EDITORIALS

An Acknowledgment

We have worked in the face of what seemed insurmountable obstacles to place this issue in the hands of our readers promptly on schedule. Its typographical shortcomings are not due to negligence on the part of our staff, for they have worked untiringly, nor through any fault of our printer, who waived his contract terms to permit the editorial sections to be printed elsewhere. Labor conditions unexpectedly intervened, and it was necessary to move the half-finished work bodily from one shop to another in the dead of night. Obviously it was impossible to match accurately the usual type styles, and conformity of detail in the third shop not to be expected. Standards have been sacrificed for promptness. We are heartily grateful to the efficient manager and capable typesetters who "delivered the goods".

Welcome to our Visitors

A hearty welcome to our British and Canadian guests! It is easy for those of us who think alike, speak alike and feel alike to get together for common good. The editorial suggestion of a year ago that the chemists of Great Britain, Canada and the United States meet together for common counsel met with sympathetic response. Correspondence and personal conferences soon made the matter an accomplished fact. Never was there better illustration of the value of personal acquaintance, and the next two weeks will afford opportunity for a wide extension of this personal contact.

The broad basis of sympathetic understanding in each of these joint meetings now in progress lies not so much in a common language as in the fact that in each of our lands the chemist, before the war, occupied a lowly plane in our body politic. His existence was known but little heeded. He was considered a man apart, no glamor attached to his accomplishments, his opinions were given but scant attention by men in power. In each country the Teuton, through cleverly fostered propaganda, was held in popular esteem as the superman in chemistry.

But the tasks of war were worthily performed. Side by side we worked on those pressing problems upon the successful outcome of which great issues hung. In the light of our accomplishments national gratitude was a not unreasonable expectation. Such a feeling would logically express itself in the form of prompt protective legislation which would safeguard the future. However, in England it was only after a great tide of imports had rushed in through the breach made in the dyke of war blockade by the Sankey decision that the gap was closed by the Licensing Act of December 1920. The British dye industry is still suffering from that devastating flood. Not before August 12, 1921, almost three years after the Armistice, was the Government's Safeguarding of Industries bill, protecting the key industries developed during the war, passed. How like the war psychology! Grave disaster was the stimulus necessary for effective measures of defense. But once aroused the British answer to the call has always been complete.

With us in America the story has been a little different, but the spirit of dallying just as evident. We have made use of the sand bags of the War Trade Board to avoid a break in our dyke against a flood of dyes, though often this temporary expedient has seemed on the point of exhaustion, but in other key industries we still await the enactment of permanent tariff legislation to check the uneven competition of longer experience and depreciated currencies. Again how like war psychology—slow in being aroused to our responsibilities.

That which gives heart and hope to all of us in each of our lands is that public understanding, though gradually, is surely arising, and we believe it a historical fact that when once the Anglo-Saxon race sees a thing clearly it sees it through.

Fortunately the visit is not to be a hurried one, for besides the opportunities of close association afforded by the week of the General Meeting with its formal program there will follow Exposition Week with its numerous occasions for informal gatherings.

While it is hoped that the social functions arranged will afford an atmosphere of good fellowship and happiness, nevertheless the period just before us is pregnant with possibilities of great good, not so much to ourselves as to the lands we love. It is a time for great things. The occasion is here. Unfetter the imagination. Let us plan for the future on broadest lines and unitedly set about to accomplish their fulfillment.

The Fight in the Senate

We call it a fight for that is the only fitting term to describe the hearings on the dye embargo held before the Senate Committee on Finance during the dog days of August 1921. The defeat of the measure in the House by such a heterogeneous vote, secured under a cloud of fake issues, "monopoly," "trusts," "corruption," etc., made certain the reopening of the question in the Senate.

While waiting for the battle to begin the opposition celebrated its victory in the House by a luncheon given in New York City on July 25, 1921, by the American Protective Tariff League in honor of Congressman Frear, the aggressive leader for the German interests. Among the other guests was Mr. Metz, assumedly representing the importers and the Democrats.

With the social festivities ended the hearings began, with the chemical interests, aided strongly by the War and Navy Departments, on the offensive to regain the ground lost in the House, while the importers and the small group of textile interests took up the defensive, Senator Moses occupying a strategic position behind the lines.

Again was covered the same ground so thoroughly thrashed out during December 1919. The outstanding features of the new hearings were the aggressive leadership of General Fries, the Chief of the Chemical Warfare Service, the letters to Senator Penrose by Secretaries Weeks and Denby (reproduced below), the admirable brief filed by Mr. Choate, the presentation of the smaller manufacturers' case by Mr. Isermann, the outspoken opposition to the embargo plan by the Amoskeag Mills (Senator Moses' chief constituent), constant questioning by Senator Smoot, and the presence of former Senator Thomas of Colorado at the hearings.

But the cleverest move in the proceedings was by Chairman Penrose. The Democrats had been called in to the hearings on the American valuation and dye embargo features of the bill. Known to be in opposition, their votes would be helpful in killing both, but Republican sentiment for American valuation developed so strongly that

a quandary presented itself. This was easily solved by the Chairman inviting the Democrats out when voting time came. Then the Republican members of the Ways and Means Committee were called in to a joint conference, and American valuation was adopted.

Meanwhile the Senate Committee received from the House the new Longworth measure extending for three months from August 27 the ad interim control of imports of dyes through license by the War Trade Board. The Senate Finance Committee voted favorably upon this bill. As soon as announcement was made of the action of the Committee, eight senators, it is reported, notified Chairman Penrose that they would filibuster against the bill. This did not disturb the wily Chairman at all. His nimble wit readily hit upon a device. The bill was broadened to include all sections of the Emergency Tariff Bill and to extend the time to January 1, 1922, unless repealed by tariff legislation in the meantime. To filibuster against the dye control in this modified bill would mean obstructive tactics against features in which some of the filibusterers are decidedly interested. In this form the bill was reported and it is believed will pass the Senate.

The joint conference of the two committees for permanent tariff legislation for dyes resulted in the appointment of a joint sub-committee consisting of Senators Smoot and Dillingham and Representatives Longworth and Frear, which was instructed to endeavor to devise some form of compromise legislation which would protect the industry and at the same time bring a united and successful vote in the Senate. The committee has not yet reported, though the composition of the committee indicates that if Mr. Longworth can succeed in saving the embargo for which he has so consistently fought, his efforts should entitle him to be considered the legislative genius of the age.

Effective Help

Two highly interesting and significant letters have had a powerful influence in directing public attention to the most important issue at stake and in changing the tide of congressional sentiment toward legislation effectively protecting the American coal-tar chemical industry.

Chairman, U. S. Senate Finance Committee,   July 26, 1921.
  Senate Office Building,
    Washington, D. C.
My Dear Senator Penrose:

My attention has been drawn to the fact that the Fordney Tariff Bill as passed by the House of Representatives will not protect the American organic chemical industry from destruction by German competition.

One of the most startling discoveries of the World War was the fact that the United States could mobilize, train and equip with clothing three or four million men far quicker than it could supply the cannon, the rifles and the ammunition for them. Notwithstanding that from 1914 to 1917 our great steel industries and our rapidly developing chemical industries had been working feverishly to increase their facilities to supply ammunition and guns to the Allies, it was more than a year after we entered the war before those industries were able to supply ammunition, war gases, guns and rifles to meet American needs. Even then our chemical industries were so undeveloped in 1917 that it was necessary for the Government to build tremendous high explosive plants as at Nitro, West Virginia, and practically all poisonous gas plants for supplying gases and smoke materials to the United States Army.

Prior to the outbreak of the war in Europe in 1914, the American organic chemical industry was very small. This was particularly true of the dye industry. At that time, the value of coal tar dyes, drugs, etc. produced in Germany was more than twice that produced by all the rest of the world, and more than twenty-one times that of the United States. The dye industry is the backbone of the organic chemical industry on which all Governments are dependent for their high explosives, their war gases, their medicines and many other materials.

So fully did Germany realize before, during and after the World War that predominance in the organic chemical industry and particularly the dye industry meant the most valuable measure of preparedness possible, that she has united all her organic chemical industries into one great trust, the Interessen-Gemeinschaft.

Not only is the German workman paid much less than the American workman, but the depreciated mark makes the difference still more pronounced. It, therefore, seems certain that the German dye trust can produce dyes and similar materials so much cheaper than the Americans can produce them that no ordinary tariff can keep the German dye trust from destroying the American dye industry and thereby crippling the whole organic chemical industry.

The use of high explosives and war gases will unquestionably be far greater in any future struggle than in the World War. Inasmuch as the coal tar industry, which is the base of all dyes, is also the base of all high explosives and most of our war gases, it is of the most vital importance to preparedness that the dye industry be developed to the fullest possible extent in this country. It is felt that this danger is so great that I urge the enactment of the embargo feature of the Fordney Tariff Bill as submitted by the Ways and Means Committee of the House as the only way to prevent crushing our chemical market by German competition.

For the above reasons, England, France, Italy and Japan have already enacted embargoes on the importation of dyes, medicinals and other organic chemicals which will remain in effect for varying periods up to ten years in the case of England.

        Very truly yours,

           (Signed) John W. Weeks
                Secretary of War

My Dear Senator Penrose: July 27, 1921

Understanding that the recommendation of the Ways and Means Committee of the House placing a limited embargo on the importation of coal-tar products (H. R. 7456 General Tariff Revision Page 6) was rejected by the House, I am earnestly requesting that your Committee give special attention to this feature.

The Longworth bill (H. R. 8078 66th Congress) included a selective embargo regulating the importation of organic chemicals particularly those useful in the preparation of explosives and toxic gases used in chemical warfare.

The Fordney bill as reported from the Committee included a modified clause to the same effect. It is of great value to the Navy to encourage the development of chemical activities in the manufacture of all products connected with the above mentioned articles, especially those manufacturers whose establishments can easily be diverted to the manufacture of war materials when needed. The restoration of the embargo clause will be of material help and I will greatly appreciate your assistance to this effect.

        Sincerely yours,

           (Signed) Edwin Denby
                Secretary of the Navy

The Passing of Secrecy

A notable example of true progressive spirit was furnished at the convention of the Biscuit and Cracker Manufacturers Association held in Atlantic City last June. From the accounts of this meeting the Technical Bureau, provided by this organization for the benefit of its members, had evidently been having some rather rough sledding in prevailing upon the several members to make full use of its possibilities of service. Evidently also the Bureau had been doing some effective work, with the aid of the officials of the Association, in developing a broad-minded spirit of progress among the members, for at the convention a majority agreed to furnish to the Technical Bureau their formulas to be passed on to such members of the Association as requested them. Furthermore it was decided to employ a field man to visit the different factories and give to the members the fullest information on the best methods and latest discoveries in the baking business.

Brought together on this fundamental basis of true progressiveness it was an easy matter to swing an initial appropriation of $300,000 for a national advertising campaign to increase the consumption of the products of the industry, to be continued for several years with expanding appropriations. Then they listened to addresses of

value to all by eminent food chemists and received new points of view for betterment of work each in his own factory.

Can anyone doubt that the net outcome of such a gathering is increased prosperity to all? And the price of it was the disclosure to the Technical Bureau of the once prized secret formulas, the guarding of which had proved a brake upon the entire industry.

Is there not food for thought in all of this for the chemical industries? Secrecy has been a part of our inheritance handed down from the age of alchemy, but the days of ultra-secrecy are passing. Not necessarily through a Technical Bureau, nor that fortunate medium which the canners found in their Research Laboratory in Washington, but certainly through some agency which will be found best adapted to the needs of their chemical staffs, a way will be found out of the fog of secrecy which now prevents full steam ahead. He who finds that way will be the true leader and benefactor of the American chemical industry.

The President Takes A Hand

The legal power of the War Trade Board to control by license importations of synthetic organic chemicals was to expire on August 27; unmistakable activity was noticeable in importing circles preparatory to the great day; Mr. Longworth, always on the watch, had introduced a resolution extending the period of this control five months; this had been reported favorably from the Ways and Means Committee, but amended to read three instead of five months.

On August 11 the resolution came up for debate before that same House which only recently had defeated the embargo provision of the tariff bill, but suddenly the atmosphere cleared and the measure was quickly passed, for Mr. Longworth read to the House the following letter from President Harding:

The White House
Washington, August 10, 1921

Hon. Nicholas Longworth,
    House of Representatives, Washington, D. C.

My Dear Congressman Longworth: I have your note calling my attention to the fact that the bill extending the provisions of the emergency tariff act relating to the protection of the American dye and chemical industry is to be before the House on the morrow. I am aware that the Secretary of the Treasury has already called the attention of your committee to the extreme desirability of extending this protective provision.

Surely we would be both unmindful and unjust if we failed in a suitable protection of this industry until the new and complete tariff revision act is made effective.

Very sincerely,
    (Signed)   WARREN G. HARDING

Never was a more complete summing up given than in the three words: "unmindful and unjust." They tell the history of yesterday, the duty of to-day and the danger of to-morrow. The President has plainly saved the day for the Emergency legislation. A still greater debt of gratitude will be owed to him if in the light of the strong letters of the Secretary of War and the Secretary of the Navy he throws his great influence to the preservation of the embargo feature in the permanent legislation, thereby assuring beyond a question the future of the industry.

Mr. Harding is looking far into the future and seeking higher ground than either trade or war. On the same day his letter to Mr. Longworth was made public there was published the text of the formal invitation to the nations to join in a disarmament conference. Evidently both the President and Secretary Hughes have been giving due thought to the question of chemical disarmament, for in the invitation it is stated: "It may also be found advisable to formulate proposals by which in the interest of humanity the use of new agencies of warfare may be suitably controlled," a cautious sentence conveying a conviction of the realities, the difficulties and the necessities of this momentous question. It may be that the President is "thinking it through."

The Meeting and the Exposition

The period, September 6 to 17, 1921, should prove historic for chemistry. Beginning with the Council Meeting on the sixth the Annual Meeting of the American Chemical Society will be held in New York City. British and Canadian chemists will join in the sessions. The advance activities of the officers of the Divisions and Sections give promise of scientific programs of unusual value, while for the general meetings with speakers of national and international distinction have been announced.

With a brief intermission for excursions there follows the Seventh National Exposition of Chemical Industries, whose doors will be open from September 12 to 17. The conversion of the Grand Central Palace into an office building made necessary the removal of the Exposition to other quarters. Fortunately, there was found in the Armory of the Eighth Coast Artillery an ideal building. Its floor space is so enormous as to admit of installation of an even greater number of exhibits than in previous expositions, all on one floor. Perhaps this may prove symbolical of greater unification in the industry.

The past year has been a trying one. Chemistry was no exception to the rule in the depression which characterized all lines of industrial effort. But we have carried an additional load of uncertainty as regards the outcome of legislation. The sky is not yet clear, but the clouds are breaking and at any time the sun of prosperity and certain future may break through. If so it will make this great gathering one long to be remembered. Frankly, we are optimistic.

Experimental Evidence

It was in Philadelphia, that city of due decorum, on July 19, 1921, some four years after the use of tear gas for dispersing men engaged in fiercest warfare, that there assembled, despite the prevalent crime wave, some two hundred members of the Police Force, with no sense of the humor of the situation, to determine definitely whether, as an organized group, they could, without gas masks, charge a given point through an atmosphere of one of the most powerful lachrymal gases known. The impossibility of such an accomplishment could readily have been attested to by the merest yardboy at Edgewood Arsenal.

Such conservatism and such slowness to utilize modern weapons suggests the attitude of those thoroughly set and comfortable officers of our Navy who still see no demonstration of anything worth while for their consideration from the recent sinking of a destroyer, a cruiser and a battleship off Hampton Roads by high explosives dropped from airplane squadrons.

Experimental evidence sometimes leads to false conclusions. The doughboys could have given advice based upon actual experience.

OUR FOREIGN TRADE IN CHEMICALS

By O. P. Hopkins 1824 Belmont Road, Washington, D. C.

The world-wide depression that overtook business during the fiscal year 1920-21 did not spare our foreign trade in chemicals and allied products. Here and there is to be found a commodity that apparently has not suffered seriously, but statistics for the year are likely to be misleading in such cases.

There are economists who say "I told you so" when the great slump is mentioned, but they certainly were not vociferous before the event. Looking backwards, it is evident that one of the chief causes of the severity of the depression was the old lack of scientific direction of production. While orders pour in, production is speeded up in every direction with no tally kept of total production or thought given to its relation to the possible consumption. After a brief boom period of high prices comes a buyers'-strike, or at any rate overproduction—then the depression.

On paper the foreign trade in chemicals was not hit so hard during the fiscal year just closed as were some other classes of commodities. A rough estimate indicates a total export of all chemicals and allied products of about a billion dollars in 1921, against something like a billion and a quarter in 1920. The decrease in imports was relatively about the same. Exports of chemicals proper, however, decreased 30 per cent, drugs, medicines, etc., about 25 per cent, and dyes nearly 27 per cent, in value, in value. Any but the most pessimistic will be encouraged by the fact that the 1921 values are still greatly in excess of those for 1914. The slump is merely from the boom year:

SUMMARY OF FOREIGN TRADE IN CHEMICALS AND ALLIED PRODUCTS
(In Millions of Dollars)

CLASSES	IMPORTS			EXPORTS		
	1914	1920	1921	1914	1920	1921
Chemicals..............	72	96	101	15	92	64
Drugs, medicines, etc....	9	22	22	11	41	31
Dyes, dyewoods.........	10	6	8	(¹)	26	19
Explosives.............	1	2	1	6	28	46
Fertilizers.............	28	39	29	12	33	25
Gums, resins, etc........	88	330	153	20	37	22
Oils, fats, waxes........	75	319	201	194	607	613
Paints, pigments, etc....	2	2	3	7	27	21
Tanning materials.......	5	12	9	1	6	2
Paper and pulp.........	30	106	159	6	33	27
Miscellaneous products¹.	120	701	689	44	324	181
Miscellaneous materials..	8	9	11	2	4	4
TOTAL.........	448	1644	1386	318	1258	1055

¹ The importance of this class is due to the inclusion of sugar. The article s making up this class are shown in the detailed table of miscellaneous products.

In the more detailed tables that follow, quantities have been given wherever possible, as values have since 1914 been comparatively worthless for purposes of comparison. All compilations are based upon statistics of the Department of Commerce, Washington, D. C.

THE TRADE IN CHEMICALS¹

With a few exceptions the trade in chemicals slumped in 1921 as compared with 1920. Even where there is apparently only a slight falling off it should be borne in mind that the market may have been affected too late in the year to make an impression on the year's total.

The exports of acids fell off in 1921, but as a whole were above those of 1914. Sulfuric acid shipments have

fallen from 68,000,000 pounds in 1918 to 32,000,000 in 1920, to 18,000,000 in 1921, but are still 6,000,000 above 1914. Imports of acids are also declining but are still above the figures for 1914.

The exports of caustic soda were cut in half during 1921, and shipments of sodium silicate decreased about one-third. There was only a slight decrease in foreign sales of sal soda, and the exports of soda ash actually increased in value, although the quantity shipped was slightly below that of 1920. The falling off in the value of "all other" soda exports was about one-third. Imports of sodium nitrate decreased from 907,000 to 844,000 tons; the 1914 imports totaled 564,000 tons.

The exports of potassium chlorate and other non-fertilizer potash salts were cut in half in 1921. Imports of potassium carbonate fell off from 22,000,000 to 14,000,000 pounds, as compared with 20,000,000 pounds in 1914. The imports of potassium nitrate went up from 27,000,000 pounds in 1920 to 31,000,000 in 1921. In 1914 the total importation was only 3,500,000 pounds.

An increase occurred in the exports of chloride of lime from 31,000,000 to 37,000,000 pounds. Imports also showed an increase—from less than 1,000,000 to more than 4,000,000 pounds, but the total imports in 1914 amounted to 47,000,000 pounds.

The growth in the imports of cyanides is shown by the fact that about 15,000,000 pounds of potassium cyanide was purchased in 1921, more than three times the figure for 1920 and fifteen times the imports in 1914. Sodium cyanide was not shown in the statistics for 1914, but the imports in 1921 were only slightly under those in 1920 and worth over a million dollars.

Of the coal-tar crudes, benzene was exported to the extent of 67,000,000 pounds in 1921, a big increase over the 17,000,000 recorded for 1920. The value of other crudes exported increased slightly. Imports of creosote oil rose from 8,000,000 gallons in 1920 to 28,000,000 in 1921. The 1914 imports totaled nearly 61,000,000 gallons.

The expansion in the domestic production of sulfur during the war is reflected in the disappearance of imports since. Exports, on the other hand, fell off only slightly in 1921 as compared with 1920, but the industry suffered during the second half of the year.

TRADE IN CHEMICALS, DRUGS, DYES, ETC.

ARTICLES Imports	1914	1920	1921
Acids (except coal-tar acids):			
Oxalic, lbs..................	8,507,850	1,401,547	2,058,907
All other, value.............	$1,133,252	$4,004,018	$2,587,571
Albumin, egg, lbs............	(¹)	8,956,845	7,889,411
Ammonia, muriate, lbs........	9,176,729	5,344,028	4,417,162
Argols, lbs..................	29,793,911	23,638,337	26,485,760
Arsenic or orpiment, lbs.......	4,432,793	6,470,700	8,801,293
Balsams, not containing alcohol, lbs.....................	(¹)	745,151	452,167
Calcium, acetate, crude chloride, carbide and nitrate, lbs......	(¹)	76,845,476	111,261,888
Chemical and medicinal compounds, n. e. s.:			
Alkalies, alkaloids, preparations, mixtures, etc., lbs....	(¹)	6,907,035	11,206,926
Medicinal preparations (see also coal-tar products), value	$1,031,054	$562,586	$1,030,551
All other...................	(¹)	$1,388,577	$1,316,937
Cinchona bark, and alkaloids or salts of:			
Barks, cinchona, or other from which quinine may be extracted, lbs...........	3,648,868	5,242,724	3,567,010
Quinine, sulfate of, and all alkaloids or salts of cinchona bark, oz..................	2,879,466	4,580,807	3,630,063

¹ The term "chemicals" is here used in the usual restricted sense, as not including drugs, medicines, and dyes.
² $400,000.

Trade in Chemicals, Drugs, Dyes, Etc., *(Concluded)*

Coal-tar products:			
Crudes			
Acid, carbolic, lbs.	8,392,995	157,319	183,709
Benzol, lbs.	(¹)	170,519	1,717,936
Cresol, lbs.	(¹)	8,188,303	6,476,140
Crecsote oil, gal.	60,900,435	8,338,761	27,779,736
Naphthalene, lbs.	(¹)	6,113,858	13,925,850
Tar and pitch, bbls.	(¹)	20,607	15,965
Toluol, lbs.	(¹)	1,195,706	
All other crudes, value	(¹)	$65,818	$159,421
Intermediates			
Acids			
Carbolic (phenol), lbs.	(¹)	30	1,260
All other, lbs.	(¹)	11,512	549
Aniline oil, lbs.	(¹)	(¹)	220
Aniline salts, lbs.	3,184,467		4
All other intermediates	(¹)	$217,653	$885,911
Finished products			
Alizarin and dyes, lbs.	2,633,414	257,841	352,173
Colors or dyes, n. e. s., value	$7,241,406	$3,775,216	$5,081,970
Indigo, synthetic, lbs.	8,125,211²	1,014,100	276,849
Medicinal preparations	(¹)	$112,611	$236,656
Other finished products	(¹)	$79,216	$82,232
All other coal-tar products, value	$1,636,750	....	....
Extracts and decoctions for dyeing, lbs.	(¹)	1,581,534	708,640
Extracts for tanning:			
Quebracho, lbs.	93,329,087	154,944,717	110,194,308
All other, lbs.	8,710,040	7,380,920	9,712,978
Fusel oil and butyl alcohol, lbs.	5,802,369	6,196,179	1,083,336
Glycerol, crude, lbs.	36,409,619	15,656,463	11,118,149
Indigo, natural, lbs.	(¹)	126,539	147,835
Iodine, lbs.	195,087	523,313	595,058
Lactarene, lbs.	10,798,614	24,039,313	14,179,764
Licorice root, lbs.	115,636,131	48,045,373	59,693,462
Lime, chloride of, lbs.	47,423,651	830,207	4,696,773
Citrate of, lbs.	3,097,265	10,431,314	5,071,504
Magnesite, not purified, tons.	289,494,316	27,503	50,352
Opium, containing 9 per cent or more morphine, lbs.	455,200	628,896	77,444
Perfumeries, cosmetics, etc., value	$2,309,027	$5,545,606	$7,078,985
Potash (not for fertilizer):			
Carbonate, lbs.	20,603,593	22,147,554	14,774,581
Cyanide, lbs.	808,721	5,175,608	13,353,268
Hydrate, not over 15 per cent caustic soda, lbs.	8,450,402	782,477	4,934,697
Nitrate, lbs.	3,516,580	26,862,012	30,868,786
All other, lbs	5,775,588	2,198,178	4,512,402
Soda:	1914	1920	1921
Cyanide, lbs.	(¹)	8,629,502	7,742,063
Nitrate, tons.	564,049	907,041	843,756
All other salts of, value	$487,038	$1,642,589	$1,343,641
Sulfur, tons	19,389	47	2
Sumac, lbs.	10,770,340	21,180,414	2,727,006
All other chemicals, drugs, dyes, etc., value.	$13,676,032	$19,076,123	$16,955,157

Exports

Acids:			
Carbolic, lbs.	(¹)	2,223,205	659,890
Nitric, lbs.	(¹)	820,517	267,119
Picric, lbs.	(¹)	8,073	3,730
Sulfuric, lbs.	12,131,750	32,336,893	18,600,704
All other, value.	$357,035	$5,291,987	$3,029,332
Alcohol, wood, gal.	1,598,776	687,008	467,763
Calcium carbide, lbs.	32,845,649	21,164,404	20,147,753
Coal tar, bbls.	22,150	81,640	128,103
Coal-tar distillates, n. e. s.:			
Benzol, lbs.	(¹)	17,282,368	66,622,862
All other, value.	(¹)	$3,611,514	$4,101,129
Copper sulfate, lbs.	7,375,775	4,511,724	4,297,378
Dyes and dyestuffs:			
Aniline dyes, value.	(¹)	$17,130,397	$13,577,788
Logwood extract, value.	(¹)	$1,832,231	$1,471,040
All other, value.	$356,919³	$6,829,937	$3,571,309
Extracts for tanning, value.	$639,941	$6,016,438	$1,732,198
Formaldehyde, value.	(¹)	$2,289,217	$1,376,281
Glycerol, lbs.	36,409,619	2,257,623	1,388,194
Infants' food, value.	(¹)	$3,032,330	$1,520,259
Lime, acetate of, lbs.	68,160,224	32,885,132	12,845,700
Chloride of, lbs.	(¹)	31,252,379	37,425,093
Medicinal and pharmaceutical preparations, value.	$6,721,978	$20,118,271	$18,038,328
Perfumery and cosmetics, value.	$2,309,027	$7,979,237	$6,236,766
Petroleum jelly, value.	$661,889	$3,156,286	$2,072,595
Potash:			
Chlorate, lbs.	(¹)	2,845,858	1,130,771
All other, value.	(¹)	$3,362,827	$1,309,852
Roots, herbs, barks:			
Ginseng, lbs.	224,605	220,970	157,351
All other, value.	$513,071	$1,793,064	$836,320
Soda:			
Bicarbonate, lbs.	(¹)	11,998,510⁴	13,353,769
Borax, lbs.	(¹)	10,943,110⁴	4,368,880
Caustic, lbs.	(¹)	229,684,163	101,021,827
Sal soda, lbs.	(¹)	12,763,399	10,376,424
Silicate, lbs.	(¹)	33,692,525	23,099,660
Ash, lbs.	(¹)	115,997,980	113,481,062
All other salts of, value.	(¹)	$7,471,808	$5,378,899
Sulfur, tons.	110,022	393,404	375,826
All other chemicals, etc., value.	$9,019,582	$42,573,500	$24,458,856

1 Not stated separately.

2 Stated as "Indigo, natural or synthetic" in 1914, but was probably largely synthetic.

3 Represents the total value of all dyes and dyestuffs in 1914.

4 Period from Jan. 1 to June 30, 1920.

DRUGS, MEDICINES AND TOILET PREPARATIONS

The trade in the products under this head seems to have held up pretty well in 1921. Exports of medicinal and pharmaceutical preparations fell off somewhat in value, but differences in prices could easily account for the drop. The total was still three times what it was in 1914. Receipts of cinchona bark and salts fell off perhaps a quarter in value, and the total is now about what it was before the war. Imports of coal-tar medicinals doubled from 1920 to 1921. Exports of perfumery and cosmetics fell off about 20 per cent in value, although still three times the total for 1914. Imports of such goods, however, increased about 20 per cent in value and were three times as great as before the war. (See table "Trade in Chemicals, Drugs, Dyes, etc.")

