromatic cushion. Treating the sclerotia with a 5 per cent. and a 30 per cent. NaCl salt solution, and then completely removing all traces of the salt and stratifying the sclerotia in the usual manner did not injure their germination power.

The rôle of manganese in plants: J. S. MCHARGUE, Kentucky Agricultural Experiment Station. The purpose of this investigation was to determine if manganese has any definite function to perform in plant economy. The method of attack has been the preparation of plant nutrient compounds and quartz sand, free from manganese, and the growing of plants in different portions of nutrient solutions or sand cultures from which manganese was withheld and in another equal number of portions of these media to which manganese was added. All the plants were grown until those that received manganese showed signs of fructification and a few to maturity. The plants from which manganese was withheld made a normal growth for about six weeks only. Thereafter they became chlorotic and the young leaves and buds died back and the plants made no further growth of any consequence, whereas the plants to which manganese was available grew in a normal way and fructified where the plants were grown to that state of maturity.

The author concludes that manganese is necessary in the plant economy and that, therefore, eleven elements are necessary for the normal growth of autotrophic plants, whereas it has been taught previously that only ten are necessary.

The hydroxy-anthraquinone derivatives in plants: JOHN ABERDEEN GUNTON, Transylvania College. A résumé was given of the various plants containing derivatives of this type as well as a description of the forms in which these occur. The cathartic principles of cascara, senna, rhubarb, aloes and buckthorn were shown to be irritant anthracene derivatives that exist in the plant in the form of glucosides to which the physiological action is presumably due. Plants containing these bodies are found widely distributed throughout the globe and present an interesting