DYES

Exports of aniline dyes decreased in value from $17,130,000 to $13,578,000 from 1920 to 1921. There was also a decrease from $6,830,000 to $3,571,000 in the exports of "All other" dyes and dyestuffs, which include synthetic dyes other than aniline. It is not possible to say just how price changes have affected these totals, but it is evident that competition from Europe is making itself felt in our foreign markets. The only country to take a notably increased amount of dyes from this country in 1921 was China, with a total of $4,809,000 as compared with $3,053,000 in 1920. Slight increases are shown for Brazil, Peru, Dutch East Indies, and Australia. There was an alarming drop in shipments to Japan from $6,727,000 in 1920 to $1,341,000 in 1921, which is attributed partly to renewed German activity and partly to distress in the textile industries. Exports to India dropped from $3,334,000 to $1,834,000. With imports it is a somewhat different story, for there was an increase from $3,775,000 to $5,082,000 in the important class, "Colors or dyes, not elsewhere specified," but there is comfort in the fact that imports of synthetic indigo fell from 1,014,000 to 277,000 pounds. In 1914 the imports of indigo amounted to 8,125,000 pounds. (Details of the dey trade are shown in "Trade in Chemicals, Drugs, Dyes, etc." and the dyewoods are mentioned in "Trade in Miscellaneous Materials.")

TANNING MATERIALS

Imports of tanning extracts fell off 25 per cent in 1921 as compared with 1920, but were still about 8 per cent above the 1914 figure in quantity. Purchases of quebracho wood fell off slightly from 1920, the quantity, however, being less than half of the total for 1914. Imports of mangrove bark went up from 2544 tons to 7156 tons, which is practically the figure given for 1914. Exports of tanning bark were under the figure for 1920, but the item is insignificant. There was a noteworthy falling off of over 70 per cent from the $6,000,000 worth of tanning extract exported in 1920. (See table "Trade in Chemicals, Drugs, Dyes, etc.," for extracts, and "Trade in Miscellaneous Materials" for bark and wood.)

FERTILIZERS

The imports of potash fertilizers are still further below the pre-war normal than they were in 1920, as the next table will show. Exports of phosphate increased 20 per cent in quantity compared with 1920, but are still about 36 per cent below the figure for 1914. Exports of superphospate, on the other hand, were only a third of the total for 1920. Shipments of ammonium phosphate showed a gratifying increase, but the sales of "all other" fertilizers

were cut in half.

TRADE IN FERTILIZERS

ARTICLES Imports	1914	1920	1921
Ammonium sulfate, tons.......	83,377	2,587	2,537
Bone dust, ash, and meal, tons...	41,450	7,340	27,413
Calcium cyanamide, tons........	(¹)	84,678	34,696
Guano, tons..................	21,887	18,796	37,570
Kainite, tons.................	541,846	274,761	204,834
Manure salts, tons............	261,342	249,348	123,273
Potash, n. e. s.:			
Muriate, tons..............	237,886	110,324	49,911
Sulfate, tons..............	45,139	6,356	12,081
All other substances used only as fertilizer, value.............	$6,199,554	$4,757,066	$5,406,764
Exports			
Phosphate rock:			
High-grade pebble rock, tons..	475,335	351,352	274,953
Land pebble, tons............	1,000,630	395,581	651,749
All other, tons.............	1,906	30,348	16,862
Superphosphates, tons.........	(¹)	93,432	29,954
Ammonium sulfate, tons.......	(²)	17,489	65,915
All other fertilizers, tons.......	61,601	239,091	108,431

¹ Not stated separately.
² Included in "all other fertilizers" prior to May 1, 1920.

GUMS, RESINS AND NAVAL STORES

Copal, kauri, and damar held their own in the import trade for 1921, but there were substantial decreases in other items of this class. Purchases of rubber fell from 632,000,000 to 357,000,000 pounds, or over 43 per cent.

The export trade in naval stores is only about half what it was in 1914 in quantity, although the sales of turpentine spirits increased 30 per cent in 1921 over 1920. Rosin exports were down one-third from 1920.

TRADE IN GUMS, RESINS, AND NAVAL STORES

ARTICLES Imports	1914	1920	1921
Camphor:			
Crude, natural, lbs.........	3,476,908	4,025,517	2,092,886
Refined and synthetic, lbs.....	566,106	1,685,633	812,865
Chicle, lbs..................	8,040,891	9,699,863	8,710,393
Copal, kauri, damar, lbs........	32,693,412	44,480,033	44,617,913
Gambier, lbs.................	14,936,129	10,207,013	6,292,780
Gum arabic, lbs..............	(¹)	6,718,308	4,416,465
Shellac, lbs.................	16,719,756	34,151,209	23,871,866
Other gums, lbs.............	....	14,641,434	10,822,198
India rubber, etc.:			
Balata, lbs.................	1,533,024	2,013,737	1,879,990
Guayule gum, lbs...........	1,475,804	1,314,913	995,123
Gutta joolatong, lbs.........	24,926,571	18,392,164	6,774,189
Gutta-percha, lbs...........	1,846,109	6,496,309	4,575,392
India rubber, lbs...........	131,995,742	632,392,636	356,975,223
India-rubber scrap, lbs.........	25,958,261	14,236,098	6,042,565
Exports			
Naval stores:			
Rosin, bbls.................	2,417,950	1,321,535	877,160
Tar, turpentine, pitch, bbls....	351,352	61,826	41,864
Turpentine, spirits of, gal.....	18,900,704	7,461,455	9,741,711

¹ Not stated separately.

OILS, FATS AND WAXES

The trade in vegetable oils fell off very badly in 1921 from the boom figures for 1920. Imports were only about a third in value of what they were the previous year, and the export trade was just about as badly hit. On the other hand, the imports of mineral oils doubled in value, while the exports increased 25 per cent.

SUMMARY OF TRADE IN OILS

ARTICLES Imports	1914	1920	1921
Oils:			
Animal..................	$1,034,000	$3,629,000	$1,388,000
Mineral.................	13,666,000	41,050,000	81,865,000
Fixed vegetable............	28,829,000	141,023,000	50,039,000
Essential...............	3,492,000	9,439,000	5,570,000
Oil-bearing materials:			
Castor beans.............	1,139,000	3,674,000	1,302,000
Copra..................	2,395,000	14,971,000	9,951,000
Flaxseed................	10,571,000	76,845,000	9,133,000
Peanuts.................	1,899,000	12,382,000	2,371,000
Exports			
Oils:			
Animal..................	822,000	3,426,000	603,000
Mineral.................	152,174,000	426,349,000	535,560,000
Fixed vegetable............	15,624,000	96,226,000	37,017,000
Essential................	628,000	2,230,000	1,177,000

The most striking development in the vegetable oil trade was the collapse of the business built up in 1920 in such Oriental oils as coconut, soy-bean, and peanut. Imports of coconut oil totaled 272,000,000 pounds in 1920 and 141,000,000 pounds were exported. In 1921 the imports were down to 165,000,000 pounds while the exports had practically disappeared. Imports of copra were fairly well maintained for the year as a whole. Imports of soy-bean oil reached 196,000,000 pounds in 1920 (which was far below the 1918 figure), and nearly 68,000,000 pounds were exported. In 1921 the imports had dropped to 50,000,000 pounds and the exports to a mere 5,000,000 pounds. The imports of these oils, however, are greatly in excess of the pre-war normal. Cottonseed oil, which was purchased abroad to the extent of nearly 25,000,000 pounds in 1920, was practically removed from the import column in 1921, whereas the exports of this typically American product actually increased from 160,000,000 pounds in 1920 to 283,000,000 pounds in 1921. This is much above the 1914 level.

TRADE IN OILS, FATS, AND WAXES

ARTICLES Imports	1914	1920	1921
Oils, animal:			
Cod and codliver, gal........	1,393,706	1,943,357	1,224,660
All other, gal...............	1,488,973	1,294,134	745,984
Oils, mineral:			
Crude, gal.................	773,052,480	2,826,860,902	5,607,124,270
Refined			
Benzene, gasoline, naphtha, gal..................	16,139,912	22,037,592	35,642,815
All other, gal..............	1,945,007	59,851,312	95,548,796
Oils, fixed vegetable:			
Chinese nut, gal.............	4,932,444	10,613,638	4,439,981
Cocoa butter or butterine, lbs..	2,838,761	41,500	915,177
Cocoanut, lbs...............	74,386,213	271,539,548	165,268,503
Cottonseed, lbs.............	17,293,201	24,164,821	1,315,265
Linseed, gal...............	192,282	4,550,391	1,996,586
Olive, non-edible, gal.......	763,924	216,145	261,689
Olive, edible, gal...........	6,217,560	6,812,596	4,443,407
Palm, lbs.................	58,040,202	50,165,387	31,076,224
Palm-kernel, lbs............	34,327,600	53,508	2,769,144
Peanut, gal................	1,337,136	22,064,363	2,421,704
Rape-seed, gal..............	1,464,265	1,229,526	1,171,930
Soy-bean, lbs..............	16,332,452	195,773,594	49,330,645
All other, value............	$439,009	$2,974,966	$791,654
Oils, distilled and essential:			
Birch tar and cajeput, value...	(¹)	$20,019	$1,829
Lemon, lbs................	385,959	870,170	626,014
All other, value............	$2,633,789	$8,370,317	$4,989,374
Oleostearin, lbs.............	5,243,553	1,307,837	742,908
Paraffin (except oil), lbs........	7,495,459	8,687,728	5,714,653
Wax:			
Beeswax, lbs...............	1,412,200	3,923,687	2,215,332
Mineral, lbs...............	8,083,422	2,816,700	4,755,396
Vegetable, lbs..............	4,255,686	9,949,567	6,235,416
Grease and oils, n. e. s., lbs......	22,322,492	42,165,287	35,106,716
Oil seeds and nuts:			
Castor beans, bu............	1,030,543	1,416,328	660,215
Cocoanuts in shell, value......	$2,133,416	$4,830,548	$2,690,723
Copra, lbs.................	45,437,155	218,521,946	196,635,315
Flaxseed, bu...............	8,653,235	23,391,934	16,170,415
Peanuts			
Not shelled, lbs...........	17,472,631	12,067,998	5,361,196
Shelled, lbs..............	27,077,158	120,344,425	42,628,034
Exports			
Oils, animal:			
Fish, gal..................	448,366	1,310,478	118,261
Lard, gal.................	110,199	130,635	89,303
All other, gal..............	891,035	1,452,489	340,329
Oils, mineral:			
Crude, gal.................	146,477,342	356,542,830	355,200,756
Refined or manufactured:			
Fuel and gas, gal..........	475,143,205	685,738,142	861,419,680
Illuminating, gal..........	1,157,283,310	914,137,071	833,194,727
Lubricating, gal...........	196,884,696	339,701,134	333,902,780
Gasoline, gal.............	151,611,537	294,949,121	382,610,683
Other naphthas, gal........	40,840,730	185,265,961	259,603,571
Residuum, gal............	113,370,245	48,300,361	9,825,633
Oils, fixed vegetable:			
Cocoa butter, lbs...........	(¹)	11,048,416	3,170,617
Cocoanut oil, lbs...........	(¹)	141,063,943	6,639,055
Corn, lbs.................	18,281,576	12,482,679	6,919,170
Cottonseed, lbs.............	192,963,079	159,400,618	283,268,025
Linseed, gal...............	239,198	1,136,585	561,277
Peanut, lbs................	(¹)	4,922,781	1,594,643
Soy-bean, lbs..............	(¹)	67,781,974	5,117,605
All other, value............	$338,956	$3,258,446	$1,013,541
Oils, distilled and essential:			
Peppermint, lbs............	117,809	90,255	50,425
All other, value............	$230,557	$1,551,992	$890,472
Grease:			
Lubricating, value..........	$2,394,918	$6,157,323	$6,851,936
Soap stock, etc., value........	$5,046,959	$8,994,603	$8,994,603
Oleo oil, lbs................	97,017,065	74,529,394	106,411,800

¹ Not stated separately.

Trade in Oils, Fats and Waxes (Concluded)

	1914	1920	1921
Oleomargarine, lbs............	2,532,821	20,952,180	6,219,165
Paraffin:			
Unrefined, lbs..............	186,357,728	79,023,341	50,121,130
Refined, lbs................	(²)	81,784,255	203,289,734
Stearin:			
Animal, lbs................	2,724,182	22,505,602	19,177,311
Vegetable, lbs.............	(²)	5,138,225	1,716,313
Wax:			
Beeswax, lbs...............	96,215	641,357	189,616
Manufactures of, value.......	$112,193	$1,203,471	$848,425
Oil seeds and nuts:			
Cottonseed, lbs.............	16,342,384	3,505,118	4,811,313
axseed, bu..............	305,546	24,044	1,481
Peanuts, lbs................	8,054,817	14,137,956	13,149,417

Period from Oct. 3, 1913, to June 30, 1914.
² Not stated separately.

ORES AND METALS

The following data on the trade in ores and metals is not included in the summary table at the beginning of the article, but may be of interest to certain branches of the chemical industry. The figures apply only to ores and metals not advanced beyond the bar and ingot stage.

SUMMARY OF TRADE IN PRINCIPAL METALS

ARTICLES	1914	1920	1921
Imports			
Antimony.....................	$696,000	$1,284,000	$937,000
Chromate of iron..............	737,000	1,419,000	1,689,000
Copper.......................	54,506,000	94,310,000	61,866,000
Iron..........................	11,879,000	12,221,000	12,215,000
Lead.........................	2,057,000	6,817,000	10,543,000
Manganese....................	1,841,000	8,086,000	10,200,000
Nickel.......................	6,110,000	6,848,000	4,971,000
Platinum.....................	3,976,000	6,990,000	6,282,000
Tin..........................	39,422,000	93,145,000	53,248,000
Tungsten ore.................	114,000	2,589,000	468,000
Zinc.........................	616,000	965,000	1,361,000
Exports			
Aluminium....................	1,102,000	5,195,000	4,107,000
Bauxite concentrates..........	616,000	1,709,000	1,067,000
Copper.......................	149,480,000	127,996,000	73,199,000
Ferrovanadium................	503,000	254,000	916,000
Iron..........................	6,261,000	14,454,000	11,238,000
Lead.........................	2,610,000	4,207,000	1,275,000
Nickel.......................	9,404,000	1,144,000	57,000
Tungsten and ferrotungsten.....	....	58,000	2,000
Zinc.........................	995,000	22,927,000	3,469,878

MISCELLANEOUS PRODUCTS

A better idea of the general depression in foreign trade can be gained from a study of the following table of miscellaneous products than from any of the other tables in this article. In nearly all cases there has been a falling off from 1920. A notable exception is gunpowder, for which there is recorded an increase from less than 2,000,000 pounds to nearly 42,000,000 pounds. Glassware did practically as well in 1921 as in 1920, so far as value is concerned, and the export total for this item is very much higher than in 1914.

TRADE IN MISCELLANEOUS PRODUCTS

ARTICLES	1914	1920	1921
Imports			
Collodion, and manufactures of, value.....................	$569,763	$82,940	$168,442
Explosives:			
Fulminates, gunpowder, etc., value...................	$256,379	$1,523,553	$189,524
All other value.............	$600,958	$765,412	$759,347
Glass and glassware, value......	$8,191,833	$3,582,403	$11,771,538
Glue and glue size, lbs........	22,714,877	1,410,194	3,561,831
Matches, value...............	$882,812	$1,096,982	$954,898
Oilcloth for floors:.............			
Linoleum, sq. yds..........	3,724,086	522,999	825,105
Oilcloth, sq. yd............	340,288	62,372	44,763
Paints, pigments, etc., value.....	$2,325,222	$1,975,769	$2,943,942
Paper and pulp:			
Printing paper			
Not over 8 c. per lb., lbs...	536,815,288¹	1,322,890,825	1,475,111,157
All other, lbs.............	6,053,429	1,371,576	4,219,925
Surface-coated paper, lbs......	6,925,505	369,211	1,157,819
Wrapping paper, lbs..........	36,515,554	4,983,817	7,444,611
Wood pulp			
Mechanical, tons...........	177,484	194,119	167,093
Chemical, unbleached, tons..	302,963	443,867	349,170
Chemical, bleached, tons....	88,917	88,564	107,904
Photographic goods:			
Dry plates, value...........	(²)	$25,808	$78,452
Motion-picture films			
Not exposed, lin. ft........	44,717,323¹	46,485,434	134,118,621
Negatives, lin. ft..........	402,704⁴	1,417,774	2,121,593
Positives, lin. ft..........	20,057,144	3,327,566	5,253,413
Other films and plates, value..	$324,535	$1,355,832	$2,724,320
Imports			
Soap:			
Castile, lbs................	4,622,082	2,352,974	1,808,872
All other, value.............	$460,485	$192,103	$319,647

¹ Valued at not above 5 cents a pound prior to April 24, 1920
² Not stated separately.
³ From Oct. 3, 1913, to June 30, 1914.
⁴ Stated as "All other" motion-picture films in 1914.

Trade in Miscellaneous Products (Concluded)

ARTICLES	1914	1920	1921
Sugar and molasses:			
Molasses, gals...............	51,410,271	154,670,200	113,413,681
Sugar			
Beet, lbs.................	2,367,708	14,270,114	22,491,771
Cane, lbs.................	5,061,564,621	7,577,698,325	6,984,195,691
Exports			
Baking powder, lbs...........	2,725,964	5,595,126	3,491,666
Blacking and polishes, value.....	$649,395	$2,845,110	$2,072,963
Candles, lbs.................	3,047,756	7,691,420	3,252,838
Celluloid and manufactures, value	$1,387,541	$10,044,242	$4,281,709
Chewing gum, value..........	$178,630	$2,617,483	$1,510,679
Explosives:			
Cartridges, loaded, value......	$3,521,533	$9,729,937	$3,099,947
Dynamite, lbs.............	14,464,601	12,566,057	11,878,600
Fuses, value..............	(²)	$709,662	$512,030
Gunpowder, lbs...........	989,385	1,721,991	43,485,291
Shells and projectiles, loaded, value..................	(²)	$12,295,519	$563,966
All other, value...........	$916,280	$2,250,566	$1,445,610
Flavoring extracts and fruit juices, value..................	(²)	$1,425,380	$1,236,135
Glass and glassware, value......	$3,729,623	$25,906,621	$25,387,607
Glucose and grape sugar:			
Glucose, lbs..............	162,680,378	219,793,235	125,972,386
Grape sugar, lbs...........	36,850,496	25,839,015	15,981,960
Glue, lbs...................	2,351,770	13,141,294	5,991,872
India-rubber manufactures, value	$12,441,220	$69,226,716	$59,565,572
Ink:			
Printers', value...........	$443,377	$1,590,096	$1,550,548
All other, value...........	$181,697	$836,436	$774,423
Matches, value..............	$77,36	$558,911	$389,064
Metal polish, value..........	$162,504	$451,934	$346,104
Mucilage and paste, value.....	$95,013	$654,827	$601,263
Oilcloth:			
For floors, sq. yds........	163,214	2,623,060	1,287,649
All other, value...........	$666,479	$2,475,699	$2,917,099
Paints, pigments, etc.:			
Dry colors			
Carbon, bone, and lampblack, value...............	$421,548	$1,959,208	$1,829,987
All other, value.........	$690,836	$2,991,618	$2,170,237
Lead			
Red, lbs.................	(²)	3,027,731	2,046,339
White, lbs...............	16,845,154	34,441,918	17,408,803
Ready-mixed paints, gal......	852,910	2,553,091	2,317,630
Varnish, gal...............	1,069,501	1,529,592	1,158,025
Zinc oxide, lbs.............	29,197,790	30,925,983	10,149,360
All other, value...........	$1,779,863	$7,756,076	$5,947,461
Paper and pulp:			
Newsprint, lbs.............	88,966,738	123,335,408	64,156,772
Other printing paper, lbs......	28,602,134	92,076,860	78,621,553
Wrapping paper, lbs..........	14,133,097	65,163,463	42,454,760
Writing paper and envelopes, value.................	$1,179,232	$7,322,859	$8,232,318
Wood pulp, tons...........	13,481	33,972	27,168
Photographic goods:			
Motion-picture films			
Not exposed, lin. ft........	155,359,550	90,398,122	53,814,601
Exposed, lin. ft..........	32,690,104	188,527,165	154,931,010
Other sensitized goods, value..	$1,348,216	$4,960,928	$5,726,611
Soap:			
Toilet or fancy, value........	$2,141,633	$6,625,259	$4,182,428
All other, lbs.............	58,547,763	155,891,586	85,830,216
Sugar and molasses:			
Molasses, gal.............	1,002,441	7,667,830	5,348,202
Sirup, gal................	11,630,528	12,278,246	4,606,261
Sugar, refined, lbs..........	50,895,726	1,444,030,665	582,698,488
Vulcanized fiber and manufactures of, value...........	$854,642	$1,859,357	$2,295,457
Washing powder and fluids, lbs..	12,761,958	6,217,201	4,021,497

¹ Not stated separately.

MISCELLANEOUS MATERIALS

The export and import trade in a number of materials that could not conveniently be grouped elsewhere is shown in the following table:

TRADE IN MISCELLANEOUS MATERIALS

ARTICLES	1914	1920	1921
Imports			
Asphaltum and bitumen, tons...	180,689	93,397	134,280
Blood, dried, value...........	$391,816	$678,307	$290,609
Bones, hoofs, horns, value.....	$1,061,466	$1,754,892	$2,936,889
Dyewoods, crude state:			
Logwood, tons.............	30,062	45,073	56,977
All other, tons.............	7,663	3,358	4,846
Fish sounds, lbs.............	(²)	79,679	127,781
Gelatin, unmanufactured, lbs...	2,341,317	1,121,117	2,396,645
Hide cuttings and other glue stock, lbs.................	2,158,514¹	26,248,159	36,104,659
Moss and seaweed:			
Crude, value..............	$301,259	$457,073	$505,808
All other, value...........	$54,376	$40,711	$47,195
Rennets, value..............	$129,720	$159,039	$72,092
Salt, 100 lbs................	3,076,071	1,756,240	2,486,091
Tanning materials, crude:			
Mangrove bark, tons........	7,689	2,544	7,156
Quebracho wood, tons......	73,956	33,672	32,901
All other, value...........	$468,230	$2,757,859	$1,393,058
Vanilla beans, lbs............	897,100	1,130,336	986,071
Exports			
Asphaltum:			
Unmanufactured, tons........	49,831	47,024	43,630
Manufactures of, value......	$362,347	$682,753	$781,947
Barks for tanning, tons........	(²)	513	382
Moss, value.................	$51,006	$141,000	$62,595
Salt, 100 lbs................	1,489,312	2,574,937	2,426,321

¹ Not stated separately.
² Quantity not given for 1914.

ORIGINAL PAPERS

A Fermentation Process for the Production of Acetone, Alcohol, and Volatile Acids from Corncobs

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The production of acetone by biochemical methods in England and Canada during the war was carried out on a large scale. In one plant,[4] operated at Toronto, Canada, from May 1916 to November 1918, more htan 6,000,000 lbs. of acetone and 12,000,000 lbs. of alcohol were obtained. The breaking down of carbohydrates into acetone can be effected by the use of *Bacillus granulobacter pectinovorum*,[1] *Bacillus macerans*,[2] *Bacillus acetoethylicum*,[3] and no doubt by other types of bacteria.

Aside from securing the proper organism and proper conditions for fermentation, an essential requirement is a cheap source of fermentable carbohydrate. The chief materials fermented have been corn meal and molasses. As a cheap substitute for these materials, the utilization of wood waste, straw, seed hulls, and corncobs is suggested.

In a recent paper[7] the authors have described the results obtained by fermenting crude corncob sirup with the pentose fermenter, *Lactobacillus pentoaceticus*. The results obtained indicate that a sirup prepared by the hydrolysis of corncobs with dilute acids offers a favorable medium for the fermentative action of these bacteria. In the present paper are given the results obtained by fermenting a similar corncob sirup with another organism, *Bacillus acetoethylicum*, whose isolation, fermentation characteristics, and commercial use have been described by Northrop and his associates. A more detailed description of the products of fermentation and conditions influencing these products was given in a later paper by Arzberger, Peterson, and Fred.[8]

The chief products formed by this organism are acetone, ethyl alcohol, formic and acetic acids, and carbon dioxide. The biochemical relations of these products to one another are very intimate, as may be seen from the fact that a high production of acetone and alcohol is accompanied by a low yield of volatile acids. Conversely, when the acid production is high, the acetone and alcohol yields are low. The condition determining this variation of the products is the reaction of the medium. An alkaline reaction, pH 8.0, favors the production of acid, while an acid reaction of pH 5 to 7 increases the yield of acetone and alcohol.

HYDROLYSIS OF CORNCOBS

A dilute sugar solution was prepared by hydrolyzing ground corncobs with sulfuric acid. After hydrolysis, the acid was neutralized with milk of lime, and the sugars were removed by pressing and washing the insoluble residue. The production of reducing sugars is influenced by the quantity of acid, the volume of water, the length of heating, and the pressure maintained during the hydrolysis. At a pressure of 20 lbs. the most efficient production of sugars was effected by heating the cobs for 1 hr. with about 8 per cent of their weight of acid. A greater quantity of acid and water increased the yield only 2 per cent. At a pressure of 100 to 115 lbs., with 2 per cent of acid, somewhat lower yields of sugar were obtained. A second hydrolysis of the residue gave only 4.4 per cent of reducing sugars. The percentages of sugar obtained and other data for the different methods of hydrolysis are given in Table I.

FERMENTATION OF PRODUCTS OF HYDROLYSIS

PRELIMINARY TESTS—To determine the fermentability of the corncob sugars, test tube cultures containing 3.0 per cent of reducing sugar, 0.5 per cent of peptone, and 0.1 per cent of solid Na_2HPO_4 (approximately $2H_2O$) were prepared. Varying amounts of sterilized sodium hydroxide were added, so that the pH value of the medium in the tubes ranged from 6.4 to 8.8. After a few days the unfermented sugar was determined, and it was found that the greatest fermentation had taken place where the pH was between 7.6 and 8.4 at the time of inoculation.

FERMENTATION SERIES, I—The effect of extracting the cobs with alkali on the fermentability of the hydrolysis products was studied in this experiment. Convenient portions of Solutions 2, 5, and 7 (Table I) were used. The solutions were placed in 500-cc. Erlenmeyer flasks, together with sufficient peptone and Na_2HPO_4 to give a concentration of 0.5 and 0.1 per cent, respectively. The flasks were stoppered with cotton plugs and sterilized for 30 min. at 15 lbs. pressure. When cold, an excess of sterilized calcium carbonate was added to the flasks, and the pH of the medium was adjusted to 7.6 to 8.0 by the addition of sterilized sodium hydroxide.[1] The flasks of media were inoculated, and the cotton plugs were covered with tin foil to prevent the loss of alcohol and acetone.

Considerable difficulty was experienced at first in securing growth in these cultures. Sugar determinations showed that little or no reducing sugars had been fermented. The

1 Received April 27, 1921.

2 This work was in part supported by a grant from the special research fund of the University of Wisconsin.

3 Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

4 H. B. Speakman, *J. Biol. Chem.*, 41 (1920), 319.

5 F. Schardinger, *Centr. Bakt. Parasitenk. I., II Abt.*, 14 (1905), 772.

6 J. H. Northrop, L. H. Ashe, and J. K. Senior, *J. Biol. Chem.*, 39 (1919), 1; J. H. Northrop, L. H. Ashe, and R. R. Morgan, THIS JOURNAL, 11 (1919), 723.

7 E. B. Fred and W. H. Peterson, THIS JOURNAL, 13 (1921), 211.

8 *J. Biol. Chem.* 44 (1920), 465.

1 In some earlier experiments, the pH was adjusted before the medium was sterilized, but it was found that the solution had become acid as a result of sterilizatson, and that from 15 to 20 per cent of the reducing sugars had been destroyed.

Table I—Reducing Sugars Obtained from Corncobs by Various Methods of Hydrolysis

No.	Material	G.	Reagent	G.	Volume of Water Cc.	Heating Time Min.	Press. Lbs.	Reducing Sugars as Glucose Per cent[1]
1	Cobs	50	H₂SO₄	4	200	60	20	24.5
2	Cobs	200	H₂SO₄	30	1500	120	20	26.7
3	Cobs	20	H₂SO₄	1.6	80	240	20	31.4
4	Cobs	100	NaOH	30	1000	120	20	10.0
5	Residue from 4		H₂SO₄	20	1000	120	20	9.1
6	Cobs	50	NaOH	2	500	15	20	2.8
7	Residue from 6		H₂SO₄	10	500	120	20	21.9
8	Cobs	100	H₂SO₄	2	200	30	100-115	20.7
9	Residue from 8		H₂SO₄	2	200	20	100-115	4.4

[1] Air dry cobs.

cultures had become acid in reaction and growth had apparently ceased. More Na₂HPO₄ was added, the pH was adjusted with sodium hydroxide, and the flasks were reinoculated. After a few days the cultures were tested for acetone, and good qualitative tests were obtained. Microscopic mounts of the cultures showed the presence of large numbers of bacteria. At the end of 10 days sugar determinations were made, and it was found that about one-half of the reducing sugars had been fermented. The cultures were analyzed for acetone, alcohol, and volatile acids.

Methods of Analysis—The acetone and alcohol were distilled from a 50-cc. portion of the culture, which had been previously neutralized with sodium hydroxide and saturated with sodium chloride in order to hasten the removal of the acetone and alcohol. An aliquot part of the distillate was used for the determination of acetone, according to Goodwin's modification[1] of the Messinger-Huppert method. In another aliquot part the alcohol was oxidized with potassium dichromate, and the resulting acids were removed by distillation and titrated.[2]

A second portion of the culture was acidified with sulfuric acid, and the volatile acids were driven out by steam distillation and titrated.

Table II—Acetone Fermentation of the Hydrolysis Products of Corncobs
(Calculated for 100 cc. of culture)

No. of Corncob Extract	Age of Culture Days	Reducing Sugar as Glucose G.	Acetone G.	Alcohol as Ethyl Gl.	Volatile Acids as Acetic G.	Sum of Products G.	Sugar Ferm. G.
Table I, No 2	10	5.02	0.320	0.854	0.636	1.810	2.73
Table I, No 5	7	4.02	0.139	0.266	0.286	0.691	1.39
Table I, No. 7	8	3.60	0.083	0.233	0.281	0.597	1.94

From the analytical data which are given in Table II, it is evident that the optimum conditions for the growth of the bacteria were not obtained. Unfavorable reaction and the tendency of the bacteria to mat together as a slime on the bottom of the flask were probably responsible.

FERMENTATION SERIES, II—The distribution of the bacteria is maintained much better if the flask is filled with some coarse, inert material to which the organisms may attach themselves. Northrop, Ashe, and Morgan[3] suggested use of broken corncobs, coke, or beech shavings. In this experiment a liter Jena bottle was two-thirds filled with coarse cinders, which were extracted with 10 per cent hydrochloric acid and washed free of acid. The bottle was closed with a 2-hole rubber stopper through which were inserted glass tubes somewhat similar to those used in an ordinary wash bottle. Instead of the short tip on a wash bottle a long glass tube was used, and a guard tube filled with cotton was attached to the second tube, which corresponded to the mouth piece of a wash bottle. During the fermentation the delivery tube was closed by a screw clamp, while the guard

[1] *J. Am. Chem. Soc.*, 42 (1920), 39.
[2] A. W. Dox and A. R. Lamb, *J. Am. Chem. Soc.*, 38 (1916), 2561.
[3] *Loc. cit.*

tube was left open as a means of escape for the fermentation gases. A sample for analysis was removed when desired by attaching a rubber force bulb to the guard tube, pumping air into the flask, and then opening the screw clamp. The first 10 cc. coming out was always discarded. When sufficient sample had been collected the screw clamp was closed, the force bulb was disconnected, and the air pressure in the flask was released through the guard tube. At the end of the fermentation all the liquid in the bottle was forced out, leaving the bacterial slime attached to the cinders. The bottle was again charged with 400 to 500 cc. of medium by sucking this into the bottle through the delivery tube. With this arrangement a rapid and continuous fermentation was maintained, the yield of products was much increased, and the time of fermentation considerably shortened. One experiment with one refill and two experiments with two renewals each were made. The results of the analyses are given in Table III. The most rapid fer-

Table III—Yield of Products by a Continuous Fermentation
(Calculated for 100 cc. of culture)

Expt.	No. of Refill	Age of Culture Days	Reducing Sugars as Glucose G.	as Acetone G.	Alcohol as Ethyl G.	Volatile Acid as Acetic G.	Total Products G.
I	1	0	2.23				
		4	0.77	0.197			
		9	0.22	0.342	0.681	0.295	1.318
I	2	0	3.28				
		3	1.84	0.390	0.570		
		6	0.46	0.502	1.051	0.561	2.114
II	1	0	3.63				
		6	0.35	0.306	0.970	0.409	1.685
II	2	0	3.42				
		4	1.00	0.309	0.810	0.408	1.527
		8	0.42	0.381	1.047	0.377	1.805
III	1	0	3.15				
		6	0.28	0.206	0.670	0.372	1.248

mentation took place in the second refill of Expt. I. In 6 days, 2.114 g. of products were obtained from the fermentation of 2.82 g. of sugar. The maximum yields of acetone and alcohol were found in this case, while the volatile acid was correspondingly low. The relation of these three products to one another and to the sugar consumed may be more clearly seen by a recalculation on a percentage basis, as has been done in Table IV. The figures previously reported

Table IV—Percentage of Products on the Basis of Sugar Fermented

Expt.	No. of Refill	Acetone Per cent	Alcohol Per cent	Volatile Acid Per cent	Total Per cent
I	1	16.1	32.1	13.9	62.1
I	2	17.8	37.3	20.0	75.0
II	1	9.3	30.0	15.5	54.8
II	2	12.7	34.9	12.6	60.2
III	1	7.2	23.3	13.0	43.5
Average		12.6	31.5	15.0	59.1
Average for 10 fermentations of purified carbohydrates[1]		8.7	25.5	21.7	55.6

[1] *Loc. cit.*

for the fermentation of the pure carbohydrates by *Bacillus acetoethylicum* are included in this table for comparison. More acetone and alcohol and less volatile acids were obtained from the fermentation of the corncob extract than had been found in the fermentation of the pure carbohydrates. In both experiments the second charge shows an increase over the first in the proportion of acetone and alcohol. These two products are characteristic of the later stages of the fermentation, and hence a method of fermentation which leaves the bacteria in the container and renews the sugar favors the formation of acetone and alcohol.

From the data of Tables I to III the yield of products may be expressed on the basis of 100 lbs. of corncobs. An average of 25 lbs. of reducing sugars were formed, and of this 90 per cent, or 22.5 lbs., were fermented, yielding about 2.7 lbs. of acetone, 6.8 lbs. of alcohol, and 3.4 lbs. of volatile acids.

Summary

Corncobs may be utilized for the production of acetone, ethyl alcohol, formic acid, and acetic acid. These products may be obtained by fermenting a sirup which is made from corncobs by hydrolysis with dilute sulfuric acid. This hydrolysis is easily brought about and, based on the weight of corncobs, yields from 25 to 30 per cent of reducing sugars, mainly xylose.

This crude xylose sirup is readily and almost completely fermented by *Bacillus acetoethylicum* with the production of the above products. On the basis of 100 lbs. of corncobs, the yield of products is 2.7 lbs. of acetone, 6.8 lbs. of alcohol, and 3.4 lbs. of volatile acids.

The best results are obtained by conducting the fermentation in a container partly filled with cinders. The bacteria become attached to these cinders, thus bringing about a good distribution of cells throughout the culture. At the end of the fermentation the solution is removed, and a fresh charge is added without disturbing the bacterial slime. An immediate and vigorous fermentation ensues. An important condition that must be observed is the reaction of the medium. This should be between pH 7.6 and 8.4 at the beginning of the fermentation, and an abundance of calcium carbonate should be present to neutralize the acids that are formed.

Alkali Fusions. III—Fusion of Phenylglycine-*o*-Carboxylic Acid for the Production of Indigo[1]

By Max Phillips

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The Gibbs and Conover[2] catalytic process for making phthalic anhydride, developed in this laboratory, has already assumed considerable industrial importance, and phthalic anhydride promises to become one of the cheapest intermediates. Of the many dyes that can be made from this compound, by far the most important one is unquestionably indigo. A process of making this dye from phthalic anhydride has been used by the Badische company for nearly twenty-five years. The various steps involved in the so-called Badische process may be represented as follows:

Phthalic Anhydride   Phthalimide   Anthranilic Acid   Phenylglycine-o-Carboxylic Acid

Indigo   Indoxyl   Indoxylic Acid
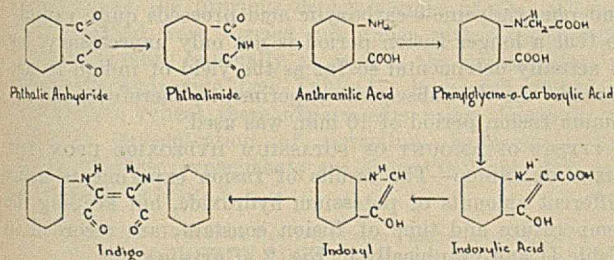
Although the chemistry involved in this process is now very generally known, the details for carrying it out have never, for obvious reasons, been published by the Badische company. A study of the various steps involved in this process has, therefore, been undertaken in this laboratory, and the present article is a report of one phase of the work.

Historical Review

The process of making indigo from phenylglycine-*o*-carbolic acid was first brought to the attention of chemists by Heumann[3] in 1890, and subsequently patented by the Badische company. According to Heumann, three parts of potassium hydroxide, one part phenylglycine-*o*-carboxylic acid, and one part of water are heated to 180° to 200°C. until the alkaline mass assumes an intense orange color, whereupon it is allowed to cool and subsequently dissolved in water, and the indigo is precipitated by passing a stream of air through the solution. The yield obtained is not given. The Badische[4] patent controlling this process fails to give any further information. In a later patent[5] it is claimed that the heating of the phenylglycine-*o*-carboxylic acid must be done in the absence of air or in an atmosphere of an inert gas. Using sodium hydroxide, a temperature range of 235° to 265°C. is given, whereas with potassium hydroxide that of 280° to 290°C. is recommended. It is also claimed that the alkali used must be as dry as possible.

According to Levinstein,[1] the conversion of phenyglycine-*o*-carboxylic acid to indoxylic acid is accomplished by heating a mixture consisting of 60 parts phenylglycine-*o*-carboxylic acid and 100 parts of sodium hyroxide for 2.75 hrs. at 260°C. No statement as to yield is given.

In a patent granted to Michel[2] it is claimed that the addition of paraffin to the alkali fusion mixture greatly improves the yield of indigo. The fusion temperature range is given as from 250° to 280°C. The end of the reaction is determined by the color of the fused mass. However, it does not appear that this method has ever found any practical application.

Materials and Apparatus

potassium hydroxide and sodium hydroxide—These chemicals were of the usual C. P. grade. The potassium hydroxide assayed 81.2 per cent KOH, and the sodium hydroxide 94.0 per cent of NaOH. In calculating the moles of alkali used in the various fusion experiments, due allowance was made for the impurities present.

phenyglycine-*o*-carboxylic acid—This acid was prepared by condensing anthranilic acid with chloroacetic acid. In preparing it by this method it is usually recommended that sodium hydroxide or sodium carbonate be used as the condensing agent. It was found, however, that a purer product could be obtained if these were eliminated. The following is a brief description of the method used: 137 g. anthranilic acid (1 mole), 94.5 g. chloroacetic acid (1 mole), and 1000 cc. of water were placed in a suitable flask attached to a reflux condenser and heated for about 3 hrs. On cooling, crystals of phenylglycine-*o*-carboxylic acid separated out. These were filtered off and recrystallized from hot water. About 1000 g. of this acid were prepared, and the same material was used in all of the experiments recorded in this paper. A nitrogen determination made on this acid gave the following results:

Found Per cent N	Calculated for $C_1H_1O_1N$ Per cent N
7.13	7.18
7.18	

apparatus—A full description of the apparatus used will be found in an earlier article.[3]

1 Received June 20, 1921.

2 U. S. Patents 1,284,888 and 1,285,117; This Journal, 11 (1919), 1031.

3 *Ber.*, 23 (1890), 3431.

4 D. R. P. 56,273.

5 D. R. P. 85,071.

1 *J. Soc. Dyers Colour.*, 17 (1901), 138.

2 *Chem. Ztg.*, 35 (1911), 735; D. R. P. 232,986.

3 This Journal, 12 (1920), 145.

EXPERIMENTAL METHODS

In working out the most favorable conditions for the conversion of phenylglycine-o-carboxylic acid to indoxylic acid and hence to indigo, a study was made of the four following factors affecting the yield of indigo:

1—The proper fusion period.
2—Ratio of alkali to phenylglycine-o-carboxylic acid.
3—The proper fusion temperature.
4—The proper condensing agent.

With the apparatus used the effect upon the yield of indigo of each of the above factors could be very conveniently studied. Thus, to determine the optimum fusion period, with potassium hydroxide as the condensing agent, experiments were performed in which the period of fusion was the only variable factor, while the temperature, as well as the ratio of phenylglycine-o-carboxylic acid to potassium hydroxide, remained constant. From the results thus obtained, the optimum fusion period with reference to the other experimental conditions was deduced. Using the optimum conditions as determined in the preceding set of experiments, and again keeping the temperature constant, experiments were performed in which the ratio of phenylglycine-o-carboxylic acid to potassium hydroxide varied. At the end of the fusion period, the tubes were rapidly cooled and their indigo content determined. To determine the optimum fusion temperature, experiments were performed at different temperatures, using the optimum conditions as to period of fusion and ratio of phenylglycine-o-carboxylic acid already determined. In a similar manner the conversion of phenylglycine-o-carboxylic acid to indigo by means of sodium hydroxide, as well as with various mixtures of potassium hydroxide and sodium hydroxide, were studied.

INDIGO DETERMINATION—The cold alkaline mass was dissolved in hot water and the solution gently boiled for about half an hour. Air was then slowly passed through the solution until no more indigo separated out. This usually required about 8 to 10 hrs. The indigo was collected on a weighed hardened filter paper, and washed with hot dilute hydrochloric acid, then with hot water, and finally with alcohol and ether. It was dried at 110°C. and its weight determined. The result thus obtained is given in the following tables under the heading "Indigo Obtained—Grams." The purity of the indigo was determined by means of the Rawson[1] potassium permanganate method. This method is unquestionably as accurate as any of the methods for the determination of indigotin and by far the simplest.[2] The potassium permanganate solution was standardized against pure indigo prepared according to the Badische[3] method. In sulfonating the pure indigo, the directions given by Rawson in connection with his method for determining indigotin were followed so as to make the results comparable. The weight of pure indigo found was calculated as per cent of the theory.

EXPERIMENTS WITH POTASSIUM HYDROXIDE

EFFECT OF TIME OF FUSION ON INDIGO YIELD—The results of several experiments in which the time of fusion was made the only variable factor, while the temperature and ratio of phenylglycine-o-carboxylic acid to potassium hydroxide remained constant, are given in Table I and shown graphically in Fig. 1.[4]

1 Chem. News, 51 (1885), 255.

2 A good review of the various methods for the determination of indigotin is given by Bergtherl and Briggs, J. Soc. Chem. Ind., 25 (1906), 729.

3 Z. Farben-Ind., 8 (1909), 121.

4 The curves given in this article were drawn by Mr. G. H. Mains of this laboratory.
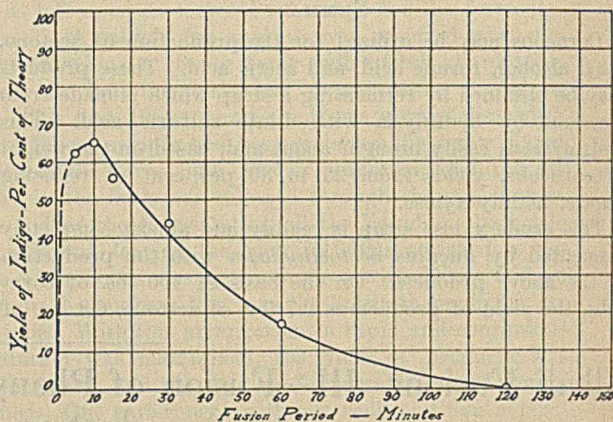
FIG. 1—FUSION PERIOD-YIELD CURVE

(Ratio of $C_6H_4(COOH)NH.CH_2.COOH : KOH = 1 : 8$. Temperature, 270° C.)

TABLE I—EFFECT OF VARYING FUSION PERIOD
Ratio $C_6H_4(COOH)NH.CH_2.COOH$: KOH = 1:8 (0.05 mole : 0.4 mole).
Fusion temperature 270°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1.........	5	4.1415	99.02	62.7
2.........	10	4.3320	99.0	65.3
3.........	15	4.2980	85.2	55.9
4.........	30	3.7530	76.6	43.8
5.........	60	2.0358	46.1	17.4
6.........	120	0.0000	00.0	00.0

This table indicates that the maximum yield of indigo was obtained when the fusion was conducted for 10 min. It appears that the reaction between potassium hydroxide and phenylglycine-o-carboxylic acid proceeds quite rapidly, so that a longer fusion period is not only unnecessary, but is actually detrimental so far as the yield of indigo is concerned. In the subsequent experiments, therefore, the optimum fusion period of 10 min. was used.

EFFECT OF AMOUNT OF POTASSIUM HYDROXIDE UPON THE YIELD OF INDIGO—The results of fusion experiments using different amounts of potassium hydroxide, but keeping the temperature and time of fusion constant, are recorded in Table II and graphically in Fig. 2 (Curve a).

TABLE II—EFFECT OF VARYING AMOUNT OF POTASSIUM HYDROXIDE
9.75 g. (0.05 mole) $C_6H_4(COOH)NH.CH_2.COOH$ used in each experiment.
Fusion temperature 270°C. Period of fusion 10 min.

No.	Moles KOH	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1.........	4	0	0	0
2.........	6	2.7816	61.7	26.2
3.........	10	5.0905	96.5	75.0
4.........	12	5.3695	99.6	81.6
5.........	14	5.6893	98.4	85.4
6.........	16	5.9396	95.8	86.8
7.........	20	5.9426	96.1	87.2
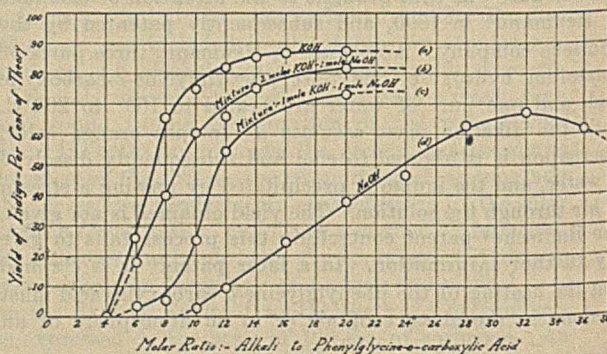
FIG. 2—CONCENTRATION-YIELD CURVES

The results show that the yield of indigo increases at first rather rapidly with the increase in concentration of

the potassium hydroxide until it reaches a maximum. Although the highest yield of indigo was obtained when 20 moles potassium hydroxide to 1 mole of phenylglycine-*o*-carboxylic acid were used, it is nevertheless apparent that practically the same yield was obtained when the molar ratio of potassium hydroxide to phenylglycine-*o*-carboxylic acid was 16:1, the difference between the two results being so small as hardly to warrant the use of the higher concentration of potassium hydroxide. In the following series of experiments, 16 moles of potassium hydroxide to 1 mole of phenylglycine-*o*-carboxylic acid were, therefore, used.
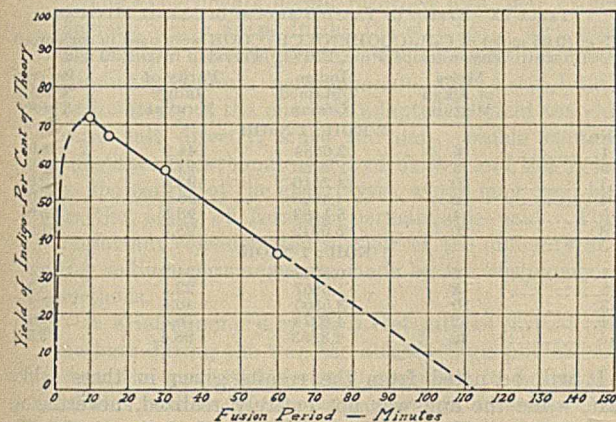
FIG. 3—FUSION PERIOD-YIELD CURVE
(Ratio of C$_6$H$_4$(COOH)NH.CH$_2$.COOH : KOH = 1 : 16. Temperature, 200° C.)

EFFECT OF TIME OF FUSION ON INDIGO YIELD. 2ND SERIES—Inasmuch as the previous determinations of the optimum fusion period were carried out under rather unfavorable conditions, more especially as regards the concentration of potassium hydroxide (see Table 1), it seemed, therefore, desirable to repeat these experiments using, however, the optimum concentration of potassium hydroxide. The results of these experiments are shown in Table III, and graphically in Fig. 3.

TABLE III—EFFECT OF VARYING FUSION PERIOD (2ND SERIES)
Ratio of C$_6$H$_4$(COOH)NH.CH$_2$.COOH : KOH =1:16 (0.05 mole:0.8 mole).
Fusion temperature 290°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	10	5.0096	93.9	71.8
2	15	4.7240	92.7	66.8
3	30	4.2240	90.0	58.0
4	60	2.7044	86.9	35.8

On comparing the results given in Tables I and III, it will be observed that in either case the maximum yield of indigo was obtained when the fusion was conducted for only 10 min. This optimum fusion period was, therefore, used in the subsequent fusion experiments with potassium hydroxide.

EFFECT OF THE TEMPERATURE OF FUSION ON YIELD OF INDIGO—The results of fusion experiments at temperatures of 240°, 260°, 270°, 290°, and 300°C. are recorded in Table IV and graphically in Fig. 4 (Curve *a*).

TABLE IV—EFFECT OF VARYING TEMPERATURE
Ratio of C$_6$H$_4$(COOH)NH.CH$_2$.COOH : KOH =1 : 16 (0.05 mole : 0.8 mole).
Fusion period 10 min.

No.	Temp. of Fusion °C.	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	240	4.6726	99.4	70.9
2	260	6.1234	95.4	89.1
3	270	5.9396	95.8	86.8
4	290	5.0096	93.9	71.8
5	300	4.1872	91.2	58.8

It appears from these results that 260°C. is the optimum temperature for the conversion of phenylglycine-*o*-carboxy-

lic acid into indigo. At higher temperatures some of the indoxylic acid formed is destroyed, so that a somewhat reduced yield of indigo is obtained.

EXPERIMENTS WITH SODIUM HYDROXIDE

EFFECT OF TIME OF FUSION ON INDIGO YIELD—The results of experiments in which the time of heating was made the only variable factor are given in Table V.

TABLE V—EFFECT OF VARYING FUSION PERIOD
Ratio of C$_6$H$_4$(COOH)NH.CH$_2$.COOH : NaOH = 1 : (0.05 mole : 0.4 mole).
Temperature 270°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	5	0	....	....
2	15	1.1940	80.3	14.6
3	30	0	....	....
4	60	0	....	....

It will be observed that indigo was obtained only in Expt. 2. Temporarily adopting 15 min. as the optimum period and using this as a basis for further study, experiments were performed in which the concentration of sodium hydroxide was the only variable factor. The results obtained are given in Table VI and graphically in Fig. 2 (Curve *d*).

TABLE VI—EFFECT OF VARYING AMOUNT OF SODIUM HYDROXIDE
9.75 g. C$_6$H$_4$(COOH)NH.CH$_2$.COOH (0.05 mole used in each experiment).
Fusion temperature 270°C. Period of fusion 15 min.

No.	Moles NaOH	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	10	0.2171	82.9	2.7
2	12	0.6506	94.5	9.4
3	16	1.7763	91.2	24.7
4	20	2.6852	91.9	37.7
5	24	3.2015	95.9	46.9
6	28	4.3519	94.9	63.0
7	32	4.7183	93.4	67.3
8	36	4.3339	93.1	61.6

In connection with these results, it will be observed that within certain limits the yield of indigo increases with the increase in the concentration of the sodium hydroxide, the maximum yield being obtained when the molar ratio of phenylglycine-*o*-carboxylic acid to sodium hydroxide is 1:32. This increase in the yield of indigo with the increase in the concentration of alkali was also found to be true in the case of potassium hydroxide (see Table II and Fig. 2, Curve *a*). With sodium hydroxide, however, the conversion of phenylglycine-*o*-carboxylic acid proceeds much more slowly than with potassium hydroxide under similar conditions. Although it may appear that a much higher molar concentration of sodium hydroxide than potassium hydroxide is necessary to get the maximum yield of indigo, nevertheless, weight for weight, the difference is not very great, more especially as ordinary C. P. potassium hydroxide usually assays about 80 per cent KOH, whereas
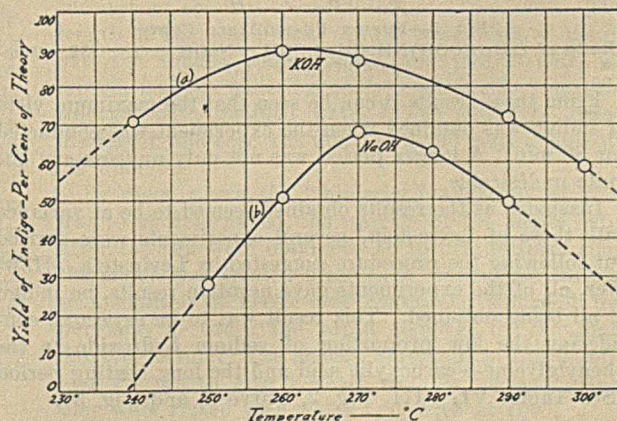
FIG. 4—FUSION TEMPERATURE-YIELD CURVES

an ordinary sodium hydroxide will assay about 95 per cent NaOH.

EFFECT OF THE TEMPERATURE ON THE YIELD OF INDIGO—Using the optimum concentration of sodium hydroxide already determined and keeping the time constant, experiments were performed at different temperatures. The results obtained are tabulated in Table VII and shown graphically in Fig. 4 (Curve *b*).

TABLE VII—EFFECT OF VARYING TEMPERATURE

Ratio of $C_6H_4(COOH)NH.CH_2.COOH : NaOH = 1 : 32$ (0.05 mole : 1.6 moles). Time, 15 min.

No.	Fusion Temperature °C.	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	250	1.9329	94.3	27.8
2	260	3.3997	97.0	50.3
3	270	4.7183	93.4	67.3
4	280	4.4239	92.5	62.5
5	290	3.6888	88.0	49.5

From these results it appears that 270°C. is the optimum temperature for the preparation of indigo from phenylglycine-*o*-carboxylic acid and sodium hydroxide.

DETERMINATION OF THE OPTIMUM TIME—Inasmuch as the experiments already made in this connection were of rather a preliminary nature (Table V), several additional experiments were performed under more favorable experimental conditions, more especially as regards temperature and concentration of sodium hydroxide. The results of these experiments are given in Table VIII and graphically in Fig. 5.

TABLE VIII—EFFECT OF VARYING TIME OF THE REACTION

Ratio of $C_6H_4(COOH)NH.CH_2.COOH : NaOH = 1 : 32$ (0.05 mole : 1.6 moles). Temperature, 270°C.

No.	Time of Fusion Minutes	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
1	10	4.0416	95.5	58.9
2	15	4.7183	93.4	67.3
3	30	5.5022	82.5	69.3
4	60	4.8816	85.9	64.0
5	120	2.7649	86.8	36.6
6	150	2.4566	84.9	31.8
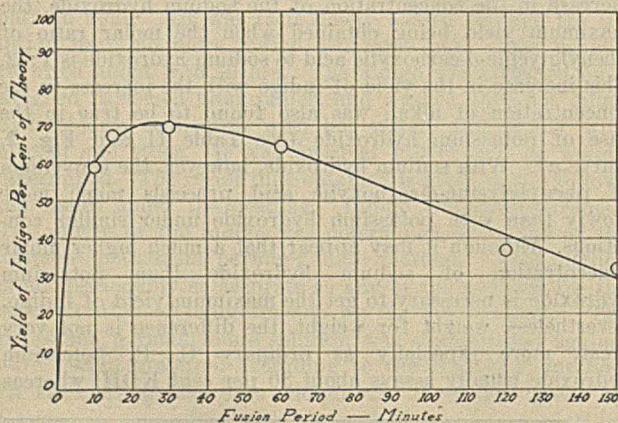
FIG. 5—FUSION PERIOD-YIELD CURVE
(Ratio of $C_6H_4(COOH)NH.CH_2.COOH : NaOH = 1 : 32$. Temperature, 270° C.)

From these results it can be seen that the maximum yield of indigo was obtained when the experiment was conducted for 30 min. A longer period was not only unnecessary, but quite undesirable.

Inasmuch as the results obtained seemed to be at variance with those of Levinstein,[1] several experiments were carried out following the procedure suggested by Levinstein. However, all of the experiments gave negative results, no indigo at all being obtained. This result was to be expected, considering the low proportion of sodium hydroxide to the phenylglycine-*o*-carboxylic acid and the long heating period (See Tables VI, VIII, Fig. 2, Curve *d*, and Fig. 5).

[1] *Loc. cit.*

EXPERIMENTS WITH MIXTURES OF POTASSIUM AND SODIUM HYDROXIDES

In view of the fact that somewhat better yields of indigo were obtained with potassium hydroxide than with sodium hydroxide, experiments were carried out with different mixtures of these two alkalies, in the hope of getting higher yields of indigo than were obtained with the pure alkalies. The results of two series of experiments utilizing two different mixtures of potassium and sodium hydroxides are given in Table IX, and are illustrated graphically in Fig. 2, Curves *b* and *c*.

TABLE IX—EFFECT OF VARYING AMOUNT OF ALKALI MIXTURE

9.75 g. (0.05 mole) of $C_6H_4(COOH).NH.CH_2.COOH$ were used in each experiment. Fusion temperature, 270°C. Period of fusion, 10 min.

No.	Moles of Alkali Mixture	Indigo Obtained Grams	Purity of Indigo Per cent	Per cent Yield of Theory
		2 KOH : 1 NaOH		
1	6	2.6684	44.2	18.0
2	8	2.8620	91.5	39.9
3	10	4.2516	93.6	60.8
4	12	4.4625	96.6	65.9
5	14	5.1433	96.3	75.6
6	20	5.5912	95.7	81.6
		1 KOH : 1 NaOH		
1	6	0.6547	34.2	3.4
2	8	1.5867	22.1	5.3
3	10	3.5805	46.4	25.3
4	12	4.6374	76.3	54.0
5	20	4.8853	98.4	73.3

It will be noted from the results given in these tables that, while the aim was not entirely realized, nevertheless much better yields were obtained than with sodium hydroxide alone under similar conditions. However, inasmuch as the results indicated that the yield of indigo obtained is a function of the quantity of potassium hydroxide present in the alkali mixture, no further experiments were carried out along this line.

SUMMARY

A study of the fusion of phenylglycine-*o*-carboxylic acid with potassium hydroxide, sodium hydroxide, and various mixtures of these two alkalies has been made, and the optimum conditions for carrying out this reaction have been determined.

The results of the experiments with potassium hydroxide as the condensing agent indicate that 260°C. is the optimum fusion temperature, 10 min. the optimum fusion period, and 12 to 16 moles potassium hydroxide to 1 mole phenylglycine-*o*-carboxylic acid, the optimum fusion mixture.

Using sodium hydroxide as the condensing agent, 270°C. has been found to be the optimum temperature, 25 to 30 min. the optimum time, and 28 to 32 moles sodium hydroxide to 1 mole phenylglycine-*o*-carboxylic acid the optimum mixture.

Potassium hydroxide has been found to give higher yields of indigo than sodium hydroxide.

Mixtures of these two alkalies give better yields of indigo than sodium hydroxide alone, the yield increasing with the increase of the ratio of potassium hydroxide with respect to the sodium hydroxide.

The zinc dust produced in the United States in 1920, as reported to the U. S. Geological Survey by 12 plants, showed an increase in 1920 as compared with 1919 of over 70 per cent, in both quantity and value.

ZINC DUST PRODUCED IN 1919-1920

	Quantity Short Tons	Value Based on Sales	Average Price per Lbs. Cents
		1919	
Prepared "blue powder"	4,083	$801,366	9.8
"Atomized" zinc dust	2,515	524,694	10.4
		1920	
Prepared "blue powder"	9,066	$2,009,117	11.1
"Atomized" zinc dust	2,273	512,833	11.3

The Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese[1,2]

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This paper deals with the formation of permanganates by the electrolytic method, in which bars of ferromanganese serve as anodes in a solution of sodium or potassium carbonate or hydroxide. The manganese is oxidized to the heptavalent state, forming permanganate directly in solution.

The experiments herein recorded owe their origin to the demand which arose during the war for a very pure grade of sodium permanganate. Of the possible methods of producing sodium permanganate, this electrolytic method undoubtedly is the one best adapted to yield the chemically pure salt directly, since the only soluble contaminating substance is carbonate (or hydroxide) and this is destroyed in the course of the electrolysis, which may even be carried to the point of forming permanganic acid. This is an important consideration in view of the difficulty of purifying sodium permanganate made by the customary chemical methods.

A brief summary of the investigations carried out by the authors during the war has already been published.[3] Since then, the authors have been interested to extend the study of this process in two respects—first, to study further the production of sodium permanganate in order to determine the optimum conditions more precisely and, if possible, to eliminate certain difficulties in its technical application, and, second, to make a careful comparative study of the process as applied to the production of potassium permanganate. Incidentally, many of the previous sodium permanganate experiments have been repeated in order that directly comparable results might be obtained with the same anodes. Both carbonate and hydroxide solutions were used as anolytes. A total of more than one hundred and eighty carefully controlled runs were made, each run having a duration, on the average, of 5 hrs. A few runs were made which lasted continuously from 7 to 10 days.

Very little work has been published on the production of permanganates electrolytically from ferromanganese. A bibliography up to 1919 is given in an article by Thompson,[4] who produced potassium permanganate in a 350-amp. cell which showed a current efficiency in K_2CO_3 anolyte of about 17 per cent at 40°. A higher efficiency would have been obtained with better diaphragms. The anodes used by Thompson contained 75 per cent Mn, 16.7 per cent Fe, 6.1 per cent C, and small amounts of Si and P, and did not show passivity under the conditions mentioned. At temperatures much above 40°, an insulating coating of oxides formed which prevented the production of permanganate. Thompson believes that the anodic behavior, as regards formation of insulating scale, is affected by small changes in the relative amounts of iron and manganese in the anode.

While this manuscript was being prepared for publication, an article by Henke and Brown[5] appeared. These authors worked with hydroxide electrolytes exclusively, and their experiments differed from those by the present authors in that no diaphragm was used and calcium hydroxide was added to the sodium hydroxide electrolyte. The calcium hydroxide apparently formed a film over the platinum cathode which acted as a diaphragm. Their experiments

showed that the current efficiency increases with the current density and diminishes with rising temperature, and that the curve of current efficiency against base concentration has a decided minimum.

APPARATUS

Except as otherwise noted, the electrolyses were carried out in a cell which consisted of a cylindrical glass jar (12.5 cm. in diameter by 15 cm. high), containing within it a porous porcelain cup (5 cm. in diameter by 12.5 cm. high) which served as a diaphragm. In this cell were placed the two electrodes, the cathode (of 16-gage sheet iron, 3 cm. by 15 cm.) being within the cup, and the ferromanganese anode standing in the jar outside, and about 3 cm. away from the cup. The freshly cast anodes had the dimensions 2.5 cm. square by 15 cm. in height. Electrical contact with the anode was made by clamping a strip of brass, carrying a binding post, against a freshly ground surface near the top.

Several cells (usually six) were operated simultaneously, being connected in series across a source of direct current. The circuit also contained an ammeter, a copper coulometer, and a rheostat. Provision was made for connecting a voltmeter across any individual cell. Readings of these several instruments furnished the electrical data.

The temperature of each cell was determined by reading a mercurial thermometer placed in the anolyte not far from the anode. In most of the experiments the temperature was controlled by placing the whole row of cells in a long water bath maintained at a temperature somewhat below that desired within the cells, and by inserting in each anolyte a cooling coil made of glass, the flow of water through which could be adjusted to compensate for irregular heating in any particular cell.

PROCEDURE

A typical electrolytic run was conducted in the following manner: Each of the cells of a series was filled with anolyte, the porous cups filled with catholyte and placed in the respective cells, the electrodes inserted, and electrical connections made. This was done as rapidly as possible, and the circuit was closed immediately afterward in order to avoid inter-diffusion of anolyte and catholyte, which usually differed from each other in composition. During the run, the electrolyte was stirred occasionally, and the temperature was observed immediately thereafter. The flow of cooling water was adjusted to keep the temperature constant within 3° or 4°C. The current was kept constant throughout the run to within about 1 per cent. The usual length of run was 5 hrs. At the conclusion of the electrolysis the anodes, cooling coils, and porous cups were removed, and the adhering anolyte was washed into the main solution with distilled water. The catholyte always was discarded, and care was taken to avoid getting any of it into the anolyte.

In cases where the "material" efficiency of the anode was to be determined, the weights of the anode before and after the run were obtained. To insure uniform conditions, the anode was treated after each electrolysis with a 2 per cent solution of acetic acid containing sufficient hydrogen peroxide to cause the rapid removal of the manganese dioxide coating. The anodes were kept in this solution just long enough to give a clean, metallic surface, after which they were rinsed with water and dried at 100°.

The gain plates of the copper coulometer were washed

[1] Received June 22, 1921.

[2] Published as Contribution No. 39 from the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.

[3] Wilson and Horsch, *Trans. Am. Electrochem. Soc.*, **35** (1919), 371.

[4] *Chem. Met. Eng.*, **21** (1919), 680.

[5] *J. Phys. Chem.*, **24** (1920), 608.

first with distilled water, then with alcohol, dried by burning the latter, and weighed. The gain in weight gave an accurate measure of the quantity of electricity passed through each cell.

The amount of permanganate produced during the run was obtained by a calculation based on the total weight of the anolyte and the analysis of a weighed sample of the latter. In order to obtain a sample which was representative, the anolyte was stirred thoroughly and allowed to stand for about 30 min. After the small amount of sludge had settled, the sample was pipetted from the clear supernatant solution.

The method of analyzing for permanganate was to wash the weighed sample (about 2 g.) into a 300-cc. flask, dilute to about 100 cc., acidify with glacial acetic acid, add an excess of potassium iodide solution, and titrate with sodium thiosulfate, using starch as an indicator. In base solutions where some manganate undoubtedly was present with the permanganate, the calculation was still made in terms of permanganate.

The total base content was determined in another sample by adding an excess of standard sulfuric acid, and a slight excess of hydrogen peroxide to reduce the permanganate, after which a titration was made with standard sodium hydroxide solution using methyl orange indicator. A blank test of the acidity of the hydrogen peroxide was made, and the amount of acid used up during the reduction of the permanganate by the H_2O_2[1] was, of course, taken into consideration in the calculation.

$$2\overset{-}{MnO_4}+5H_2O_2+6\overset{+}{H}=2\overset{++}{Mn}+5O_2+8H_2O.$$
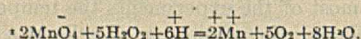
Results and Calculations

general discussion—The main reaction which takes place in the cell as a whole may be represented by the equation:

$$Mn+\overset{-}{OH}+3H_2O = \overset{-}{MnO_4}+\tfrac{7}{2}H_2$$
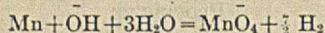
This is accompanied by the passage of 7 faradays of electricity. At the cathode the only reaction is the evolution of hydrogen.

In addition to the oxidation of Mn to $\overset{-}{MnO_4}$, a number of other reactions always take place at the anode. The principal side reactions are the formation of oxides of manganese, iron, and perhaps silicon and carbon, and the evolution of oxygen. (In strongly alkaline solutions some $\overset{-}{MnO_4}$ is also formed.) The mixture of the three metallic oxides is deposited as a sludge. Considerable oxygen was evolved in all the runs made.

The current used up in these side reactions represents the degree of inefficiency of the process. There is little chance of being able to oxidize the manganese of the anode without simultaneously oxidizing its other constituents. Consequently, the losses might be divided into two classes—those theoretically avoidable and those probably unavoidable. The evolution of oxygen and the formation of manganese dioxide belong to the former; the other side reactions mentioned, to the latter. In this paper, however, the calculation of the current efficiency is based on the assumption that the passage of one faraday would produce, in a perfect electrolytic process, one-seventh of a mole of permanganate.

Current efficiency is influenced mainly by variations, in four factors, namely, anode composition, electrolyte, temperature, and current density. These are considered below in the order named. Besides the current efficiency, the cell voltage, material efficiency of the anode, and the energy consumption per unit weight of product also are influenced by these four factors. The voltage, and consequently the energy consumption, may be affected somewhat by the material of which the cathode is composed, as a result of the change in hydrogen overvoltage thereby produced. This effect is relatively small, however, and practical considerations limit the choice to iron.

Material efficiency is taken as the per cent of anode manganese which is converted to permanganate. This quantity is not easily determined with precision, owing to the difficulty of reproducing the same anode conditions before and after a run, for the purpose of obtaining the loss in weight. Thus, there is no way, apparently, of removing the coating which always collects on the anode without also removing a small amount of the metal; sometimes solution is absorbed by the anode as a result of its porosity, and this changes its apparent weight on drying; finally, even with physical conditions at their best, there exists the mathematical disadvantage that the difference between initial and final weights was in the neighborhood of 1 g., while the weight of the anode itself was about 800 g., so that errors of weighing were highly magnified.

In spite of these difficulties, however, fairly concordant values were obtained by treating the anode after each run in the manner described above. The results obtained in carbonate solutions showed better concordance than those in base solutions.

effect of anode composition—The anodes used in these experiments were made by casting ferromanganese in graphite molds, the castings being cooled slowly over a period of 15 hrs. by burying them in asbestos-magnesia powder while they were still at a red heat. Unless this precaution was taken, the castings cracked spontaneously. Using this method, however, it was found possible to cast alloys containing manganese to the extent of 95 per cent.[1]

The most important variable in the composition of the anode is the ratio of manganese to iron present. The effect of varying the manganese content of the ferromanganese was studied in this laboratory,[2] electrolyses being conducted with anodes containing from 60 to 94 per cent manganese. The anolyte was 12 per cent sodium carbonate solution (previously found to give about the optimum results), and the catholyte was 8 per cent sodium hydroxide solution.

Table I—Effect of Variations in Anode Composition on Current Efficiency, Voltage, and Energy Consumption
Initial anolyte, 12 per cent (1.3M) Na₂CO₃ solution.
Temperature, 25° C.
Current density, 10 amp./sq.dm.

| Constituents of Anode Per cent | | | | Current Efficiency | Cell | Energy Consumption |
Mn	Si	C	Fe	Per cent	Voltage	Kw.Hr.-Kg.
60.2	2.07	5.86	31.8	10.34	5.63	71.9
70.4	1.88	4.93	22.8	28.0	5.84	27.6
75.3	0.64	5.98	18.0	34.0	5.98	23.2
80.4	1.62	3.53	14.4	38.7	5.93	20.3
89.2	1.43	2.65	6.7	45.3	5.57	16.2
94.4	0.68	5.08	0.0	50.1	6.18	16.3

The current density was 9 to 10 amp. per sq. dm.; temperature, 25° C.; the results are given in Table I and are shown graphically in Fig 1. It will be noted from the table that the percentages of silicon and of carbon are nearly the same in all the electrodes, the small differences probably being insufficient to produce a noticeable effect on the results. The percentage of iron, therefore, increased as that

[1] The casting process consisted simply in heating the alloy in a graphite crucible in an electric furnace of the resistant type and pouring the melt directly into the open mold. For the 2.5 cm. × 2.5 cm. × 15 cm. electrodes, no scavenger was necessary. In order to cast large bars (4 cm. × 12.5 cm. × 100 cm.) of 80 per cent manganese content, Dr. C. J. Fink (who gave assistance in this phase of the war problem) showed that it was necessary to employ aluminium as a scavenger during the melting and also just before pouring.

[2] Thesis by A. J. Hartsook, M. I. T., 1920.
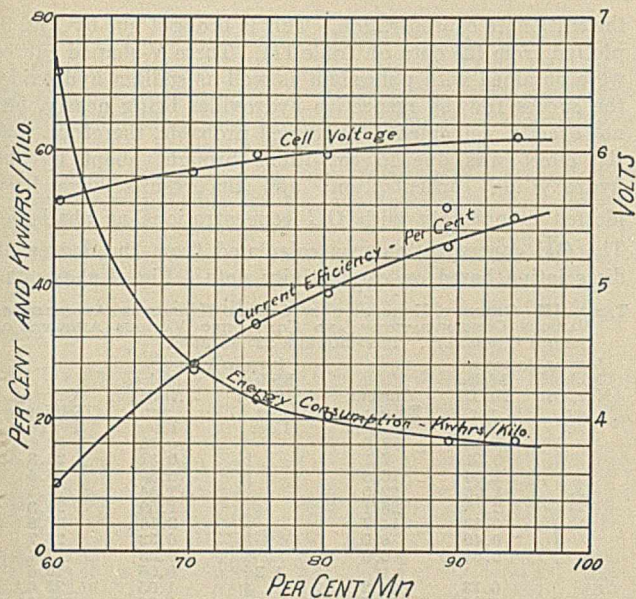
Fig. 1—Showing relation of cell voltage, current efficiency, and energy consumption to manganese content of ferromanganese anode. Temperature, 25° C. Initial anolyte, 12 per cent Na$_2$CO$_3$ solution

of manganese diminished. The ratio of manganese to iron in the anode has a marked effect on the current efficiency, the latter increasing with increase in this ratio, as would be predicted. An experiment with spiegel iron (about 40 per cent Mn) showed practically zero yield of permanganate. The effect on cell voltage is small. There is, however, a definite upward trend in the voltage curve with increase in the manganese content. Since the dilution of manganese with iron ought to decrease rather than increase the tendency of the manganese to form permanganate, the slight increase in cell voltage as the manganese content increases appears to be due to a change in overvoltage. The increase in current efficiency, then, apparently is due to the combined effect of two factors, *viz.*, the higher concentration of manganese in the anode and the higher oxygen overvoltage.

The highest concentration of manganese which is readily obtainable commercially is 80 per cent. Higher concentrations are occasionally obtainable, but usually recourse must be had to the expensive "thermit" process. The additional cost for, say, 95 per cent manganese as against 80 per cent would more than offset the gain in production, for, although the current efficiency increases from 40 per cent to 50 per cent, the energy consumption is reduced only from 20 to 18 kw.hr. per kg.

Besides being more costly, the alloys of high manganese content have the mechanical disadvantage of being much more brittle. Hence, commercial ferromanganese was employed in the present investigation (except for the work by Mr. Hartsook just described), the composition being approximately

	Per cent
Mn	75
Fe	16.2
Si	2.3
C (by difference)	6.5

A small amount of work also was done to show the effect of adding other metals to the ferromanganese. The addition of a small percentage of copper had an unnoticeable effect on the current efficiency. Cobalt, when present to the extent of 1 or 2 per cent, reduced the efficiency practically to zero.

EFFECT OF ANOLYTE COMPOSITION—In general, it may be stated that suitable initial anolytes are the solutions of any

salts which hydrolyze to give a basic reaction. Thus, in some unpublished work by Dr. B. F. Lovelace at Johns Hopkins University, it was found that with sodium acetate solution a current efficiency of 32 per cent could be obtained. Borax solution gave 35 per cent and disodium phosphate 22 per cent. Using ammonium carbamate solution, the authors were able to obtain fair yields provided the temperature was kept low (around 10°C.). At room temperature, ammonium permanganate decomposes rapidly.

In the practical production of sodium or potassium permanganate, it is desirable to use the solution of a salt, the anion of which will be eliminated automatically, if possible, in the ordinary course of the electrolysis. This may be accomplished by employing the carbonate or hydroxide of the alkali metal, which also has the advantage of being cheaper than any of the other possibilities. The present work is concerned chiefly with experiments with these two species of solution.

TABLE II—RELATION OF CURRENT EFFICIENCY, CELL VOLTAGE, AND ENERGY CONSUMPTION TO THE CONCENTRATION OF CARBONATE IN THE ANOLYTE
Temperature, 25°C., Current density, approx., 7.5 amp. sq. dm.

Average Conc. Moles per Liter	Carbonate Per cent	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr.Kg.
		NaMnO$_4$		
0.28	2.88	35.5	15.3	57.0
1.10	10.50	32.7	10.0	40.5
1.50	14.1	30.3	8.4	36.6
2.11	18.4	28.5	7.9	36.7
		KMnO$_4$		
0.30	4.07	36.1	12.2	46.5
0.60	7.97	31.3	8.7	33.0
1.55	18.25	28.3	6.3	26.4
2.34	25.9	31.2	5.9	22.4
2.81	29.95	28.5	5.4	22.5
3.26	33.5	29.3	6.1	24.7
3.87	38.3	19.8	6.1	36.5
5.48	49.3	13.2	7.1	63.8
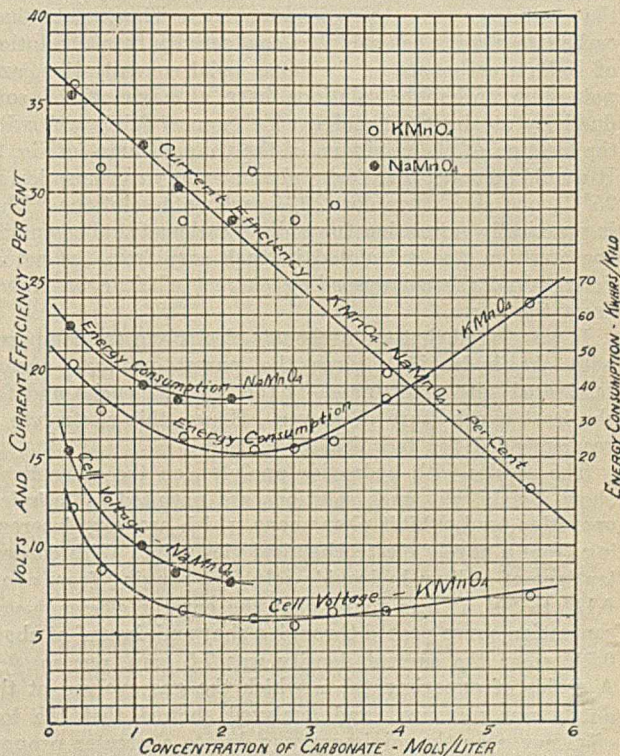
FIG. 2—VARIATION OF CURRENT EFFICIENCY, VOLTAGE, AND ENERGY CONSUMPTION WITH CONCENTRATION IN PURE CARBONATE ANOLYTE. TEMPERATURE, 25° C. C.D., 7.5 AMP. PER SQ. DM.

¹ The current density in runs recorded in this and the following section was estimated on the assumption that the front face and one-half the two side faces of the anode were active. In other words, with an anode of square cross section, the active surface was taken as approximately twice the submerged area of the face toward the cathode. This was justified by the appearance of the anode after electrolysis. While this method of calculation may not be very accurate, it does not alter the *relative* magnitude of results.
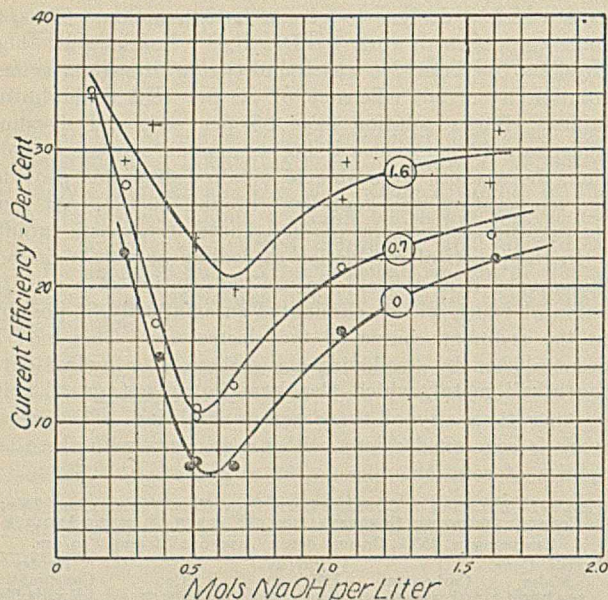
FIG. 3—CURRENT EFFICIENCY IN SODIUM HYDROXIDE ANOLYTES OF VARIOUS CONCENTRATIONS CONTAINING VARIOUS AMOUNTS OF SODIUM CARBONATE. CIRCLED NUMBERS INDICATE MOLAL CONCENTRATION OF CARBONATE. TEMPERATURE, 22° TO 25° C.

The effect of varying the concentration of pure carbonate anolytes is shown by the results given in Table II, which are also presented in graphical form in Fig. 2.[1]

Although the results with potassium carbonate are not as uniform as could be desired, there is no doubt about the general character of the curves. The variations in voltage between the different solutions are due almost entirely to the variations in their conductivity. Thus, potassium carbonate always has a higher conductivity than a solution of sodium carbonate of the same molal concentration, and potassium carbonate solutions have a maximum of conductivity at about 3.1 molal, which agrees fairly well with the location of the minimum of the voltage curve in Fig. 2. It should be noted that for minimum energy consumption at 25°C., one should employ 2.1M carbonate solutions. This is practically saturation for sodium carbonate. The energy consumption was calculated in each case from the actual voltage and the corresponding current efficiency as taken from the curve.

It was found that the carbonate electrolyte (as compared with the hydroxide) gives the purest product—uncontaminated with manganate—at the best efficiencies and for the least expenditure of power. Hence, this electrolyte is recommended for technical operation.

The results with hydroxide anolytes, on the other hand, show clearly why such solutions are unsuited to technical operation, and exhibit phenomena which are very interesting from a purely electrochemical viewpoint. With concentrations of sodium hydroxide solutions ranging from about 0.1M to 8M, it was found that the current efficiency-concentration curve passed through a sharp minimum[2] at about 0.5M when the current density was 7.5 amp. per sq. dm. A series of experiments[3] in which the gas evolved at the anode was measured and analysed showed that the low efficiency near the minimum was due to a greater proportion of the current going to oxygen evolution. If carbonate was present in addition to hydroxide, the only effect on this curve was to raise it as a whole without changing its general V-shape. The amount of raising was greater the higher

the carbonate concentration. This is brought out by Fig. 3, plotted from the data of Table III. These V-shaped curves were obtained with potassium as well as sodium hydroxide, the curves for the respective hydroxides being nearly, but not exactly, coincident. It seemed probable, therefore, that the effect was due to conditions brought about by the hydroxyl-ion concentration; and the results have been plotted accordingly with $\overline{OH}$ concentrations as abscissae. The $\overline{OH}$ concentration was calculated from the degree of dissociation based on conductivity data. Fig. 4 shows the

TABLE III—CURRENT EFFICIENCY IN SODIUM HYDROXIDE ANOLYTES OF VARIOUS CONCENTRATIONS[1] AND CONTAINING VARIOUS AMOUNTS OF SODIUM CARBONATE. TEMPERATURE 22° TO 26°C.

INITIAL ANOLYTE			INITIAL ANOLYTE		
Moles Na_2CO_3 per Liter	Moles NaOH per Liter	Current Efficiency Per cent	Moles Na_2CO_3 per Liter	Moles NaOH per Liter	Current Efficiency Per cent
	0.25	22.6		0.13	32.6
	0.51	7.1		0.31	26.8
	1.04	16.6		0.52	15.6
0.0	1.60	22.0		1.04	23.5
	2.18	26.1		1.59	26.3
	0.38	14.7		2.10	27.8
	0.49	6.9		0.33	28.7
	0.65	6.9		0.53	17.4
			1.3	0.66	16.6
	0.13	34.2		1.05	25.0
	0.25	27.5		1.59	29.2
	0.51	10.7		2.19	29.1
	1.04	21.6		0.27	34.8
0.7	1.59	23.8		0.47	24.0
	2.25	27.3		0.53	15.6
	0.36	17.2		1.04	27.2
	0.51	10.9		1.60	29.3
	0.65	12.8			
	0.15	33.2		0.13	33.8
	0.28	31.7		0.25	29.3
	0.51	23.6		0.51	23.1
	1.00	24.4		1.04	26.4
	1.60	26.9		1.59	27.7
	2.00	28.3	1.6	2.14	26.9
1.0	0.13	35.1		0.36	31.8
	0.25	32.4		0.51	23.7
	0.51	19.8		0.65	19.9
	1.04	24.6		1.06	29.2
	1.58	26.7		1.02	31.5
	2.09	28.3		2.19	32.8

[1] In these experiments the sodium hydroxide content was not maintained constant during a run as it was in the experiments of Tables IV and V.
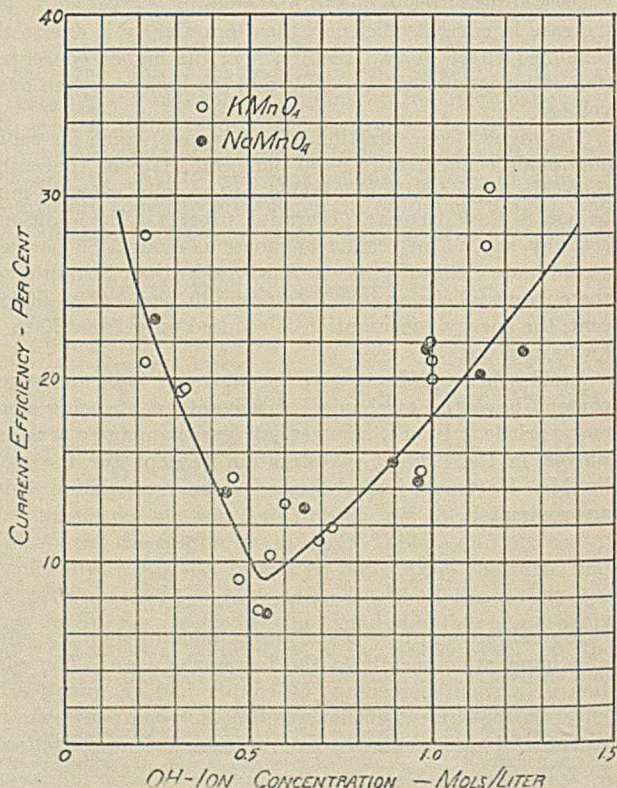
FIG. 4—CURRENT EFFICIENCY VS. OH-ION CONCENTRATION FOR BOTH $NaMnO_4$ AND $KMnO_4$ PRODUCTION IN PURE HYDROXIDE ELECTROLYTES. TEMPERATURE, 25° C. C.D., 7.5 AMP. PER SQ. DM.

[1] See second column, page 765.
[2] In similar electrolyses where anodes of ferrochromium were oxidised to chromic acid in alkaline solution a similar minimum was found at certain concentrations of hydroxide. (Unpublished thesis by R. R. Ridgway, M. I. T., 1920.)
[3] Thesis by M. M. Whitaker, M. I. T., 1920.

results for pure sodium and potassium hydroxides. The two sets of data for this curve are given in Table IV. In each run, the hydroxide concentration was kept sensibly constant by adding the proper amount of concentrated caustic solution at small, regular time intervals (about 20 min.). The impossibility of accomplishing this accurately is probably responsible for the unusually large deviations observed in these experiments.

Certain theories as to the fundamental cause of the minimum point and peculiar shape of these curves are being tested out, and will probably form the basis of a later article.

TABLE IV—RESULTS OF EXPERIMENTS WITH PURE HYDROXIDE SOLUTIONS AS ANOLYTES
Temperature—25° C.; cell current—5 amp.; current density—7.5 amp./eq. dm

Final Conc. KMnO₄ (NaMnO₄) Per cent	Av. Conc. KOH (NaOH) Per cent	Av. Conc. KOH (NaOH) mole/liter	Degree of Dissociation	Av. Conc. OH Moles/Liter	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr./Kg.	Material Efficiency Per cent
				KMnO₄				
0.345	1.43	0.26	0.858	0.22	21.2	10.0	55.8	61.0
0.447	1.45	0.26	0.858	0.22	27.9	9.7	41.2	65.6
0.317	2.16	0.39	0.830	0.32	19.4	7.9	48.3	56.6
0.317	2.25	0.40	0.830	0.33	19.6	8.4	50.8	56.7
0.234	3.12	0.57	0.804	0.46	14.5	6.2	50.8	53.5
0.141	3.21	0.59	0.802	0.47	9.0	6.2	88.3	48.6
0.123	3.53	0.65	0.797	0.52	7.4	6.2	99.3	100+
0.170	3.88	0.71	0.790	0.56	10.3	5.9	67.9	51.3
0.202	4.24	0.77	0.780	0.60	13.4	5.4	47.8	79.4
0.177	4.77	0.90	0.765	0.69	11.2	5.3	56.2	52.6
0.179	5.20	0.96	0.760	0.73	11.9	5.1	50.8	86.2
0.255	6.97	1.35	0.718	0.97	15.0	5.1	40.4	48.7
0.304	7.19	1.38	0.716	0.99	22.0	5.3	28.6	...
0.269	7.25	1.40	0.715	1.00	20.0	5.6	33.2	...
0.281	7.36	1.41	0.715	1.01	20.5	5.3	30.7	...
0.435	8.48	1.64	0.695	1.14	27.3	4.4	19.1	72.0
0.510	8.67	1.68	0.688	1.16	30.5	4.3	16.7	83.6
0.384	12.25	2.48	0.622	1.61	27.0	4.1	18.0	91.5
				NaMnO₄				
0.352	1.17	0.295	0.802	0.237	23.2	10.5	59.8	68.5
0.205	2.24	0.572	0.763	0.437	13.8	7.3	70.0	78.4
0.120	2.82	0.73	0.742	0.541	7.16	6.9	127.5	70.0
0.187	3.52	0.915	0.713	0.653	13.0	5.8	59.1	61.4
0.219	5.08	1.34	0.670	0.898	15.6	5.3	44.9	69.3
0.221	5.46	1.45	0.660	0.960	14.7	5.0	45.0	65.2
0.269	5.64	1.50	0.655	0.984	21.9	5.3	32.1	...
0.304	6.83	1.85	0.610	1.13	20.3	5.0	32.6	74.0
0.279	7.83	2.13	0.585	1.25	21.5	4.7	29.0	76.0

FIG. 5—VARIATION OF CURRENT EFFICIENCY, VOLTAGE AND ENERGY CONSUMPTION WITH TEMPERATURE. ANOLYTES : K₂CO₃, 14 PER CENT, NA₂CO₃, 12 PER CENT ; C. D., 6 TO 9 AMP. PER SQ. DM.

EFFECT OF TEMPERATURE—The effect of variation in temperature upon current efficiency, voltage, and energy consumption is shown graphically in the plot in Fig. 5 (data in Table V). These experiments were made with carbonate solution (K₂CO₃ and Na₂CO₃) for anolyte, since carbonate was found to be the best anolyte for commercial use, and gave no peculiar variations as did hydroxide solutions. All

the runs were of 5 hrs. duration, with an anodic current density of 6 to 9 amp. per sq. dm. Each result in the table represents the average for *six* cells in series, except at 40° where three cells were operated for NaMnO₄ and three for KMnO₄. The anolyte concentrations were 14 and 12 per cent potassium and sodium carbonate, respectively. The variation in current density was due to differences in size of electrodes. As will be seen later, variation of current density between these limits has little effect on current efficiency.

TABLE V—RESULTS OF EXPERIMENTS AT VARIOUS TEMPERATURES
Cell current—5 amp.; current density—6 to 9 amp./sq. dm.

Anolyte	Temp. °C.	Current Efficiency Per cent	Cell Voltage	Energy Consumption Kw.Hr./Kg.	Material Efficiency Per cent
14%K₂CO₃	10	36.4	7.2	21.3	86.8
	20	33.9	6.5	22.1	....
	30	27.0	5.8	24.2	....
	40	24.8	5.9	27.9	70.6
	50	14.9	5.4	36.3	....
12%Na₂CO₃	20	35.9	8.6	32.7	....
	27.5	30.5	8.3	35.4	57.0
	30.5	30.7	9.8¹	36.3	68.2
	40	26.7	7.5	42.4	67.6

¹ Exceptionally high for some unknown reason and hence not plotted.

It will be noted that both current efficiency and cell voltage are reduced as the temperature increases. The cell voltage is lower chiefly because of the lessened resistance of the solution, but the oxygen overvoltage is also less at high temperature. This latter lowering and the more rapid decomposition of permanganate at high temperatures are responsible for the decrease in efficiency as the temperature increases, the former being the more important.

Although these results seem to indicate that the efficiency of sodium permanganate production is slightly greater than for potassium, the difference is probably not greater than the experimental error; furthermore it did not show up in other series. Only one curve is drawn to represent the average results.

In plotting the data, the best current efficiency-temperature and voltage-temperature curves were drawn through the points obtained, and values read from these curves were used in calculating the values for energy consumption which consequently lie upon a smooth curve.

The results indicate that the maximum current efficiencies and minimum energy consumptions are obtained at temperatures below 10°C., although the energy consumption varies but little up to 20°C.

EFFECT OF CURRENT DENSITY—By passing various currents through a cell of given dimensions the effect of varying the current density has been determined. In this way both the anodic and cathodic current densities were altered simultaneously, but since it is inconceivable that the cathodic current density can have any effect on the current efficiency, the results are interpreted to represent the effect of variations in anodic current density.

In the case of these experiments a different set of anodes and a different size and type of cell were used. This was done partly in order to obtain more accurate figures for current density, and partly in order to see whether the results obtained up to this time could be duplicated with much larger cells. The cell was constructed of concrete lined with paraffin. A diaphragm composed of a sheet of asbestos paper between two supporting sheets of asbestos cloth divided the cell into two compartments. The anode was made up of two bars each about 12 cm. in width, submerged to a depth of about 25 cm. This was placed close to the diaphragm so that only the front surface was very active. The value of the anodic current density is taken as the apparent current density obtained by dividing the cell current by the actual area of the submerged portion of the anode on the side toward the diaphragm.

Fig. 6—Showing the Effect of Variations in Current Density on Current Efficiency, Cell Voltage, and Energy Consumption. Initial Anolyte, 15 Per cent Na₂CO₃ Solution. Temperature—30° C.; initial anolyte—15 per cent Na₂CO₃ solution

The runs were all made at a temperature in the neighborhood of 30° and the results corrected to this temperature on the basis of the data given in Table VI. The initial anolyte in each run was approximately 15 per cent Na$_2$CO$_3$ solution. No experiments were made with the potassium salt. The final permanganate content of the runs reported here never exceeded about 3 per cent NaMnO$_4$.

The data given in Table VI are plotted in Fig. 6. The plot shows the energy consumption curve to possess a minimum of 23.5 kw. hr. per kg. when the current density is 6 amp. per sq. dm. The energy consumption increases gradually with increase in current density beyond this point. Since the current efficiency also continues to increase, the

Table VI—Effect of Variations in Current Density

Temperature—30° C.; initial Anolyte—15 per cent Na₂CO₃ solution

Current Density Amp./Sq. Dm.	Current Efficiency Per cent	Cell Voltag	Energy Consumption Kw.Hr./Kg.
2.69	14.8	4.22	37.6
2.9	20.3	4.30	28.0
2.9	17.8	4.60	34.2
3.0	18.0	4.25	31.2
4.51	27.6	4.95	23.7
4.51	30.9	4.90	21.0
4.73	26.0	5.00	25.5
4.73	24.8	5.00	26.7
5.70	26.6	5.30	26.4
5.91	26.1	5.70	28.9
9.03	34.7	6.25	23.8
9.03	28.9	5.90	27.0
9.46	36.7	6.30	22.7
9.46	30.4	6.75	29.4
11.3	32.3	6.70	27.5
11.8	35.2	7.20	27.1
12.1	37.0	6.90	24.7
12.5	34.8	6.80	25.9
13.5	36.0	6.40	23.5
14.3	31.9	7.45	30.9
17.0	37.5	7.30	25.8
17.8	35.6	8.50	31.6

optimum current density for technical operation will be somewhat above 6 amp. per sq. dm. because of the saving in cost of installation thereby effected.

Extrapolation of the voltage-current density curve in-

dicates that the cell voltage when C. D. = 0 is 3.4 volts as compared with a theoretical value[1] of 1.07 volts. The overvoltages probably are large, but several other effects undoubtedly enter to help make up the 2.3 volts difference between these two values.

Two other series of runs were made in which the average permanganate concentrations were about 4 and 8 per cent, respectively. On account of inaccuracies introduced in the analytical determinations, the results were not even as concordant as those where the permanganate concentration was low. Within the experimental error there was substantially the same current efficiency at all concentrations of permanganate. This conclusion is substantiated by the results obtained in the long-time runs discussed below.

THE "SKIN EFFECT" AND ITS ELIMINATION—The requirement of simplicity in commercial operation demands that the anodes may be kept in action continuously until they have been reduced to a small fraction of their initial size. In the earlier stages of this investigation, a good deal of trouble was encountered, in runs of more than a few hours' duration, by a "skin effect" which was exhibited by the ferromanganese anode. The anodes always became covered with a coating of oxide which, when thin, adhered too firmly to be scraped off. The coating developed more rapidly, and to a greater extent, in caustic than in carbonate anolytes. In carbonate anolytes, electrolysis would proceed smoothly, in spite of the coating, for 25 or 30 hrs., after which the voltage would commence to rise rapidly and severe heating ensue so that the cell had to be shut down. In the semi-plant scale experiments which were conducted in connection with the war work, a sharp rise in the voltage-time curve of a given cell was the signal for the removal of its anode and the substitution of a fresh one, the particular cell being meantime by-passed so that the current in the series was not interrupted. The "fresh" anode was prepared by removing the coating with a sandblast, which made it ready for another 30-hr. operating period. It should be understood that this active operating period was not absolutely regular, but 30 hrs. represents a fair average. As the permanganate concentration increased, the period became somewhat shorter.

Other methods than sandblasting were tried for removing the coating. Thus, the coating formed in carbonate electrolytes became very flaky on drying and was nearly all easily removed by scraping with a cold chisel. The surface of the anode was then ground slightly all over with a carborundum wheel. Another method was to "pickle" the anode in hydrochloric acid. Sandblasting was the least undesirable of all these methods from the technical viewpoint.

It was attempted to obviate the formation of the oxide coating by the use of "addition agents" in the electrolyte. No improvement was brought about, however, by the use in this way of such salts as chlorides, chlorates, perchlorates, sulfates, and nitrates. Incidentally, it was found that perchlorates and nitrates to the extent of about $1M$ in $2M$ hydroxide solutions reduced the efficiency to zero, while with sulfate and chlorate in similar concentration, the

[1] For the calculation of the theoretical value the cell was considered to be constituted as follows:

Mn$_2$ MnO$_4$ (0.1M), CO$_2$ (0.5M) || OH (1M), H$_2$ (1 atm.) Pt.
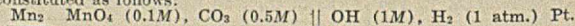
The liquid junction potential, which would be of the order of magnitude of two or three hundredths of a volt, was neglected. It was assumed that the potential of manganese vs. MnO$_4$ in a half-molal carbonate solution would be the same as in a base solution where the O-H concentration is 10⁻⁶M. The potentials involving manganese were calculated from data in *Abhand deutsch. Bunsen-Ges.*, II, 5 (1911), 201. The potential ½ H$_2$ + ⊕ = H · (1-M), was taken as zero. The e. m. f.'s of the two "half" reactions are:

Mn + 7⊕ + 8 O-H (10⁻⁶M) = MnO$_4$ (0.1M) + 4H$_2$O : E$_1$ = − 0.243 volt

H$_2$O = O-H (1M) + ⊕ + 8 OH + ½ H$_2$: E$_2$ = − 0.826 volt.

From the whole cell, therefore, E = E$_1$ + E$_2$ = 1.069 volts.

current efficiency was only about 2 per cent less than with carbonate.

The clue which led to the discovery of the conditions for eliminating the coating was furnished by a 5-hr. electrolysis with a potassium carbonate solution of higher concentration than had been used previously (namely, 30 per cent K_2CO_3), at the end of which it was found that the anode surface, after the adhering permanganate solution had been rinsed off, was brightly metallic and free from the usual coating. Further experiments showed that under the following conditions of temperature and *initial* anolyte, electrolysis proceeds smoothly and continuously for an indefinite length of time without coating formation:

PRODUCT	ANOLYTE	TEMPERATURE
$KMnO_4$	30% K_2CO_3 solution	28° C. or lower
	15% K_2CO_3 solution	12° C. or lower
$NaMnO_4$	Saturated (7%) Na_2CO_3 solution	10° C. or lower

Short periods of operation at 10° higher than the above temperatures were harmless in the case of potassium.

If it is desired to build up a concentration of *sodium* permanganate above about 3 per cent, however, it is necessary to add solid Na_2CO_3 to the anolyte from time to time. While not many of these long, continuous runs (7 to 10 days in duration) were made, nevertheless sufficient data were obtained to indicate that the current efficiency and energy consumption under such conditions are about the same as in the runs on which the curves presented in this paper are based, and the anodes are clean and bright at the end of the operation.

Summary

1—The foregoing article presents in tabular and graphic form the results of extensive experimental work on the more important factors involved in the electrolytic production of sodium and potassium permanganates from ferromanganese anodes.

2—In the investigation of the effect of *anode composition* it was found that the higher the manganese content of the electrode, the higher the current efficiency, anodes containing less than 40 per cent giving practically no yield under any conditions. Other constituents at the anode seem to have comparatively little effect except in the case of cobalt, about 2 per cent of which practically destroys the permanganate producing power of a ferromanganese electrode. In view, however, of the greater cost and brittleness of anodes containing more than 80 per cent manganese, the commercial 80 per cent ferromanganese appears to be the best anode material for technical operation, and most of the experiments were made with such anodes.

3—Possible *anolytes* are alkali metal salts of weak acids, and alkali metal hydroxides. The best anolyte appears to be a solution of alkali metal carbonate, the carbonate being destroyed in the course of electrolysis and replaced by permanganate uncontaminated by manganate or other salts. Hydroxide solutions are interesting from the theoretical viewpoint, in that they give a sharp minimum in current efficiency at an intermediate OH concentration.

4—The operating *temperature* should be as low as possible (10° to 20°C.). Low temperature gives highest efficiency and lowest energy consumption, and makes possible the continuous operation of the anode (provided the initial carbonate concentration is high). High temperature gives lower current efficiency and promotes a "skin effect" on the anode surface which gives rise to excessive voltages.

5—A *current density* of about 6 amp. per sq. dm. gives the minimum energy consumption. The optimum operating current density is somewhat higher than this. At lower current densities the current efficiency falls off rapidly; at higher current densities it rises slowly, but the increased I. R. drop through the solution results in somewhat higher energy consumption.

6—It is believed that the effect of practically all variables (such as temperature, current density, anolyte composition, etc.) on the current efficiency is in reality due to the variations which these factors cause in the oxygen overvoltage, a high oxygen overvoltage being necessary for high current efficiencies in permanganate production. It is hoped to present further evidence bearing upon this point in a later paper.

7—The essential conclusions as to the optimum operating conditions and the efficiencies obtainable have all been confirmed by continuous operation of a full-sized commercial cell, using five ferromanganese bars, each 5 in. $\times$ 1.5 in. $\times$ 35 in., as the anode.

Bakelite Company Wins Decree

The General Bakelite Company of New York was awarded a decree in its suit against the General Insulate Company of Brooklyn charging infringement of three Bakelite patents. The decision against the defendant was handed down by Judge I. Chatfield of the United States District Court, Eastern District of New York, on August 2, 1921.

The three Bakelite patents involved were No. 942,699, 492,852 and 939,966 commonly designated as the Heat and Pressure Patent, the Fibrous Materials or Indurated Product Patent and the Comminuted Mixture or Molding Patent, all of which have been sustained and declared infringed by the Court.

The decision is remarkable for the comprehensiveness and the clearness with which Judge Chatfield has handled a highly technical subject, involving fine distinctions between chemical and physical processes and between actual inention and the manufacture of a known substance by variations in technique of production. Particular interest is attached to this decision because the defendant in the case—General Insulate Company—is a molding concern doing business in Brooklyn, New York, and using the products manufactured by the Redmanol Chemical Products Company of Chicago and as Judge Chatfield said in his opinion:

"The record shows that in fact the Redmanol Company has stood behind the defendant in the trial of this action, and in so far as investigation of the prior art and discussions of questions of patentability are concerned, the Redmanol Company has as freely and fully presented its evidence as if the action had been against the Redmanol Company for infringement of the plaintiff's patents in the manufacture of the synthetic gum itself."

The Redmanol Company had no office in New York—hence the indirect action of the General Bakelite Company in filling a Bill of Complaint against one of the users of the Redmanol products. The Bill of Complaint was filed September 18, 1917, but a trial could not be obtained until March 31, 1919. The trial lasted many weeks in open court, the final arguments taking place on June 22, 1919.

The decision itself covers 36 printed pages, and reviews the various patents that have been issued both in the United States and foreign countries for the preparation of materials generally classified as synthetic resins. The fact that the Baekeland patents go further than any previous patents in covering the preparation of materials that are of practical value and prepared according to exact processes yielding definite products, is definitely shown. The decision is a valuable contribution to chemical patent literature.

The Detection of Carbon Monoxide[1,2]

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The problem of detecting quantities of carbon monoxide too small to be determined accurately by the ordinary methods of gas analysis, yet sufficiently large to produce harmful physiological effects, has been attacked by a number of investigators.

Several forms of portable apparatus for the detection of carbon monoxide in houses, mines, factories, etc., have been devised.

Racine[3] attached a filament of guncotton dusted with platinum black to the terminals of an electric circuit in such way that as the guncotton was ignited by the heat of absorption of the carbon monoxide on the platinum black, the circuit was closed and a signal given. This device is capable only of detecting quantities of carbon monoxide greater than 0.75 per cent and is therefore not sufficiently sensitive for the hygienic testing of air.

Guasco[4] constructed a toximeter for carbon monoxide consisting of two glass bulbs, one coated with platinum black, connected by a U-tube containing a colored liquid. Temperature changes produced by the absorption of carbon monoxide on platinum bulb altered the level of the liquid in the U-tube. Although Guasco claims to be able to recognize 0.01 per cent of carbon monoxide with this apparatus, it is difficult to manipulate, and useless in most industrial gas mixtures.

Lamb and Larson[5] have recently investigated the thermometric principle and propose two accurate methods very well adapted t othe continuous analysis of a gas mixture containing carbon monoxide. Their apparatus is not intended to be readily portable, but it would seem to be of special value for stationary use in laboratories and industrial plants for the analysis of combustible gases which can be freed from catalytic poison.

Nowicki[6] patented a pocket apparatus in which strips of paper moistened with palladium chloride solution are placed in a glass tube through which the suspected gas is drawn. However, the slowness of the reaction, the need of freshly preparing the paper to be used out of contact with reducing substances, and the wide variety of reducing substances that produce similar changes to those produced by carbon monoxide, have prevented any considerable practical use of this type of detector.

Harger[7] designed a portable apparatus for the detection of carbon monoxide in mines. The variation in the conductivity of a solution of hydrogen iodide formed from the iodine liberated by the action of carbon monoxide on heated iodine pentoxide is employed to indicate the quantity of the gas present. This method is obviously difficult of manipulation, and the apparatus is expensive and cumbersome.

Teague[8] of the Bureau of Mines has adapted the iodine pentoxide method of analysis to the determination of carbon monoxide in automobile exhause gases by using liquid air to remove interfering substances. A form of portable apparatus has been described, but the manipulation is rather more difficult than can be carried out by the average working man.

In practical use none of the chemical or thermometric detectors mentioned have been found to be as generally successful as small animals, especially canaries, as suggested by Burrell, Seibertl and Robertson of the Bureau of Mines.[9] That small animals, are, however, unsatisfactory in some cases was first pointed out by the same investigators. A man moving or at work may be overcome before a small animal quietly confined, and a person may be seriously affected by long breathing of low concentration of gas which causes no appreciable symptoms of distress in small animals. Among the other objections, the following may be

mentioned: The detection by small animals is applicable only to a limited range of concentration of carbon monoxide, and there is an appreciable difference in sensitiveness of different animals of the same kind. The uncertainty and slowness of recovery of small animals unless placed in pure air or oxygen makes it impossible to make tests at frequent intervals in impure air, or after passing through impure air, without a large number of birds and special containers. When not in use, animals must be cared for at places that are readily accessible. It can therefore be concluded that there is need in many industrial operations of a more reliable, more rapid, and simpler method of detecting carbon monoxide than any yet proposed.

HOOLAMITE

Lamb, Bray and Frazer[4] have summarized the work done by the Defense Chemical Research Section of the Chemical Warfare Service upon the absorption of carbon monoxide. One of the absorbents developed, Hoolamite,[5] was the result of an investigation of the action of carbon mono..ide on mixtures of iodine pentoxide and other substances begun in this laboratory during the summer of 1917. This work was continued after September 1917 with the personal coöperation of Lieut. Col. A. B. Lamb, director of Defense Research, as a part of the general investigation described in the article just mentioned. Subsequent to the signing of the armistice and the resulting curtailment of the activities of the Chemical Warfare Service, the problem was continued in this laboratory and the detectors described in this article developed.

COMPOSITION—Hoolamite is prepared by mixing fuming sulfuric acid with iodine pentoxide and an inert supporting material. During the early stages of the development of this absorbent it was noticed that carbon monoxide imparted to the white Hoolamite of certain range of composition colors varying from pale bluish green to brownish black, the depth of the color depending upon the amount of the gas present. The nature of the compounds of iodine and oxides of iodine with sulfur trioxide and sulfuric acid is being investigated, but has not yet been definitely determined. The green color is due to an unstable substance which can be formed from iodine and sulfur trioxide. On standing or gentle warming in the presence of sulfur trioxide, the green material changes to orange yellow and finally, upon the addition of iodine pentoxide, to a white substance. Since at ordinary temperatures Hoolamite oxidizes carbon monoxide to carbon dioxide with the liberation of iodine, if an excess of sulfur trioxide is present, the green substance will be formed and is thus indicative of the presence of carbon monoxide.

Iodine pentoxide and fuming sulfuric acid of high sulfur trioxide content form solid bodies if the weight of acid does not exceed 70 per cent of the weight of the mixture, but in order to produce the green body a greater proportion must be present and such mixtures, being pasty, must necessarily be supported on an inert porous material in order to expose them efficiently to the action of carbon monoxide. Asbestos fiber gives the most active material, but it is difficult to handle, and irregular in surface and, consequently, in action. However, a material almost as active can be prepared with granular pumice stone, and this supporting material is used for all mixtures.

Table I shows the composition of the mixtures found to be best suited to the detection of small amounts of carbon monoxide.

1 Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

2 Published by permission of the Director of the Chemical Warfare Service.

3 Bull. soc. chim. (3), 1 (1889), 555.

4 Compt. rend., 155 (1912), 282.

5 J. Am. Chem. Soc., 41 (1919), 1908.

6 Chem.-Ztg., 35 (1911), 1120.

7 Iron Coal Trades Rev., 88 (1914), 912.

8 THIS JOURNAL, 12 (1920), 964.

9 Bureau of Mines, Technical Paper, 62 (1914).

1 THIS JOURNAL, 12 (1920), 213.

2 Lamb and Hoover, U. S. Patents 1,321,061 and 1,321,062.

TABLE I—COMPOSITION OF DETECTOR MATERIAL

Use	Method of Preparation	Iodine Pentoxide Per cent	Pumice Stone Per cent	Fuming Sulfuric Acid Per cent
Approximately quantitative detection of reducing gases—Detector B	Mixed in open vessels	12.0	35.0	53.0(60%SO₃)
Quantitative detection of carbon monoxide—Detector C	Mixed in closed vessels or in air of low humidity	10.6	33.3	56.1(60%SO₃)
Quantitative detection of carbon monoxide—Detector C	Mixed in open vessels High humidity	11.0	34.0	55.0(30%SO₃)

Since Hoolamite is a corrosive, deliquescent material, it must be preserved in closed vessels which are not attacked by acids or oxidizing agents. When so preserved, it gradually increases in activity for several days, finally remaining unchanged apparently indefinitely. The material is usually employed in small glass tubes which are sealed after filling and opened just before use.

SENSITIVITY—Under favorable conditions concentrations of carbon monoxide as low as 0.005 per cent can be detected by the passage of 500 cc. of a gas mixture through a glass tube containing a 50 mm. $\times$ 5 mm. column of Hoolamite. The color developed is proportional to the amount of carbon monoxide present and the cross-sectional area of the detector material, for concentrations of carbon monoxide of 3 per cent or less. The rate at which the gas is passed can vary considerably, but for quantitative results it should be kept between 30 and 60 sec. for a 500-cc. sample through a tube of 5-mm. inside diameter. The depth of the detector material should be at least 2.5 cm., 5 to 7 cm. being commonly used. Carbon monoxide reacts readily with the detector material at —10° C. Since the action is strongly exothermic the color produced is largely independent of the temperature. As a result of chemical changes such as were mentioned above, the green color indicating the presence of carbon monoxide disappears in a few minutes and the material can again be used as before. After twelve positive tests, with concentrations of carbon monoxide not greater than 0.2 per cent, the color produced becomes somewhat irregular in shade and a new sample should be employed. With higher concentration of carbon monoxide proportionately less tests can be made with one tube. Twenty to thirty negative tests in ordinary air can be made before the activity of the Hoolamite has been destroyed.

COLOR STANDARDS—Permanent color standards consisting of granules of pumice stone, normal or basic copper acetate, and chromium oxide can be prepared which match closely the colors produced in Hoolamite by a 500-cc. sample of gas containing amounts of carbon monoxide from 0.03 to 0.17, or 0.2 per cent. Above 0.2 per cent for a 500-cc. sample the colors are more irregular, and other methods than direct color comparison give better results.

ACTION WITH OTHER GASES—A substance capable of rapidly oxidizing carbon monoxide at low temperatures can also be expected to react with oxidizable gases and vapors other than carbon monoxide. Unsaturated hydrocarbons, gasoline vapor, hydrogen sulfide, arsine, hydrogen cyanide, and various complex organic compounds, especially those containing halogens or amino nitrogen, are similar in action to carbon monoxide. In the absence of carbon monoxide the material is a sensitive detector for such substances. Fortunately all interfering substances investigated are absorbed by dry active charcoal. Hydrogen, methane, sulfur dioxide, nitric acid, ammonia, and other common gases and vapors are without action.

For the determination of small amounts of carbon monoxide in the laboratory, any simple container from which definite volumes of gas can be forced under a pressure of several inches of water, appropriate color standards, and a few tubes of Hoolamite are all that are necessary.

If other reducing gases are present, it is necessary only to pass the mixture to be examined over a column of active charcoal before it comes into contact with the Hoolamite. It may be noted here that a method of determining large amounts of carbon monoxide in the usual type of absorption pipet by means of Hoolamite is also being developed.

POCKET DETECTOR FOR INDUSTRIAL USE

The most important application of Hoolamite that has yet been made is to the industrial detection of carbon monoxide. A simple and durable form of pocket detector, Type B, is shown in Fig. 1. This device is 24 cm. long
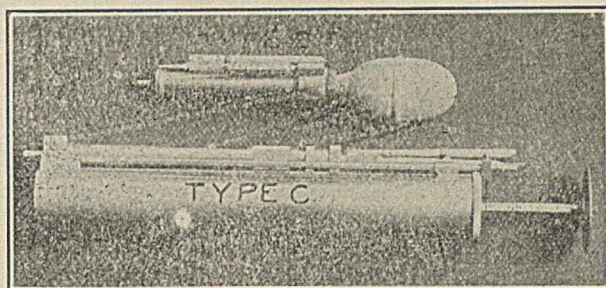
FIG. 1

over all and weighs 260 g. Its construction and operation are explained by Fig. 2. A 250-cc. sample of the gas to be examined is drawn through the guard tube, A, containing active charcoal, by means of ten compressions of the rubber bulb, B, and forced out through the detector material in the glass tube, D. The green color produced in the detector tube is compared with color standards contained in an adjoining tube as shown in Fig. 1. The range of approximately quantitative detection with this instrument is from 0.05 to 1 per cent.

In practical use this instrument (Type B) has been successful as a qualitative and approximately quantitative detector for carbon monoxide. It is sufficiently sensitive to detect in a few seconds quantities of the gas less than are harmful to men, or capable of causing symptoms of distress in small animals. The directions for use are simple and the instrument can be used by the average workman. With improved Hoolamite and revised directions to insure more definite volumes of gas and rates of passage, it should be increasingly valuable.
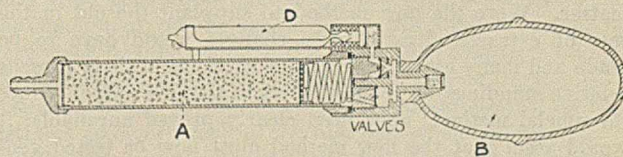
FIG. 2—TYPE B
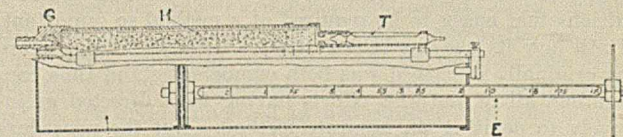
FIG. 3—TYPE C

IMPROVED APPARATUS

It is evident that if the volume of gas and its rate of passage can be regulated more accurately than is possible with the device just described, analytical results of correspondingly greater accuracy will be secured. With this object in view a metal cylinder and piston were substituted for the aspirator bulb and a positively operated stopcock for the rubber valves. The exterior appearance of the im-

proved apparatus is shown in Fig. 1 (Type C). The construction and operation can be understood by referring to Fig. 3. Outward movement of the piston rod, E, draws 500 cc. of gas to be examined through the valve, G, into the cylinder, F. As the piston reaches the end of its travel a rod connected by track and gear to the valve, G, turns it 90°, thus connecting the cylinder with the guard tube, H, and the detector tube, T, through which the gas is passed by the return stroke of the piston. Completion of the stroke moves the valve to its original position.

Among the advantages of this type of instrument may be noted: Definite volume of sample, regular rate of passage governed by the size of the opening into the guard tube, the sample can be taken quickly in a dangerous atmosphere or in the dark, and the analysis made at leisure in a safe, better lighted spot.

As previously stated, concentrations of carbon monoxide greater than 0.2 per cent give somewhat irregular colors when a 500-cc. sample is forced through a 5-mm. tube of Hoolamite; hence with the type C detector the color comparison scale covers only the range from 0.03 to 0.17 per cent. Quantities of carbon monoxide greater than 0.17 per cent are determined by taking advantage of the fact that the color change produced in Hoolamite by a given quantity of carbon monoxide is independent, within the limits previously stated, of the volume of the gas sample, provided the rate of passage is properly regulated. When a sample containing more than 0.17 per cent is being expelled from the cylinder, the color corresponding to 0.17 per cent will be reached before the stroke is completed. Hence by graduating the piston rod of the apparatus (E, Fig. 3) in per cent carbon monoxide, quantities up to 3 per cent can be determined with a good degree of accuracy.

The improved detector has not yet been put upon the market, but practical tests indicate that it is superior in accuracy and range to the smaller, type B, instrument, although somewhat more cumbersome. Table II gives the results of comparative tests of the two detectors which support the statements just made.

TABLE II—COMPARATIVE TESTS OF DETECTORS

Source of Carbon Monoxide	Detector B Per cent	Detector C Per cent	Iodine Pentoxide Laboratory Analysis Per cent
Pure gas	0.5	0.6	0.583
Flue gas	0.5	0.4	0.431
Illuminating gas	0.3	0.2	0.181
Pure gas	0.2	0.12	0.127
Illuminating gas	0.1	0.07	0.069
Illuminating gas[1]	0.0	0.04	0.034

[1] Charging floor, water gas plant.

The two devices are designed to supplement each other, the simpler being suited to occasional use in the hands of persons engaged in work exposing them to the danger of breathing carbon monoxide such as is met in mines; producer, water, and blast furnace gas plants; garages; boiler rooms; tunnels and excavations near gas mains; army and navy work, etc. The more accurate device is intended to meet the needs of chemists, engineers, inspectors, and other persons responsible for the welfare of workmen, the regulation of plant operations, laboratory tests, and the conduct of industrial research.

SUMMARY

1—A mixture of pumice stone, iodine pentoxide, and fuming sulfuric acid reacts with carbon monoxide to give a green color varying in depth with the concentration of the gas.

2—Two portable devices by means of which this reaction can be applied to the approximately quantitative determination of carbon monoxide are described.

The Determination of Tannin[1,2]

By John Arthur Wilson and Erwin J. Kern

LABORATORIES OF A. F. GALLUN & SONS CO., MILWAUKEE, WISCONSIN

A rather widespread controversy has arisen over a new method of tannin analysis described by the authors in two previous papers,[3] in which it was shown that the methods adopted as official both here and abroad are greatly in error, exceeding 200 per cent in some cases. Changing a method of analysis upon which millions of dollars of tanning materials are bought and sold annually is admittedly a serious matter. Were the new method to supplant the old in the sale of extracts, drastic price changes would have to be made and many extracts would no longer hold their present relative standings or reputation as to tanning value. Since the official methods have been clearly proved unreliable, it would seem that the new method must now be tested generally to determine whether or not it will meet all the conditions that ought to be required of a method so important. Until now its use has been restricted because the procedure as originally described was both cumbersome and time consuming, all of the first efforts having been directed exclusively to devising an accurate method. But the procedure has since been developed until it is now quite as simple as that of any method in general use. In this paper we describe the simplified procedure, and also refute the objections which have been raised against the new method.

DEFINITION OF TANNIN

A thorough review of the literature shows that it has

been generally agreed to class as tannin that portion of the water-soluble matter of certain vegetable materials which will precipitate gelatin from solution and which will form compounds with hide fiber which are resistant to washing. Much confusion would have been avoided in discussion by making it clear whether the criticism was directed against the definition or the method.

CHANGES IN PROCEDURE

In the method as originally described, the tanned hide powder had to be washed by shaking with water for 30 min., squeezing through linen, and repeating with fresh water until free from soluble matter, which usually required about twelve washings. This is now accomplished with very little effort in a washing apparatus to be described later. The washed powder, after drying, was analyzed for water, ash, fat, and hide substance (N×5.62), and the percentages of these subtracted from 100 gave the per cent of tannin in the powder. It was suggested earlier that this figure might be obtained simply by noting the increase in weight of the dry powder after tanning and washing, provided the washing operation were so conducted that no powder was lost, making the determination direct instead of by difference and increasing the accuracy for unskilled analysts. The new washing apparatus not only makes this possible, but reduces the amount of hide powder required for a determination to one-sixth.

PRESENT PROCEDURE

A solution of the tanning material is prepared of such

strength that 2 g. of hide powder will detannize 100 cc. in 6 hrs. of shaking. With a little experimenting, safe limits are easily determined for all ordinary materials so that the need for repetition will be rare. For the extracts used in this work, suitable concentrations in grams per liter are 20 for hemlock, larch, oak, and sumac, 16 for gambier, and 7 for solid quebracho. The solution must be freed from insoluble matter, which may be done in the usual manner by adding kaolin, filtering through a thin paper, returning the filtrate to the paper for an hour to tan it, then discarding all liquor which has touched the paper, pouring fresh liquor on to the filter and collecting when the filtrate comes through clear. For materials which filter with difficulty, time can be saved by setting up several filters at one time. Standard hide powder,[1] or its equivalent, is extracted with chloroform to remove all extractable matter, and is then freed from solvent and stored ready for use. This treatment is chiefly to remove fatty matters, and it may be found convenient to treat a year's supply at once. Two grams of this powder, of known moisture content, are put into a 6-oz., wide-mouth bottle, 100 cc. of tan liquor are added, and the whole is put into a rotating box and shaken for 6 hrs. It is advisable to keep the liquor and wash water cool to guard against any tendency towards decomposition of the untanned portion of the hide powder. This matter requires attention only in hot weather.

The essential part of the washing apparatus is shown in Fig. 1 and consists of three glass parts fitting tightly into one another by means of ground joints. A small piece of fine filter cloth is stretched tightly over the bottom outlet of part B and is firmly secured by winding and tying strong thread around the groove. Parts B and C are then put together and the stopcock is opened. The tan liquor and hide powder, after the 6-hr. shaking, are washed into part B, the liquor being allowed to run through the open cock into a beaker and returned until reasonably clear.[2] The stopcock is then closed and B is half filled with water and then fitted to part A with stopcock closed.

The remaining part of the washing apparatus is a reservoir of water set high enough from the table to exert a pressure equal to a column of about 4 ft. of water upon the glass receptacle, which is connected to the reservoir by means of a rubber tube attached to A. The stopcock in A is opened wide, and the rate of flow of water is regulated to about 500 cc. per hr. by means of the stopcock in C, which is connected to the drain. Since the washing is usually complete in about 12 hrs., it is convenient to start it just before leaving the laboratory in the evening so that it will be complete at the start of the next day. However, washing should not be stopped until the wash water is colorless and does not darken upon the addition of a drop of ferric chloride.

The powder is then washed on to a Büchner funnel and freed from as much

Fig. 1—Glass Washing Apparatus for Use in Wilson-Kern Method of Tannin Analysis or in Determination of Water-Soluble Matter in Leather. Scale 1:4.

1 Prepared by the Standard Mfg. Co., Ridgway, Pa.

2 This liquor must always be tested for tannin by adding, one drop at a time, a freshly prepared solution of 10 g. gelatin and 100 g. sodium chloride per liter. A precipitate indicates that tannin is present, in which case the determination must be repeated, using a more dilute solution of the tanning material.

water as possible by suction. It is then allowed to dry in the air over night, after which it is completely dried in a vacuum oven for 2 hrs., desiccated and weighed. It is returned to the oven and reweighed as a check against insufficient drying. The increase in weight of the dry powder represents the amount of tannin present in 100 cc. of the original tan liquor.

We have found it very convenient to have rotating boxes capable of holding twelve bottles each and cylindrical stands equipped with twelve washing devices each. Given twelve filtered liquors Monday morning, the powders would be tanned and ready for washing before evening, ready for drying next morning, and the tannin values available before noon Wednesday. With one such outfit an analyst can easily complete twelve determinations every day and still have time for other work.

COMPARATIVE ANALYSES

The analyses of six typical extracts given in Table I show that there is practically no difference in results obtained by the original and revised procedures of the new method. Analyses by the official method of the American Leather Chemists Association, widely used in this country, are given for comparison.

TABLE I—COMPARATIVE ANALYSIS OF EXTRACTS BY A. L. C. A. METHOD AND THE ORIGINAL AND REVISED PROCEDURES OF THE NEW METHOD

| | | A. L. C. A. METHOD | | | NEW METHOD Tannin | |
| | | | | | Original Procedure (By Difference) | Revised Procedure (Direct) |
EXTRACT	Water	Insoluble	Non-tannin	Tannin (By Difference)		
Gambier	48.84	7.58	15.78	27.80	7.32	7.44
Hemlock	51.76	7.32	15.04	25.88	16.38	16.39
Larch	51.63	5.41	20.00	22.96	12.70	12.82
Oak	53.51	2.55	18.35	25.59	11.63	11.42
Quebracho	19.41	9.50	6.86	64.23	44.33	44.03
Sumac	49.44	2.86	22.56	25.14	13.10	13.04

DISCUSSION

A common objection to the new method has been that it appeared inconceivable that leather chemists everywhere should have been so misguided as to accept as official a method liable to a 200 per cent error. The fallacy in the argument put forward lies in its assumption that leather chemists everywhere have found the official methods to be borne out quantitatively in practice. When data were called for to prove this assumption, apparently none were available. On the contrary, we have been able to secure data from both upper and sole leather yards showing that the amount of tannin appearing in the finished leather is very much less than entered the yards according to the A. L. C. A. method, and that the apparent loss of tannin corresponds closely to the difference in tannin content of the extracts as determined by the new and official methods.

After some experimenting with the new method, Schultz and Blackadder[1] raised a number of objections to it. Their first was that it was difficult to obtain concordant results, which they explained as being due in part to the fact that the tannin was determined by difference and was subject to the errors involved in determining the water, ash, fat, and hide substance in the tanned powder. This appears to us rather a matter of skill in manipulation, but in any event the cause has vanished with the revision of the procedure.

Their second objection was that the detannized liquor and wash waters gave a test for tannin when concentrated to small bulk. In an earlier paper[2] we showed that certain nontannins are converted into tannin when their solutions are evaporated and that this transformation can be fol-

1 *J. Am. Leather Chem. Assoc.*, 15 (1920), 654.
2 THIS JOURNAL, 12 (1920), 1149.

lowed by means of the new method, but not by the A. L. C. A. method.

Their third objection was that the degree of subdivision of standard hide powder is not uniform, that the finer portions become more heavily tanned but are more easily lost during the washing operation or in later handling, thus tending to give low results for tannin as a result of making the analyses on the portions of powder less heavily tanned. In the revised procedure no loss of powder during the washing is possible, and all of the powder is weighed after drying. It is worthy of note, however, that the results we obtained by the original and revised procedures are practically identical.

Schell[1] has raised an objection to the method that involves the definition of tannin. Following the work of Meunier,[2] he conceives the existence of two kinds of tannin which may be likened to quinone and hydroquinol. Meunier showed that quinone has tanning properties, while hydroquinol apparently has none. Given plenty of access to the air, however, solutions of hydroquinol become capable of tanning because of oxidation. According to Schell, the new method determines only the quinone-like tannin and fails to include hydroquinol-like bodies.

But hydroquinol admittedly has no tanning properties. It seems to us that the method is all the more accurate for not including as tannin, those bodies which are not tannin, although convertible by oxidation or otherwise into tannin. The existence of these substances in tanning materials has been recognized and discussed in our last paper, in which it was shown that the tannin content of a tan liquor is increased by boiling. There is good reason to believe that the new method can be developed to determine the amount of substances convertible into tannin as well as of actual tannin. This might be done simply by analyzing the liquor both before and after some special treatment, such as oxidation, that will convert into tannin all substances capable of such conversion. However, the data available to us indicate that only a fraction of these substances really appear as tannin in the finished leather.

Schell is right in insisting that these nontannins have a value which should be recognized in judging the value of an extract, but the values should be recognized also of those substances which aid in the diffusion of the tannins into the hides and the sugars which form the necessary acids. Two extracts of apparently the same tannin content may have very different properties. The tannin content alone is no sure guide to the value of an extract; much importance is attached to the reputation of the extract manufacturer. It is not improbable that it will eventually be found preferable to sell extracts on a basis of total solid matter, leaving the extract men to compete with each other in establishing a reputation for producing extracts of high quality and constant composition.

In speaking of hydroquinol-like bodies, Schell implies the suggestion that what the official method really determines is the sum of these and the true tannins, but this is not so. Gallic acid belongs to the class of nontannins capable of conversion into tannin, but when added to a tan liquor only a variable fraction of it appears as tannin by the A. L. C. A. method, which makes the method quite unreliable and often very misleading. This is strikingly shown with gambier extract. The method calls for 12.5 g. of dry hide powder to detannize 200 cc. of tan liquor, which amount was assumed to be correct because the nontannin filtrate gave no test with the gelatin-salt reagent. Using this method on a gambier extract we found 26 per cent tannin. But we then

reduced the amount of hide powder to 1.5 g.; the nontannin filtrate gave a negative test with the gelatin-salt reagent, but the per cent of tannin found was only 13. The extract is listed as containing 26 per cent tannin simply because a group of men were more favorably disposed to make 12.5 g. of hide powder official than some other amount. This is treated more fully in our first paper.

The A. L. C. A. method is based upon a principle often employed in adsorption experiments. It falsely assumes that the decrease in concentration of a tan liquor upon shaking with hide powder is a measure of the tannin content and that the solution absorbed by the substance of the hide is of the same composition as the remaining liquor. Thomas and Kelly[1] have shown to what ridiculous conclusions this can lead. In studying the effect of concentration of chrome liquor upon the adsorption of its constituents by hide substance, they had occasion to use very strong liquors. Hide powder was treated with a chrome liquor containing 14.75 g. of chromic oxide per liter, but after 48 hrs. the concentration had *risen* to 15.40 g., although the hide powder had actually removed chromium from solution. This would correspond to a negative value for tannin by the A. L. C. A. method. What happened was that the hide powder absorbed a solution more dilute than the remaining chrome liquor and therefore concentrated the liquor more than enough to offset the chromium removed by combination with the hide substance. It is quite clear that one cannot determine the amount of matter removed from solution by noting the decrease in concentration of the liquor and calculating according to the instructions of the A. L. C. A. method.

Synthetic Tannins

A representative of a firm manufacturing synthetic tanning materials of the Neradol type informed us that the use of the official method on their product meant nothing as it could be made to give any results desired. He was anxious to learn if the new method would indicate the per cent of matter capable of forming a stable compound with hide substance. While we have done no work with syntans, as they are called, it is obvious that they differ from ordinary tan liquors in that they usually contain a large amount of free sulfuric acid. In using the new method on such materials there is the possibility that the acid might cause the hide substance to swell considerably during washing. This would slow down the washing action and tend to favor decomposition of hide substance, with a consequent loss in accuracy of the method. It seems possible that this might be avoided by using tap water saturated with salt for the first washings, until all sulfuric acid was removed, and then completing the washing with distilled water.

Summary

A modification of the authors' new method of tannin analysis is described which results in a great saving of time and labor, and tends towards increased accuracy.

Objections raised against the new method are refuted.

It is shown that the principle underlying the present official methods is unsound.

A suggestion for using the new method with snytans is made.

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[1] *Le Cuir*, 9 (1920), 491.
[2] *Chimie & industrie*, 1 (1918), 71.

[1] This Journal, 13 (1921), 31.

The Preparation of Ethylene by Hydrogenation of Acetylene[1,2]

By William H. Ross, James B. Culbertson and J. P. Parsons

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The earliest work on the hydrogenation of acetylene was done by Sabatier and Senderens during the course of their general investigations on the hydrogenation of organic compounds by catalysis.[3] It was observed that when one volume of acetylene and three volumes of hydrogen were passed through a tube containing reduced nickel the temperature rose to 100° to 150°, and the recovered gas consisted almost entirely of ethane and hydrogen. When the proportion of hydrogen was reduced to two volumes, the recovered gas consisted of 5.3 per cent acetylene, 15.0 per cent ethylene, and 79.1 per cent ethane. On reducing the proportion of hydrogen still further, the nickel became hotter, aromatic hydrocarbons were formed, and the recovered gas analyzed as follows: acetylene, 23.0 per cent, ethylene 18.3 per cent, ethane 61.0 per cent, and hydrogen 2.5 per cent.[4]

A similar result was obtained with platinum, but at the same temperature this catalyst is slower in its action.[5] Reduced copper at temperatures of 150° or above also acts as a catalyst in bringing about the combination of hydrogen and acetylene to form ethylene mixed with other hydrocarbons. It was found, however, that when the mixture contained half its volume of acetylene the reaction was attended by the formation of cuprene and that this metal was therefore less promising than nickel for the hydrogenation of acetylene.[6]

Paal and his co-workers found that combination of hydrogen and acetylene occurs when a mixture of these gases is shaken with a colloidal solution of platinum or palladium in water.[7] Using equal volumes of the gases mentioned, there was recovered in this way a gas which analyzed 80 per cent ethylene.[8]

The reaction between the gases in this process is a relatively slow one, however, and when an excess of hydrogen is used ethane is formed, as in the case of nickel catalyst.

The present paper describes experiments that were undertaken to increase the yield of ethylene in the hydrogenation of acetylene by means of nickel.

Preparation of Nickel Catalyst

The catalyst was prepared from pure nickel nitrate, according to the method of Sabatier and Espil.[9] The oxide prepared from the nitrate was reduced to metallic nickel with hydrogen in the apparatus represented in Fig. 1. In order to remove the last traces of moisture and of oxygen from the hydrogen it was passed through sulfuric acid in the wash bottle E, over copper gauze, G, heated to redness in the electric furnace F_1, and finally over sticks, H, of solid potassium hydroxide. At this point the flow of hydrogen was divided and directed into teach of four tubes, I, containing the nickel oxide to be reduced. The tubes were placed in an electric furnace, F_2, and during he reduction were maintained at a temperature of 300°, as indicated by a thermometer placed in one of the tubes. The reduction of the oxide to metallic nickel was assumed to be complete when the moisture which first formed on the walls of the tubes leading to the absorption traps had com-

pletely disappeared. When the furnaces were shut off for the night or at the end of the reduction, the outlets of the traps J were closed, the hydrogen cylinder was shut off, and in its place there was joined in with the apparatus by means of the 3-way stopcock the reservoir of hydrogen, D. In this way the catalyst could be cooled in hydrogen without any decrease in pressure occurring in the tubes.

A-HYDROGEN CYLINDER   F-ELECTRIC FURNACE
B-HYDROGEN REGULATOR   G-COPPER GAUZE
C-THREE-WAY STOPCOCK   H-NaOH STICKS
D-HYDROGEN CONTAINER   I-CATALYST TUBES
E-H₂SO₄ WASH BOTTLE   J-WASH-BOTTLES
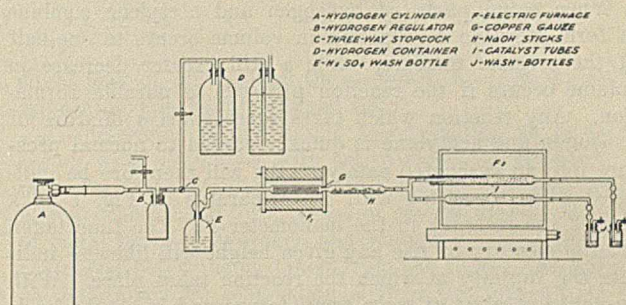
Fig. 1

Each tube in which the nickel oxide was reduced was about 30 cm. long and 2 cm. in diameter, and was sealed at each end to a coarse capillary tube about 10 cm. long. The nickel oxide was placed in the tube after one of the capillary tubes had been sealed on. The quantity of oxide taken amounted to about 20 g., sufficient to fill the tube about one-third full. This was spread out in a train covering the whole length of the tube when placed horizontally. Metallic nickel deposited on 20-mesh pumice was also used.

Apparatus and Method

In testing out the action of nickel catalyst on mixtures of hydrogen and acetylene use was made of the apparatus represented in Fig. 2. The two gases were measured and mixed in the graduated gas buret C, of 300-cc. capacity. The tube containing the reduced nickel is represented at G in the figure. F is a manometer in connection with the tube, and H is a graduated receiver in which the gases could be collected over mercury after passing through or over the catalyst.

A - TWO-WAY STOPCOCKS
B - GAS OUTLETS
C - GRADUATED GAS HOLDER
D - REVERSIBLE Hg TRAP
E - STOPCOCK
F - MANOMETER
G - CATALYST
H - GRADUATED GAS RECEIVER
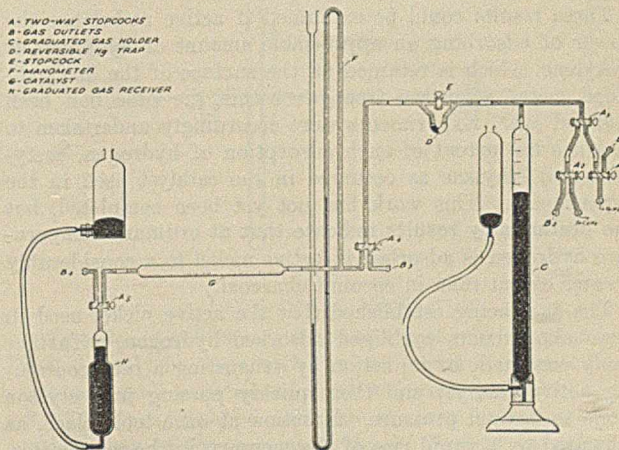
Fig. 2

Before introducing the hydrogen-acetylene mixture into the catalyst tube, the hydrogen remaining in the tube after the reduction of the nickel was pumped out to a pressure of about 6 cm., as indicated by the manometer. This was done by closing the stopcock A_4 and opening A_3. The leveling bottle of the receiver H was then lowered so as to create a

[1] Received June 15, 1921.

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] Paul Sabatier, "La catalyse en chimie organique."

[4] *Compt. rend.*, **128** (1899), 1173.

[5] *Compt. rend.*, **131** (1900), 40.

[6] *Compt. rend.*, **130** (1900), 1559.

[7] *Ber.*, **48** (1915), 275, 1195, 1202.

[8] *Chem.-Ztg.*, **36** (1912), 60.

[9] *Compt. rend.*, **155** (1914), 668.

decrease in pressure within the catalyst tube. The gas withdrawn into H was discharged through the outlet B₄, and the process was repeated if necessary until the desired vacuum was obtained.

By cautiously turning stopcock A₄ the gaseous mixture from the buret C could be passed over the catalyst at any desired rate, as indicated by the mercury trap D; or by opening stopcocks E and A₄ the mixture could be passed quickly into the catalyst tube to normal pressure and left in contact with the catalyst as long as desired. This latter procedure was followed in most of the experiments.

When equal parts of hydrogen and acetylene combine to form ethylene a reduction in volume occurs to one-half of the original mixture, while a still greater decrease in volume occurs if the reaction proceeds to paraffin formation. Any reaction which takes place when a mixture of hydrogen and acetylene is quickly passed to normal pressure into an evacuated catalyst tube will therefore be indicated when connected with the apparatus of Fig. 1 by a rise of the mercury in the manometer F. The time taken for the mercury to rise any given height will likewise indicate the rapidity at which the reaction takes place. With an active catalyst at room temperature and in a tube holding about 75 cc. of free gas, the column of mercury in the manometer after adding a mixture of equal volumes of hydrogen and acetylene was often observed to rise to a height of 38 cm. in 1.5 min. With an inactive catalyst, on the other hand, no change took place in the level of the mercury.

Adsorption of Hydrogen

At the end of the first day's experiments the hydrogen-acetylene mixture that had been in contact with the catalyst was pumped out, and hydrogen was added to normal pressure, with a view to decreasing the danger of any leak into the apparatus while standing over night. Instead of the pressure remaining constant as was expected, the manometer indicated almost as great a degree of exhaustion within the tube as before the hydrogen was added. A similar result was also observed, but to a less marked extent, when acetylene was passed into an evacuated tube that had previously contained hydrogen. However, when a tube containing freshly reduced nickel was exhausted in the same way and hydrogen was introduced again, no decrease in pressure occurred.

These results could be explained if active nickel has the power of adsorbing an appreciable amount of hydrogen or acetylene, which is retained on the surface of the finely divided metal after the free gas within the tube had been pumped out. Experiments were accordingly undertaken to measure the extent of such adsorption of hydrogen, acetylene, and ethylene as occurred in the catalyst used in the experiments. This work has not yet been completed, but the preliminary results indicate that at ordinary temperature hydrogen is adsorbed in active nickel to a considerably greater extent than in coconut charcoal.[1]

The fact being established that the active nickel used in these experiments contained adsorbed hydrogen, a further study was made of its action by exhausting a tube containing active catalyst and then quickly passing in acetylene alone to normal pressure. Reaction at once took place, as indicated by a rapid rise of the mercury in the manometer. The tube was then pumped out as before, and acetylene was again added. On repeating this treatment a number of times it was found that acetylene could be left in con-

tact with the catalyst indefinitely without any change taking place in its composition. That the catalyst still remained active was shown by pumping out the acetylene and filling the tube with hydrogen. A marked reduction of pressure quickly took place, hydrogen disappeared, and the recovered gas consisted largely of ethane. By repeating the treatment with hydrogen, the acetylene in turn was eliminated and hydrogen could then be left in contact with the catalyst without any reduction in pressure taking place. These results indicate that acetylene will react with the hydrogen adsorbed in nickel catalyst; that the adsorbed hydrogen in an active catalyst can be removed by repeated treatment with acetylene without destroying its activity; that an active catalyst from which the adsorbed hydrogen has been removed has no action on acetylene; and that acetylene as well as hydrogen is adsorbed in active nickel.

Measurement of Relative Activity of Catalysts

These results suggested a simple method of measuring the relative activity of different nickel catalysts by connecting each tube in turn in the apparatus, exhausting to a given pressure, quickly passing in a mixture of equal parts of hydrogen and acetylene to normal pressure, and noting the time taken for the mercury to rise to a given height while the tube was maintained at constant temperature. The activity of the different catalysts was assumed to be proportional to the rate at which the mercury rose in the manometer. Having made these determinations in portions of different catalysts, steps were also taken to determine the adsorbed hydrogen by combustion in the remaining portion of each, with a view to ascertaining if the activity of a catalyst in the hydrogenation of acetylene is proportional to its capacity for adsorbed hydrogen. This work has not yet been completed.

Formation of Ethane

Since reduced nickel contains adsorbed hydrogen it will follow that a catalyst tube that has been evacuated and filled with a hydrogen-acetylene mixture of equal parts will actually contain an excess of hydrogen over that required for ethylene. Reduction of the latter to ethane would therefore be expected. This was found to be the case in a set of experiments in which a mixture of equal parts of hydrogen and acetylene were passed over a new catalyst at ordinary temperature at the rate of 2 cc. per min. The recovered gas was found to contain only a trace of acetylene, 8.7 per cent of ethylene, and over 80 per cent of paraffins. The experiments were repeated with the reacting tube maintained at a temperature of — 10° by surrounding it with a freezing mixture. It was thought that at this temperature the reduction of ethylene to ethane might possibly be diminished or entirely inhibited. At the lower temperature the activity of the catalyst was found to have decreased somewhat. By regulating the flow of the gas, samples were sometimes recovered containing upwards of 50 per cent ethylene, but in every case a considerable percentage of ethane was also present. Mixtures of equal volumes of ethylene and hydrogen were substituted for the acetylene-hydrogen mixtures and passed over the catalyst at the same temperature as before. It was found that when the flow of the gas was sufficiently reduced almost complete conversion into ethane took place. This shows that ethylene as well as acetylene will undergo hydrogenation at a temperature as low as — 10°.

Since there is a reduction in volume to one-half when equal parts of hydrogen and acetylene combine to form ethylene while the decrease in volume is still greater if the reaction proceeds to paraffin formation, it was thought that possibly the pressure of the gases in the catalyst tube might

[1] Cf. L. Troast and P. Hautefeuille, *Compt. rend.*, 80 (1875), 788; G. P. Baxter, *Am. Chem. J.*, 22 (1899), 351; Adolf Sieverts, *Z. physik. Chem.*, 60 (1907), 129; 77 (1911), 591; M. Mayer and V. Altmayer, *Ber.*, 41 (1908), 3062; G. Neuman and F. Streintz, *Monatsh.*, 12 (1891), 642; T. W. Richards and A. S. Cushman, *Proc. Am. Acad.*, 34 (1899), 333.

TABLE I.—PERCENTAGE COMPOSITION OF COMPOSITE SAMPLES OF GAS COLLECTED WHEN MIXTURES OF HYDROGEN AND ACETYLENE WERE PASSED OVER NICKEL CATALYST.

Component	A		B		C		D		E		F		G	
	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered	Original Gas Mixture	Gas Recovered
Ethylene, C_2H_4	...	66.8	...	71.1	...	73.0	...	74.7	...	77.8	...	81.5	...	82.2
Acetylene, C_2H_2	41.7	0.0	48.4	8.9	48.2	11.0	49.4	13.1	48.8	9.1	45.2	0.6	47.4	1.1
Ethane, C_2H_6	...	16.3	...	10.6	...	3.6	...	6.6	...	7.1	...	11.9	...	8.6
Hydrogen, H	55.3	1.0	49.1	3.5	49.6	0.4	49.3	0.0	49.9	0.3	53.5	0.0	51.3	0.6
Oxygen, O	0.4	2.8	0.4	0.7	0.4	0.3	0.2	0.5	0.2	0.5	0.2	0.6	0.2	0.4
Nitrogen, etc. (by difference)	2.6	13.1	2.1	5.2	1.8	11.7	1.1	5.1	1.1	5.2	1.1	5.4	1.1	7.1

have some effect on the reaction as suggested by Le Chatelier's principle. The experiments were accordingly repeated by passing the gaseous mixture over the catalyst at room temperature but at different pressures below normal. It was not noticed, however, that the change in pressure, which was varied from normal to one-twelfth of an atmosphere, had any appreciable effect, under the conditions of the experiment, in decreasing the proportion of ethane formed.

YIELD OF ETHYLENE

The experiments were repeated with a freshly reduced catalyst from which all adsorbed hydrogen was removed by repeated treatment with acetylene. The tube was then exhausted, and equal volumes of hydrogen and acetylene were passed in quickly to normal pressure and allowed to remain until the pressure decreased to half an atmosphere. The resulting gas was then pumped out and analyzed. By this treatment there was obtained a marked increase in the percentage of ethylene formed. Results of analyses of composite samples collected over several days are given in Table I.

From the results given in Table I it is seen that a comparatively small variation in the proportion of hydrogen to acetylene in the mixture taken produces a marked change in the composition of the recovered gas. Best results seem to be attained when the hydrogen in the mixture is slightly in excess of the acetylene. A further increase in the proportion of hydrogen, however, results in a decrease of ethylene with a corresponding increase of ethane. When a considerable excess of acetylene is taken, no hydrogen is found in the recovered gas and very little ethane. In a series of experiments in which the proportion of acetylene to hydrogen in the mixture varied up to two parts of the former to one of the latter it was found that the acetylene and ethylene in the recovered gas amounted to 91.5 per cent. The impurities in the gas which came from that occurring in the original mixture amounted to 5.4 per cent, which leaves a total of only 3.1 per cent for the ethane and other constituents which make up the balance of the gas.

The acetylene used in these experiments was obtained from an ordinary acetylene cylinder. An analysis of the gas at the beginning of the experiments showed 94.7 per cent of acetylene which later increased to 96.4 per cent, and finally to 98.1 per cent. The purity of the hydrogen amounted to 99.3 per cent. If one volume of hydrogen were to combine with one volume of acetylene to give one volume of ethylene, then the impurities in the product, which owe their source to that occurring in the original mixture, would amount at first to 6.0 per cent, and with the gases finally used, to 2.6 per cent. The excess of the nonabsorbable and noncombustible components found in the recovered gas, over what was to be expected from the impurities in the original mixture, was no doubt due to a

slight leak of air through the stopcock A_5 (Fig. 2) as the apparatus was being pumped out.

To determine if any slight decomposition of acetylene occurs when in contact with active nickel, an analysis was made for carbon and hydrogen in a catalyst that had been in almost constant use for a period of several weeks. Mixtures of equal parts of hydrogen and acetylene were passed over the nickel before being taken from the tube. The analysis as determined by combustion showed the presence in the nickel of 1.09 per cent of carbon and 0.41 per cent of hydrogen by weight. The ratio of hydrogen to carbon in the sample was therefore even greater than that corresponding to methane. If the carbon occurred in the sample analyzed in the free state, then the hydrogen would have a volume under standard conditions of about 400 cc. per unit volume of the nickel. This is greatly in excess of the quantity found adsorbed in a freshly prepared catalyst. It must therefore be concluded that no appreciable amount of carbon was deposited on the nickel and that the carbon and hydrogen found owe their source to free hydrogen and to hydrocarbons which are either adsorbed in, or deposited on, the nickel.

A-RUBBER BAG GASOMETER   F-BY-PASS WITH STOP COCK
B-WATER OUTLETS   G-CATALYST
C-TWO-WAY STOP-COCKS   H-MANOMETER
D-GAS INLET   I-GAS OUTLETS
E-MERCURY TRAP   J-CONTAINER FOR SUPPLYING WATER-HEAD
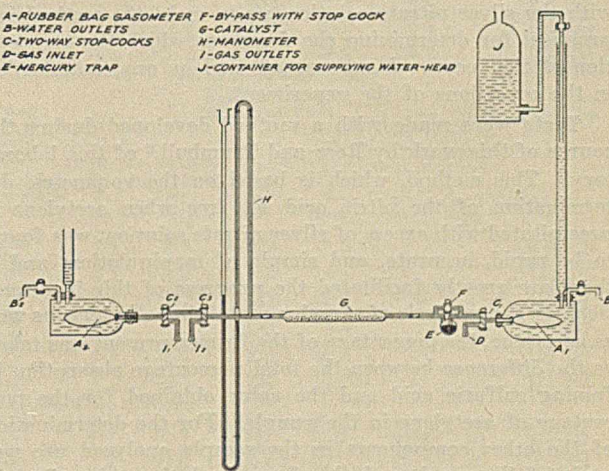
Fig. 3

LARGE-SCALE APPARATUS

In order to collect larger quantities of ethylene than could conveniently be done with the equipment shown in Fig. 2, use was made of a second apparatus as represented in Fig. 3. The hydrogen and acetylene mixture was stored in the rubber bag of the gasometer A_1, of 2000-cc. capacity. By means of the pressure supplied by the head of water in the aspirator bottle J, the gas in the bag could be passed at any rate through the stopcock C_1, the mercury trap E, and the catalyst G, and be collected in the bag of the gasometer A_2. The water of this gasometer was displaced through B_2. The rate at which the gas was passed over the catalyst could be roughly measured by counting the

bubbles per second passing through E. On an average each bubble had a volume of 0.06 cc. To remove the adsorbed hydrogen from a freshly prepared catalyst, the tube in which it was contained was evacuated through the outlet I_2, after closing C_1 and opening C_3. The latter stopcock was then closed, and the pressure within the tube was brought to normal again by passing in a portion of the hydrogen-acetylene mixture from A_1 through the by-pass F. When the mercury rose to a constant height in the manometer the gas was again pumped out, and the process was repeated until the composition of the recovered gas became constant. The same mixture was now passed slowly at practically normal pressure over the catalyst, and the product of the reaction was collected in the gasometer A_2. With an arrangement of this kind the reaction could be allowed to proceed at night, as the flow of water from J automatically stopped when the bag in the gasometer A_1 became empty.

Sample A, Table I, represents the average of several samples collected while the rubber bag of the gasometer A_2 was suspended in the air. The analysis would seem to indicate that a slight exchange of gas had taken place through the walls of the bag. Sample B represents the mean of several collected with the bag in the gasometer as shown.

Methods of Analysis

In the preliminary experiments described in the early part of this work, use was made of the Tucker and Moody method for determining ethylene in the presence of acetylene.[1] This method consists in passing the gases through an ammoniacal silver nitrate solution, which is claimed to remove the acetylene completely, but only a relatively small amount of ethylene. It was found, however, that the quantity of ethylene absorbed so varied with different conditions, particularly with the time the mixture was shaken with the silver nitrate solution, as to make the method impractical for determining the degree to which the composition of the recovered gas was affected by any modification in the conditions of the experiment.

Tests were made with a method developed during the course of this work by Ross and Trumbull,[2] of this laboratory. This method, which is based on the volumetric determination of the nitric acid set free when acetylene is precipitated with excess of silver nitrate solution, was found to be rapid, accurate, and simple of manipulation, and it therefore greatly facilitated the progress of this investigation. In the analysis of samples containing ethylene, as well as acetylene, the percentage of the former present was taken as the difference between the total percentage absorption in fuming sulfuric acid and the value obtained for the percentage of acetylene in the sample. For the determination of the other components in the sample analyzed use was made of the usual methods of gas analysis as described in Dennis' "Gas Analysis."

Experiments with Filchar as Catalyst

Since charcoal is known to act as a catalytic agent in bringing about reactions between different gases, as for example in the combination of carbon monoxide and chlorine to make phosgene, it was thought advisable to test any effect which the material might have on the hydrogenation of acetylene. The material selected for the experiments consisted of screened filchar of medium-sized grains. This was placed in a Pyrex glass tube similar to that used in the experiments with nickel catalyst. The tube was heated

to 700°, and chlorine was passed through until the charcoal had undergone complete chlorination and all tarry matter present in the pores of the material had been destroyed. Nitrogen was then passed through the tube at the same temperature as before, followed by enough hydrogen to drive out the nitrogen, after which the tube was allowed to cool down in an atmosphere of hydrogen. The tube containing the filchar was then placed in an apparatus similar to that represented in Fig. 2. The gas was pumped out to 6 cm. of mercury, and a mixture of hydrogen and acetylene in equal volumes was added at normal temperature. After standing for several hours the rise of mercury in the manometer amounted to only a few millimeters. At 50° and even at 100° the rise of mercury was still less than at normal temperature. This shows, as was also confirmed by an analysis of the gas, that under the conditions of the experiment filchar is without action in bringing about the combination of hydrogen and acetylene.

Summary

Metallic nickel reduced from the oxide at 300° has a greater capacity than coconut charcoal for adsorbing hydrogen at ordinary temperature. When a mixture of equal volumes of hydrogen and acetylene is passed into an evacuated tube about one-third filled with freshly reduced nickel, the hydrogen adsorbed in the nickel, together with that added, may be sufficient to bring about the complete reduction of the acetylene to ethane. By repeating the process of evacuating the tube and passing in the hydrogen-acetylene mixture until the excess of hydrogen is used up, a product may be obtained which contains upward of 80 per cent of ethylene. A comparatively small variation in the composition of the mixture taken produces a considerable change in the composition of the recovered gas. Best results seem to be obtained when the hydrogen in the mixture is slightly in excess, but as this is further increased the ethylene decreases, with corresponding increase of ethane. As the acetylene in the mixture is increased the ethane in the product decreases, and the sum of the ethylene and acetylene increases.

The adsorbed hydrogen in an active nickel catalyst may be eliminated without destroying its activity by repeated treatment with acetylene. The catalyst is then without action on either ethylene or acetylene.

A simple apparatus is described for measuring the relative activities of different nickel catalysts.

VULCANIZATION OF RUBBER

A new method for the vulcanization of rubber is described in a recent article by Professor Bruni of the Pirelli Research Laboratories, Milan, Italy. He states that if certain accelerators such as thiocarbanilide which are formed by the action of an organic amine and carbon bisulfide are produced relatively to the rubber in the nascent state, particularly in the presence of zinc oxide, curing takes place at ordinary temperatures.

[1] *J. Am. Chem. Soc.*, 23 (1901), 671; see also Dennis, "Gas Analysis," p. 249.
[2] *J. Am. Chem. Soc.*, 41 (1919), 1130.

Viscosity-Temperature Curves of Fractions of Typical American Crude Oils[1,2]

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Published information regarding the variation of the viscosity of petroleum oils with temperature is, according to the observations of the authors, notably inadequate. Relatively few data are available in print, and in all cases there is a decided absence of information regarding the origin and history of the samples on which tests were made. The investigation reported in the present paper was undertaken by the Bureau of Mines for the purpose of obtaining figures showing the viscosity-temperature relationships of a reasonably wide range of petroleum fractions of known origin and of accurately determined physical properties.

SCOPE AND GENERAL METHOD OF PROCEDURE

The following three crude oils were selected for the present series of tests:

1—A sample of Pennsylvania crude petroleum obtained from a small refinery located in Pittsburgh, Pa. This oil was regarded as representative of the so-called "paraffin base" class.

2—A sample of crude petroleum from the Sunset Field, Kern County, Cal., which was regarded as representative of the class of so-called "naphthene base" oils.

3—A sample of crude petroleum from the Salt Creek Field, Natrona County, Wyo., which was regarded as representative of the class of so-called "intermediate base" oils.

Analyses of these samples according to the Bureau of Mines procedure for crude oil appear in Table I.

The viscosity determinations recorded in subsequent tables were made on fractions distilling at atmospheric pressure between limits of 100° to 125° C. (212° to 257° F.) 125° to 150° C. (257° to 302° F.), etc., up to 250° to 275° C. (482° to 527° F.), and on all the "vacuum" fractions. These fractions are designated hereafter by letters and numbers indicating the crude from which they were derived, the pressure under which they were distilled, and the upper (centigrade) distillation limit. Thus, for example, "W-V-250" represents a fraction from Wyoming crude, separated between limits of 225° to 250° C. (437° to 482° F.) in the "vacuum" distillation at 40 mm.; "C-A-175" indicates a fraction from California crude, distilling between 150° and 175° C. (302° to 347° F.) at atmospheric pressure, etc.

Viscosity determinations were made at the following temperatures: 0° C., 10° C., 20° C., 30° C., 40° C., 50° C., 60° C., 80° C., and 100° C. (32° F., 50° F., 68° F., 86° F., 104° F., 122° F., 140° F., 176° F., and 212° F.). For obvious reasons, tests were not made at all points on all fractions; some of the fractions distilling at atmospheric pressure have excessive vapor pressures at 80° C. and 100° C., and some of the "vacuum" fractions solidify partly or totally at temperatures as high as 30° C.

The determinations of viscosity-temperature curves for distillation fractions were supplemented by tests on the following oils: (1) The residuum (designated as "P-R") from the distillation of the Pennsylvania crude, (2) a mixture (designated as "P-mixt") of this residuum and the Pennsylvania fraction "P-V-225," and (3) a mixture (designated as "P-C-mixt") of "P-R" and the California fraction "C-V-250."

Results in terms of kinematic viscosity (absolute viscosity divided by density) are given in full. Saybolt Universal equivalents are given for the majority of figures representing kinematic viscosities in excess of 0.0142 (32 sec., Say-

TABLE I—RESULTS OF ROUTINE ANALYSES OF SAMPLES OF CRUDE PETROLEUM FROM WHICH WERE OBTAINED THE FRACTIONS USED FOR VISCOSITY-TEMPERATURE MEASUREMENTS

SAMPLE No. 640

Pennsylvania
Specific gravity—0.809　　Baumé gravity—43.1°
Per cent sulfur—0.16　　Per cent water—Nil

DISTILLATION, BUREAU OF MINES HEMPEL METHOD
Air distillation, first drop, 24°C. (75°F.)

Temperature °C.	Per cent Cut	Sum Per Cent	Sp. gr. Cut	°Bé. Cut	Viscosity[1]	Cloud Test °F.	Temperature °F.
Up to 50	1.5	1.5	0.639	89.1			Up to 122
50- 75	2.8	4.3	0.662	81.5			122-167
75-100	3.3	7.6	0.702	69.4			167-212
100-125	7.2	14.8	0.728	62.3			212-257
125-150	6.0	20.8	0.746	57.?			257-302
150-175	6.5	27.3	0.760	54.2			302-347
175-200	5.5	32.8	0.773	51.1			347-392
200-225	6.5	39.3	0.785	48.3			392-437
225-250	5.9	45.2	0.797	45.7			437-482
250-275	7.0	52.2	0.810	42.8			482-527
Vacuum distillation at 40mm.							
Up to 200	4.6	4.6	0.829	38.9	39.1	16	Up to 392
200-225	5.2	9.8	0.834	37.9	44.5	36	392-437
225-250	5.2	15.0	0.842	36.3	53.5	55	437-482
250-275	5.2	20.2	0.850	34.7	71.2	74	482-527
275-300	6.0	26.2	0.859	33.0	109.5	90	527-572
Residuum			0.894	26.6	726.8		Residuum

Carbon residue of residuum—2.3 per cent

SAMPLE No. 474

California　　Sunset Field　　Kern County
Specific gravity—0.878　　Baumé gravity—29.5°
Per cent sulfur—0.73　　Per cent water—Nil

DISTILLATION, BUREAU OF MINES HEMPEL METHOD
Air distillation, first drop—26°C. (79°F.)

Temperature °C.	Per cent Cut	Sum Per cent	Sp. gr. Cut	°Bé. Cut[1]	Viscosity	Cloud Test °F.	Temperature °F.
75-100	1.3	1.3	0.742	58.7			167-212
100-125	3.9	5.2	0.761	54.0			212-257
125-150	4.5	9.7	0.782	49.0			257-302
150-175	4.0	13.7	0.805	43.9			302-347
175-200	3.7	17.4	0.818	41.1			347-392
200-225	4.8	22.2	0.844	35.9			392-437
225-250	5.5	27.7	0.860	32.8			437-482
250-275	5.9	33.6	0.874	30.2			482-527
Vacuum distillation at 40mm.							
Up to 200	3.6	3.6	0.891	27.1	42.5		Up to 392
200-225	4.8	8.4	0.904	24.9	53.8		392-437
225-250	4.9	13.3	0.917	22.7	89.4		437-482
250-275	5.3	18.6	0.932	20.2	203.1		482-527
275-300	8.3	26.9	0.942	18.6	427.3		527-572

Carbon residue of residuum—16.4 per cent

SAMPLE No. 561

Wyoming　　Salt Creek Field　　Natrona County
Specific gravity—0.841　　Baumé gravity—36.5°
Per cent sulfur—0.18　　Per cent water—Nil

DISTILLATION, BUREAU OF MINES HEMPEL METHOD
Air distillation, first drop—25°C. (77°F.)

Temperature °C.	Per cent Cut	Sum Per cent	Sp. gr. Cut	°Be. Cut	Viscosity[1]	Cloud Test °F.	Temperature °F.
Up to 50	1.4	1.4	0.669	79.3			Up to 122
50- 75	1.8	3.2					122-167
75-100	4.5	7.7	0.716	65.5			167-212
100-125	6.7	14.4	0.744	58.2			212-257
125-150	5.1	19.5	0.764	53.2			257-302
150-175	5.8	25.3	0.783	48.8			302-347
175-200	4.0	29.3	0.797	45.7			347-392
200-225	4.4	33.7	0.810	42.8			392-437
225-250	5.4	39.1	0.822	40.3			437-482
250-275	6.3	45.4	0.833	38.1			482-527
Vacuum distillation at 40mm.							
Up to 200	4.1	4.1	0.849	34.9	40.1	19	Up to 392
200-225	6.1	10.2	0.852	34.3	45.2	39	392-437
225-250	6.1	16.3	0.860	32.8	57.6	63	437-482
250-275	5.6	21.9	0.865	31.9	80.2	77	482-527
275-300	5.4	27.3	0.874	30.2	130.8	90	527-572

Carbon residue of residuum—6.1 per cent
[1] Viscosity figures are Saybolt Universal sec., at 100°F.

bolt Universal). Transformations were made by the use of the Bureau of Standards equation[1]

$$V_k = 0.00220\, t_s - \frac{1.80}{t_s}$$

in which V_k is kinematic viscosity and t_s Saybolt Universal viscosity.

EXPERIMENTAL

The distillation methods used for preparing the various fractions are to be described in full in Bureau of Mines *Bulletin* 207, which will be published at a slightly later

Capacity about 3 CC.

Capacity about 1.2 CC

Capillary 0.5 M.M. diameter

Capacity about 1.2 CC

Capillary 1 M.M. diameter

Capacity about 5 CC

Capacity about 10 CC.

Fig. 1—Form and approximate dimensions of two extremes of set of Ostwald viscosimeters used in present series of experiments

constructed Ostwald viscosimeters, about a dozen of which were used. These instruments varied somewhat in the size of the upper bulb and the length and bore of the capillary. The approximate dimensions of two extremes of the set are shown in Fig. 1. Viscosimeters having relatively large bulbs and long, fine capillaries were, of course, used for the less viscous fractions, whereas for viscous oils the small-bulbed instruments with shorter, wider capillaries were more convenient.

METHOD OF FILLING VISCOSIMETERS—The problem of filling viscosimeters offered a little difficulty, as the conventional procedure of introducing a known volume of liquid from a pipet is obviously unsatisfactory in the case of the more viscous fractions. The scheme finally adopted involved using the lower reservoir of the viscosimeter as a measuring container. The process of filling was accomplished by setting up a viscosimeter in a vertical position and introducing oil through the wider arm by means of a pipet or pressure injector equipped with a long, slender tip. The oil was run in " drop-wise " after the reservoir had become approximately three-quarters full and the flow was stopped as soon as the level of the liquid reached the junction of the capillary and the reservoir. This point was indicated very accurately by a " shooting up " when the oil first entered the capillary.

STANDARIZATION OF VISCOSIMETERS—Each viscosimeter was standardized by determining the efflux time with each of at least two liquids of known viscosity, the " known " liquids being distilled water, and samples of oil for which kinematic viscosity figures were supplied by the Bureau of Standards. The selection of calibrating liquids was determined by the " rapidity " or " slowness " of the viscosimeter under test. For the " slower " instruments, that is,

date. The method involves distilling a 300-cc. charge of oil in a special glass flask, equipped with a 6-in. Hempel column, until a vapor temperature of 275° C. (527° F.) is reached. The flask and its contents are then allowed to cool. The Hempel column is removed and replaced by a "spray catching" device consisting of three inverted gauze cones. The flask is attached to a properly designed "vacuum" system, and the distillation is continued at a reduced pressure of 40 mm. absolute until a vapor temperature of 300° C. (572° F.) is reached. Fractions are separated at temperature limits that are multiples of 25° C. (The respective Fahrenheit limits are 45° apart.)

Viscosity determinations were made by means of specially

the ones with large bulbs and long, fine capillaries, water and one of the less viscous " standard " oils were used. The more " rapid " viscosimeters were standardized with two oil samples. The method of standardization involved the assumption of the following relationship:

$$V_k = At \qquad (1)$$

in which V_k is kinematic viscosity, t the efflux time and A a constant characteristic of the viscosimeter. The general equation is

$$V_k = At - \frac{B}{t} \qquad (2)$$

in which the term $\frac{B}{t}$ (the kinetic energy correction) is negligible if the rate of flow of liquid through the capillary is sufficiently slow. The employment of two liquids in the standardization of each viscosimeter indicated the negligible magnitude of the " kinetic energy correction " for when two liquids of differing viscosity give the same value for A in Equation 1 it is obvious that neither of them flows with sufficient rapidity to necessitate the use of Equation 2.

THE " FILLING FACTOR "—In case a viscosimeter is filled at one temperature and the efflux time is determined at some other temperature, it is obvious that some sort of a correction factor must be employed to compensate for the change in " head " brought about by thermal expansion or contraction of the oil. For purposes of operating convenience the authors usually filled viscosimeters at temperatures of either 25° C. (77° F.) or 100° C. (212° F.). Actual determinations of viscosity were, of course, made at temperatures ranging from 0° C. (32° F.) to 100° C. (212° F.). It was necessary, therefore, to use a series of so-called filling factors to compensate for the errors that would otherwise have been introduced by this detail of procedure. An average factor was determined for the whole set of instruments by making viscosity tests on certain oils at 100° C. (212° F.) with filling temperatures of 25° C. (77° F.) and 100° C. (212° F.). The average ratio for this difference in filling temperature was 1.023 at 100° C. Using this figure as a basis, the set of " filling factors " given in Table II was calculated.

TABLE II—FILLING FACTORS USED WHEN VISCOSIMETERS ARE FILLED AT 25°C. (77° F.) OR 100° C. (212° F.) AND VISCOSITY DETERMINATIONS A MADE AT OTHER TEMPERATURES

Temperature at which Viscosity Determination is Made		"Filling Factor" when Pipet is Filled at 25° C. (77° F.)	"Filling Factor" when Pipet is Filled at 100° C. (212° F.)
°C.	°F.		
0	32	0.992	....
10	50	0.995	...
20	68	0.999	....
30	86	1.002	0.979
40	104	1.005	0.982
50	122	1.008	0.985
60	1r0	1.011	0.988
70	158	1.014	0.991
80	176	1.017	0.994
100	212	1.023	1.000

The equation actually used for the calculation of results therefore takes the form:

$$V_k = Atf \qquad (3)$$

in which V_k is kinematic viscosity, A the constant characteristic of the viscosimeter used, and f a properly selected filling factor from Table II.

It should perhaps be stated that the authors recognize the fact that their method of standardization and calculation involves certain approximations that would not be justifiable if the highest possible degree of precision were necessary. It has seemed, however, that the consumption of time necessary for increased accuracy is greater than is warranted through any possible advantage that could be gained.

MISCELLANEOUS OPERATING DETAILS—Actual determinations were made with the viscosimeters immersed in constant temperature baths. A vigorously stirred mixture of cracked ice and distilled water gave a temperature of 0° C. (32° F.), while temperatures from 10° C. (50° F.) to 70° C.

Fig. 2—Viscosity-temperature curves of sets of distillation fractions derived from Pennsylvania and California crude petroleum

vania residuum and the two mixtures previously referred to.

Fig. 2 shows graphically the majority of the data included in Table III, *A* and *B*, and indicates the similarities and differences of the viscosity-temperature curves for fractions from two extreme types of crude oil. It will be observed that the curves representing low boiling ranges and low viscosities are not unlike, but that there are impressive differences in the "higher" fractions. The curves for the California oil are much steeper than those for Pennsylvania cuts and indicate a greater variation of viscosity with temperature. Curves for the Wyoming oil are not shown. They have characteristics intermediate between those of the Pennsylvania and California curves and resemble the former more closely than they do the latter.

While it is felt that the method of plotting the results adopted in Fig. 2 is the most effective way of illustrating the points emphasized above, another scheme of graphic representation has certain advantages.[1] If the reciprocals of the kinematic viscosities as ordinates are plotted against the temperatures as abscissas, the resulting lines are straight for the lighter fractions, and only slightly curved for the heavier fractions. A plot so constructed permits easier interpolation than the type of diagram shown in Fig. 2. For the gasoline fractions, a straight line drawn through two experimental points will represent satisfactorily the viscosity temperature relationship while for the heavier oils, three or more points obviously will be required to determine the curve. This subject is considered from a mathematical standpoint in a later connection.
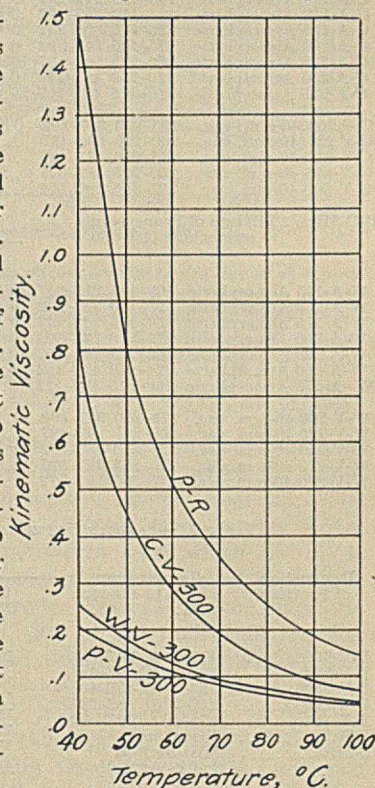
Fig. 3—Viscosity-temperature curves of several of the more viscous products derived from Pennsylvania, California and Wyoming crude petroleum.

(158° F.) were maintained by the use of water baths equipped with the conventional devices for thermostatic control. The baths for 80° C. (176° F.) and 100° C. (212° F.) consisted of glass jackets through which benzene vapor and steam were passed. Both of these baths were maintained under pressures so regulated as to give the precise temperatures desired.

At least three determinations of the efflux time were made for each oil at each temperature, and the viscosity figures reported were calculated from the mean of these experimental values.

Discussion of Results

The calculated figures for the kinematic viscosities are given in Table III. Table IV shows equivalent Saybolt Universal figures for the "vacuum" fractions, the Pennsyl-

Fig. 3 shows in detail a comparison of curves characteristic of viscous oils derived from Pennsylvania and California crude petroleums. The upper curve, marked "P-R" represents the residuum from the combined "air" and "vacuum" distillations of the Pennsylvania crude. This residuum is a product the properties of which approach those of so-called steam cylinder stock. Its viscosity is high throughout the entire range of temperature, but it belongs to the same family as the lowest two curves of the diagram, marked "W-V-300" and "P-V-300," and representing respectively vacuum distillation fractions cut between limits of 275° to 300° C. (527° to 572° F.) from the Wyoming and Pennsylvania crudes. The intermediate curve, marked "C-V-300," representing the highest vacuum fraction from the California crude, shows at 100° C. (212° F.) a viscosity slightly higher

[1] The authors are indebted to Professor Robert E. Wilson, of the Massachusetts Institute of Technology, for bringing to their attention the practical advantages of this method.

TABLE III—KINEMATIC VISCOSITIES AT VARIOUS TEMPERATURES OF A SERIES OF PRODUCTS DERIVED FROM CRUDE PETROLEUM

Designation of Product	Description under which Distilled	Temperature Limits of Cut	0° C. 32° F.	10° C. 50° F.	20° C. 68° F.	30° C. 86° F.	40° C. 104° F.	50° C. 122° F.	60° C. 140° F.	80° C. 176° F.	100° C. 212° F.	37.8° C. 100° F.	54.4° C. 130° F.	98.9°C 210° F.
		°C. °F.												
						A—Pennsylvania Crude								
P-A-125	Atmospheric	100–125 212–257	0.00880	0.00780	0.00703	0.00643	0.00593	0.00542	0.00508	0.00456	......	......	......	......
P-A-150	Atmospheric	125–150 257–302	0.0111	0.00957	0.00869	0.00780	0.00708	0.00649	0.00603	0.00524	0.00467	......	......	......
P-A-175	Atmospheric	150–175 302–347	0.0141	0.0121	0.0106	0.00946	0.00849	0.00769	0.00702	0.00618	0.00548	......	......	......
P-A-200	Atmospheric	175–200 347–392	0.0199	0.0166	0.0142	0.0123	0.0110	0.00964	0.00871	0.00737	0.00642	......	......	......
P-A-225	Atmospheric	200–225 392–437	0.0298	0.0236	0.0196	0.0167	0.0145	0.0127	0.0112	0.00926	0.00781	......	......	......
P-A-250	Atmospheric	225–250 437–482	0.0454	0.0345	0.0277	0.0227	0.0191	0.0164	0.0143	0.0115	0.00958	......	......	......
P-A-275	Atmospheric	250–275 482–527	0.0729	0.0529	0.0407	0.0322	0.0265	0.0221	0.0188	0.0147	0.0120	......	......	......
P-V-200	40 - mm. vac.	175–200 347–392	0.1296	0.0884	0.0642	0.0489	0.0384	0.0315	0.0259	0.0195	0.0152	0.0400	0.0289	0.0153
P-V-225	40 - mm. vac.	200–225 392–437	......	0.1372	0.0962	0.0704	0.0544	0.0432	0.0356	0.0247	0.0186	0.0574	0.0394	0.0188
P-V-250	40 - mm. vac.	225–250 437–482	......	......	0.1533	0.1079	0.0798	0.0609	0.0484	0.0327	0.0238	0.0841	0.0546	0.0242
P-V-275	40 - mm. vac.	250–275 482–527	......	......	......	0.1746	0.1225	0.0899	0.0694	0.0448	0.0312	0.1314	0.0797	0.0318
P-V-300	40 - mm. vac.	275–300 527–572	......	......	......	......	0.2044	0.1444	0.1064	0.0654	0.0441	0.2245	0.1248	0.0450
P-R	Residuum		......	......	......	......	1.498	0.8064	0.5248	0.2581	0.1468	1.596	0.6780	0.1512
P-Mixt.	Mixture residuum and fraction P-V-225		......	......	......	0.1669	0.1208	0.0918	0.0570	0.0396	......	......	......	
						B—California Crude								
C-A-125	Atmospheric	100–125 212–257	0.0103	0.00902	0.00807	0.00735	0.00665	0.00610	0.00565	0.00488	......	......	......	......
C-A-150	Atmospheric	125–150 257–302	0.0124	0.0108	0.00957	0.00860	0.00775	0.00711	0.00661	0.00570	0.00505	......	......	......
C-A-175	Atmospheric	150–175 302–347	0.0162	0.0128	0.0120	0.0106	0.00942	0.00847	0.00773	0.00651	0.00568	......	......	......
C-A-200	Atmospheric	175–200 347–392	0.0223	0.0185	0.0158	0.0135	0.0119	0.0105	0.00943	0.00781	0.00673	......	......	......
C-A-225	Atmospheric	200–225 392–437	0.0332	0.0263	0.0215	0.0180	0.0154	0.0134	0.0120	0.00961	0.00817	......	......	......
C-A-250	Atmospheric	225–250 437–482	0.0523	0.0396	0.0312	0.0252	0.0210	0.0179	0.0154	0.0121	0.00987	......	......	......
C-A-275	Atmospheric	250–275 482–527	0.0935	0.0656	0.0486	0.0375	0.0302	0.0249	0.0209	0.0158	0.0124	......	......	......
C-V-200	40-mm. vac.	175–200 347–392	0.2142	0.1328	0.0902	0.0645	0.0485	0.0383	0.0308	0.0217	0.0165	0.0510	0.0348	0.0166
C-V-225	40-mm. vac.	200–225 392–437	......	0.2825	0.1717	0.1136	0.0803	0.0596	0.0459	0.0303	0.0219	0.0848	0.0529	0.0222
C-V-250	40-mm. vac.	225–250 437–482	......	0.8393	0.4360	0.2548	0.1628	0.1122	0.0807	0.0482	0.0322	0.1766	0.0962	0.0328
C-V-275	40-mm. vac.	250–275 482–527	......	......	......	0.0926	0.3877	0.2372	0.1572	0.0825	0.0502	0.4380	0.1961	0.0514
C-V-300	40-mm. vac.	275–300 527–572	......	......	......	......	0.8282	0.4612	0.2836	0.1305	0.0736	0.9363	0.3686	0.0757
P-C-Mixt.	Mixture of Pennsylvania residue and C-V-250		......	......	......	......	0.3228	0.2108	0.1465	0.0811	0.0517	......	......	......
						C—Wyoming Crude								
W-A-125	Atmospheric	100–125 212–257	0.00927	0.00829	0.00741	0.00675	0.00609	0.00567	0.00533	......	......	......	......	......
W-A-150	Atmospheric	125–150 257–302	0.01141	0.00999	0.00890	0.00803	0.00730	0.00669	0.00622	0.00547	0.00489	......	......	......
W-A-175	Atmospheric	150–175 302–347	0.0151	0.0129	0.0113	0.0100	0.00895	0.00808	0.00752	0.00628	0.00547	......	......	......
W-A-200	Atmospheric	175–200 347–392	0.0207	0.0173	0.0148	0.0128	0.0114	0.0101	0.00907	0.00760	0.00646	......	......	......
W-A-225	Atmospheric	200–225 392–437	0.0299	0.0241	0.0200	0.0169	0.0146	0.0127	0.0114	0.00919	0.00773	......	......	......
W-A-250	Atmospheric	225–250 437–482	0.0452	0.0348	0.0281	0.0231	0.0193	0.0165	0.0143	0.0114	0.00935	......	......	......
W -A-275	Atmospheric	250–275 482–527	0.0737	0.0542	0.0414	0.0327	0.0268	0.0224	0.0191	0.0146	0.0116	......	......	......
W-V-200	40-mm. vac.	175–200 347–392	0.1432	0.0976	0.0698	0.0526	0.0412	0.0330	0.0274	0.0199	0.0155	0.0433	0.0303	0.0157
W-V-225	40-mm. vac.	200–225 392–437	......	0.1491	0.1026	0.0743	0.0563	0.0442	0.0356	0.0251	0.0188	0.0596	0.0401	0.0101
W-V-250	40-mm. vac.	225–250 437–482	......	......	0.1792	0.1227	0.0892	0.0672	0.0528	0.0356	0.0257	0.0955	0.0600	0.0260
W-V-275	40-mm. vac.	250–275 482–527	......	......	......	0.2070	0.1418	0.1033	0.0774	0.0483	0.0334	0.154	0.0905	0.0340
W-V-300	40-mm. vac.	275–300 527–572	......	......	......	......	0.2501	0.1701	0.1230	0.0723	0.0470	0.274	0.146	0.0480

TABLE IV—SAYBOLT UNIVERSAL VISCOSITIES AT VARIOUS TEMPERATURES OF A SERIES OF PRODUCTS FROM CRUDE PETROLEUM
(Fractions distilled at 40-mm. vacuum)

Designation of Fraction	Temperature Limits of Fraction °C. °F.	0°C. 32°F.	10°C. 50°F.	20°C. 68°F.	30°C. 86°F.	40°C. 104°F.	50°C. 122°F.	60°C. 140°F.	80°C. 176°F.	100°C. 212°F.	37.8°C. 100°F.	54.4°C. 130°F.	98.9°C. 210°F.
						A—Pennsylvania Crude								
P-V-200........	175–200 347–392	70.5	55.0	46.7	41.8	38.6	36.6	35.1	33.4	32.3	39.1	35.9	32.3
P-V-225........	200–225 392–437	....	73.5	·57.9	48.8	43.5	40.1	37.8	34.8	33.1	44.5	38.9	33.2
P-V-250........	225–250 437–482	....	....	79.9	62.2	52.0	45.6	41.7	37.0	34.5	53.5	43.6	34.6
P-V-275........	250–275 482–527	....	....	....	88.6	67.8	55.6	48.4	40.5	36.6	71.2	52.0	36.7
P-V-300........	275–300 527–572	....	....	....	....	101.0	76.4	61.6	47.1	40.3	109.5	68.7	40.6
P-R...........	Residuum	....	....	....	....	682.2	368.8	241.6	123.9	77.3	726.8	310.8	79.1
P-Mixt........	Mixture P-R and P-V-225	....	....	....	....	85.5	67.1	56.2	44.3	39.0	....	....	
						B—California Crude								
C-V-200........	175–200 347–392	105.1	71.8	55.7	46.8	41.7	38.6	36.4	33.9	32.6	42.5	37.6	32.6
C-V-225........	200–225 392–437	....	134.5	87.4	64.3	52.2	45.2	40.9	36.3	34.0	53.8	43.1	34.1
C-V-250........	225–250 437–482	....	383.5	202.2	122.5	83.8	63.8	52.3	41.6	36.8	89.4	57.9	37.0
C-V-275........	250–275 482–527	_....	383.5	....	317.5	180.7	114.9	81.5	53.0	42.2	203.1	97.5	42.6
C-V-300........	275–300 527–572	....	....	....	....	378.7	213.5	135.0	70.8	49.9·	427.5	172.3	50.6
P-C-Mixt.......	Mixture P-R and C-V-250	....	....	....	....	152.1	103.7	77.2	52.5	42.8	....	....	
						C—Wyoming Crude								
W-V-200......	175–200 347–392	75.9	58.4	48.6	43.0	39.5	37.1	35.5	33.5	32.3	40.1	36.3	32.4
W-V-225......	200–225 392–437	....	78.3	60.2	50.1	44.2	40.3	37.8	34.8	33.3	45.2	39.1	33.3
W-V-250......	225–250 437–482	....	....	90.5	67.8	55.3	47.6	43.0	37.8	35.0	57.6	45.3	35.1
W-V-275......	250–275 482–527	....	....	....	102.1	75.3	60.5	51.2	41.6	37.2	80.2	55.8	37.4
W-V-300......	275–300 527–572	....	....	....	....	120.5	86.7	68.0	49.4	41.2	130.8	77.0	41.5

than those of the corresponding Pennsylvania and Wyoming products, whereas at the lower temperatures it approaches more closely the viscosity of the Pennsylvania residuum.

Fig. 4 shows viscosity-temperature curves for typical kerosene fractions ("P-A-225," "C-A-225," and "W-A-225") from the Pennsylvania, California, and Wyoming crudes. Viscosity differences are of the same type as those shown for higher boiling, more viscous fractions, but are of a lesser order of magnitude.

Fig. 5 gives interesting indications regarding the viscosity-temperature curves of mixtures. It has just been pointed out (refer to Fig. 3) that the viscosity-temperature curve of the Pennsylvania residuum resembles the curves for the distillates from the same crude. In Fig 5 the curve marked "P-mixt" represents a blend of Pennsylvania residuum and the Pennsylvania vacuum fraction "P-V-225." It will be noted that this curve is entirely similar to those obtained from the fractions "P-V-300" and "P-V-275," between which it lies. The curve marked "P-C-mixt" represents

Fig. 4—Viscosity-temperature curves of typical kerosene fractions derived from Pennsylvania, California and Wyoming crude petroleum

Fig. 5—Showing that the viscosity-temperature curve of a mixture of Pennsylvania distillate and Pennsylvania residuum has the same form as curves for unblended Pennsylvania distillates, whereas the curve for a mixture of California distillate and Pennsylvania residuum varies appreciably from the form of a curve for unblended California distillate.

[1] Compare Basler chemische Fabrik, D. R. P. 205,377, and 211,696.

a mixture of the Pennsylvania residuum and one of the lighter vacuum fractions of the California crude. It will be noted that its slope is not as steep as that of the adjacent curve " C-V-275," representing a " straight " California distillate.

The indications furnished by these comparisons point to the fact that the viscosity-temperature curves of the important group of commercial lubricating oils made by blending " paraffin base " distillates and " paraffin base " residuums show the same characteristics as the corresponding curves for "straight" distillates. When blends are composed of oils derived from different types of crude petroleum the characteristics of the curves are intermediate between those of the constituents.

GENERAL CHARACTERISTICS OF VISCOSITY-TEMPERATURE CURVES

From the data presented in Tables III and IV, and in Figs. 2 to 5, inclusive, two conclusions may be drawn. In

the first place, the work done apparently indicates the nonexistence of any simple rule by means of which the variation of viscosity with temperature can be predicted. The ratio between viscosities at different temperatures varies with the type of crude petroleum from which the oil is derived and also with the physical and chemical properties of fractions from a given crude. For example the kinematic viscosity at 100° C. (212° F.) of the California fraction " C-V-300 " is 8.9 per cent of the figure determined for 40° C. (104° F.). A corresponding ratio for the Pennsylvania fraction " P-V-300 " is 21.6 per cent. It may be noted further that for the Pennsylvania fraction " P-V-250 " the ratio between kinematic viscosities at the same two temperature points is 29.8 per cent. Similar variations may be discovered when comparisons are made of products derived from different crudes and having equal viscosities at any given temperature. This matter is discussed in more detail in a later connection.

TABLE V—VALUES OF THE CALCULATED CONSTANTS K,[1] A AND B REPRESENTING THE VISCOSITY TEMPERATURE CURVES OF THE DISTILLATION FRACTIONS DERIVED FROM PENNSYLVANIA AND CALIFORNIA CRUDE PETROLEUM

Temperature Limits of Fraction		Pressure under which Distilled	Pennsylvania Fractions			California Fractions		
°C.	F°.		K	A	B	K	A	B
100–125	212–257	Atmospheric	113.2	1.498	—0.00200	97.60	1.287	+0.000688
125–150	257–302	Atmospheric	90.19	1.300	—0.000591	80.74	1.204	—0.000298
150–175	302–347	Atmospheric	70.30	1.250	—0.000126	61.32	1.108	+0.000450
175–200	347–392	Atmospheric	49.60	1.072	—0.0000380	44.14	0.989	+0.000623
200–225	392–437	Atmospheric	33.50	0.865	+0.000794	29.57	0.853	0.000813
225–250	437–482	Atmospheric	21.37	0.751	+0.000840	18.61	0.661	0.00169
250–275	482–527	Atmospheric	12.97	0.583	0.00130	10.29	0.488	0.00217
175–200	347–392	40-mm. vacuum	7.21	0.400	0.00189	4.242	0.309	0.00259
200–225	392–437	40-mm. vacuum	4.45	0.252	0.00243	1.254	+0.178	0.00269
225–250	437–482	40-mm. vacuum	1.88	0.182	0.00219	0.550	+0.0319	0.00274
250–275	482–527	40-mm. vacuum	+0.810	0.0994	0.00213	1.070	—0.0629	0.00252
275–300	527–572	40-mm. vacuum	—0.010	0.0522	0.00175	1.967	—0.109	0.00225
Residuum			+0.881	—0.0468	+0.00106			

[1] The viscosity temperature curves can be represented in terms of an equation of the general form

$$V_k = \frac{1}{K + At + Bt^2}$$

in which V_k is kinematic viscosity, t the centigrade temperature and K, A, and B constants characteristic of each individual fraction from each oil.

Secondly, an outstanding similarity is found in the general form of the various viscosity-temperature curves. These can be represented by equations of the form:

$$V_k = \frac{1}{K + At + Bt^2} \qquad (4)$$

in which V_k is kinematic viscosity, t the centigrade temperature and K, A and B, constants characteristic of each individual fraction from each crude.[1] The values of the constants for the products derived from the Pennsylvania and California crudes have been calculated by the method of least squares and are shown in Table V. The excellent agreement between experimental and calculated values is illustrated by Table VI, which includes figures for several typical fractions.

TABLE VI—AGREEMENT BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF KINEMATIC VISCOSITY OF SELECTED FRACTIONS FROM PENNSYLVANIA AND CALIFORNIA CRUDE PETROLEUM

Temperature °C.	Fraction A-150 Kinematic Viscosity Exp.	Calc.	Fraction A-275 Kinematic Viscosity Exp.	Calc.	Fraction V-225 Kinematic Viscosity Exp.	Calc.	Fraction V-300 Kinematic Viscosity Exp.	Calc.
				Pennsylvania Fractions				
0	0.0111	0.0111	0.0729	0.0771	....	....	....	....
10	0.00957	0.00970	0.0529	0.0528	0.1327	0.1386	....	....
20	0.00869	0.00862	0.0407	0.0398	0.0962	0.0956	....	....
30	0.00780	0.00777	0.0322	0.0316	0.0701	0.0708	....	....
40	0.00708	0.00708	0.0265	0.0261	0.0544	0.0543	0.2044	0.2048
50	0.00649	0.00651	0.0221	0.0220	0.0432	0.0433	0.1444	0.1433
60	0.00603	0.00602	0.0188	0.0190	0.0356	0.0353	0.1064	0.1061
80	0.00524	0.00525	0.0147	0.0147	0.0247	0.0249	0.0654	0.0651
100	0.00467	0.00467	0.0120	0.0119	0.0186	0.0186	0.0441	0.0441
				California Fractions				
0	0.01235	0.01239	0.0935	0.0972	....	....	....	....
10	0.01080	0.01076	0.0656	0.0650	0.2825	0.3030	....	....
20	0.00957	0.00955	0.0486	0.0478	0.1717	0.1700	....	....
30	0.00860	0.00858	0.0375	0.0372	0.1136	0.1111	....	....
40	0.00775	0.00779	0.0302	0.0300	0.0803	0.0791	0.8282	0.8230
50	0.00711	0.00713	0.0249	0.0249	0.0596	0.0593	0.4612	0.4651
60	0.00661	0.00658	0.0209	0.0211	0.0459	0.0163	0.2836	0.2826
80	0.00570	0.00571	0.0158	0.0158	0.0303	0.0306	0.1305	0.1306
100	0.00505	0.00505	0.0124	0.0124	0.0219	0.0218	0.0736	0.0735

It will be understood that the constants for the viscosity-temperature equation of any oil can be calculated from the experimentally determined viscosities at three suitable temperatures. The method of calculation involves the solution of three simultaneous equations, and does not require the use of the more accurate but decidedly tedious method of least squares.

Obviously, the values for the constants are useful in calculating viscosities at temperatures, within the experimental range, for which actual determinations are lacking. The reliability of such calculated viscosities can be accepted without question; but the use of the constants at temperatures considerably below or above the extremes represented by the experimental data is not to be recommended on account of a possible change in state of the oil, or a change in the viscosity-temperature relationship. While the equations would seem to offer an effective method for estimating solidification temperatures (at which the kinematic viscosity becomes infinite), it is felt that the significance of such calculations is open to question because of the fact that partial solidification so often takes place. In the authors' opinion, it is equally unjustifiable to attempt the calculation of viscosities for temperatures at which the oils have appreciable vapor pressures, and hence are changed in properties through partial distillation.

As an indication of the validity of the equations at temperatures considerably above those covered by the foregoing experimental data, two viscosity determinations were made

[1] This is in effect the Slotte equation (See A. E. Dunstan and F. B. Thole "The Viscosity of Liquids," London, 1914, 4; Schlotte, *Wied. Ann.*, 14 (1881), 13, *Beibl.* 16 (1892), 182; Thorpe and Rodger, *Phil. Trans. A.*, 185 (1894), 397, which is usually employed to indicate the relation between absolute viscosity and temperature but which the authors have found equally useful as applied to kinematic viscosity.
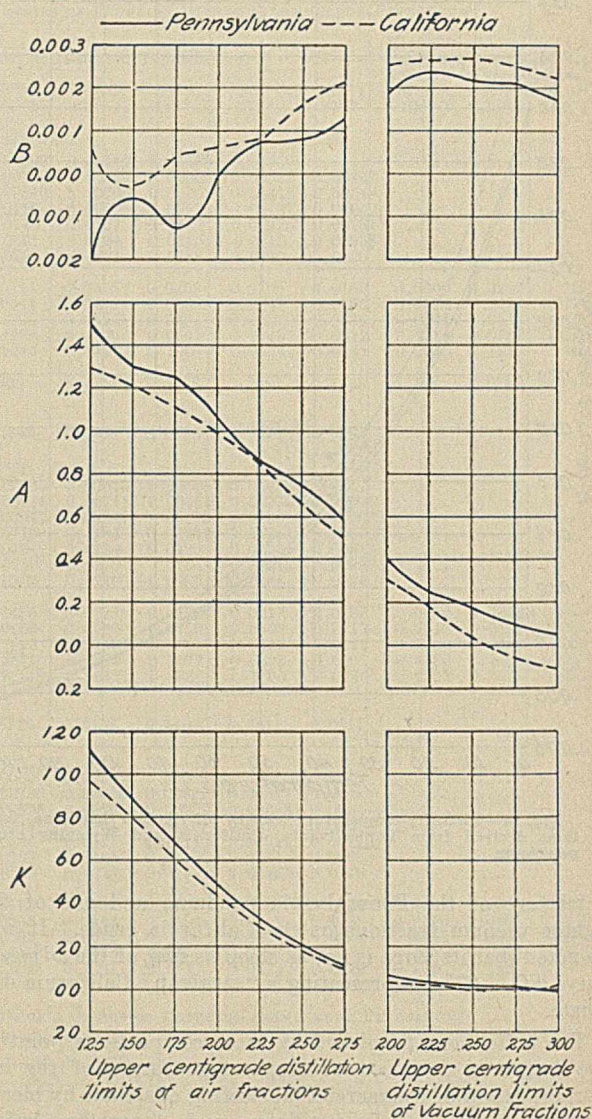
Fig. 6—Showing similarities in curves obtained by plotting against upper distillation limits the values of the constants K, A and B from the equations representing viscosity-temperature curves of the series of fractions from Pennsylvania and California crude petroleum

at approximately 180° C. (356° F.) and compared with the calculated figures based on the experimental range 40° to 100° C. (140° to 212° F.). Table VII (part A) shows the agreement to be satisfactory in both cases.

TABLE VII—CALCULATED AND EXPERIMENTAL VISCOSITY FIGURES FOR RELATIVELY HIGH TEMPERATURES

		Part A	
PRODUCT	Temperature °C.	Kinematic Viscosity Experimental	Calculated
P-R	181.7	0.0363	0.0366
C-V-300	182.5	0.0171	0.0175

	Part B		
PRODUCT	—Kinematic Viscosity at Temperature Indicated—		
	Experimental 100°C. (212°F.)	Calculated 200°C. (392°F.)	300°C. (572°F.)
P-R	0.1468	0.0295	0.0122
P-V-300	0.0441	0.0124	0.00578
C-V-300	0.0736	0.0142	0.00582

Assuming the validity of the equations for temperatures considerably above those of the experimental range, it is interesting to consider the values so calculated as indicating whether viscosity actually becomes constant at higher temperatures. Table VII (part B) shows the calculated values at 200° C. (392°F.) and 300° C. (572° F.) as compared with the experimental figures at 100° C. (212° F.). These figures seem to indicate that viscosity continues to decrease even at temperatures as high as 300° C. (572° F.).

The constants for the equations may also possess addi-

Fig. 7—Showing curves obtained by plotting Saybolt viscosities at 210°F. against aSybolt viscosities at 100°F. for the series of products obtained from Pennsylvania and California crude petroleums.

Table VIII—Comparative Saybolt Universal Viscosities at 210°F., 130°F., and 100°F. for Oils Derived from Pennsylvania and California Crude Petroleum

| A—Figures for Pennsylvania and California Oils | | | | | B—Figures for Pennsylvania Oils Only | | |
| Saybolt Viscosity at 210°F. | Saybolt Viscosity at 130°F. | | Saybolt Viscosity at 100°F. | | Saybolt Viscosity at 210°F. | Saybolt Viscosity at 130°F. | Saybolt Viscosity at 100°F. |
	Pa.	Cal.	Pa.	Cal.			
33	37	38	41	42	56	˙45	291
34	40	41	47	49	57	151	306
35	44	45	53	58	58	157	321
36	48	50	61	69	59	163	337
37	52	56	70	82	60	170	353
38	56	61	79	99	61	176	369
39	60	68	89	119	62	183	385
40	64	74	99	139	63	189	401
41	68	81	109	160	64	195	419
42	73	89	119	181	65	202	437
43	78	97	129	202	66	209	455
44	82	106	139	224	67	216	473
45	87	116	150	249	68	223	491
46	92	125	161	277	69	230	510
47	97	135	172	307	70	237	529
48	102	145	184	337	71	244	548
49	107	154	196	367	72	252	567
50	112	163	209	396	73	259	587
51	117	...	222	422	74	267	...
52	123	...	235	459	75	274	...
53	128	...	˙249	498	76	282	...
54	134	...	263	537	77	290	...
55	139	...	277	574	78	299	...
					79	307	...
					80	316	...

case any oil under consideration is known to be of the same type as either of the two crudes studied by the authors. Such a happy coincidence is, unfortunately, not likely to be a frequent occurrence, and the table is of greatest significance as indicating possibilities of variation when it is attempted to estimate viscosity at one temperature from figures determined at some other temperature. It appears, for example, that Pennsylvania and California products, having at 210° F. a viscosity of 50 sec. Saybolt Universal, have at 100° F. respective viscosities of 209 and 396 sec.

It is possible that a proper use of figures for other physical properties of oils might permit reasonably accurate interpolation between limits such as have just been indicated. The data at present available have not, however, seemed adequate to permit formulating any rule for interpolation that would be satisfactorily reliable.

Summary

1—Viscosity-temperature curves have been determined for series of products derived from samples of Pennsylvania, California, and Wyoming crude petroleum.

2—The California fractions show a greater change in viscosity with temperature (the curves are steeper) than the corresponding Pennsylvania products. Differences are most impressive for fractions of high viscosity. Viscosity-temperature curves for the Wyoming fractions show characteristics which are intermediate between those of the California and Pennsylvania curves; but they resemble the latter more closely than they do the former.

3—The viscosity-temperature curve of the undistilled residuum from the Pennsylvania crude is of the same type as the curves for the distillation fractions.

4—The viscosity-temperature curve for a mixture of Pennsylvania residuum and Pennsylvania distillate shows the same characteristics as the curves for unblended distillates. Furthermore, the curve for a mixture of Pennsylvania residuum and California distillate apparently averages the characteristics of the curves of the two constituents.

5—The viscosity-temperature curves for the Pennsylvania, Wyoming, and California kerosene fractions show the same qualitative relationships as those for the lubricating fractions.

6—Viscosity-temperature curves can be represented by an equation of the general form:

$$Vk = \frac{1}{K + At + Bt^2}$$

tional theoretical or practical significance, and the authors have under consideration several possibilities that will be investigated as soon as further experimental data are available. For the present, attention is called only to an interesting relationship indicated by the curves in Fig. 6, which were obtained by plotting values of the constants for the series of fractions from Pennsylvania and California crudes against the upper (centigrade) distillation limit for each cut. An interesting similarity will be noted in the form of the curves representing values of the constants K and A for equivalent fractions from each of the two types of crude petroleum. The similarity becomes equally striking in the curves for the constant B if, instead of adhering so closely to the plotted points as has been done in Fig. 6, more general curves are drawn.

Relation Between Saybolt Viscosities at Different Temperatures

It has already been stated that no simple general rule has been discovered which may be applied to estimate viscosity at one temperature from determinations made at some other temperature.[1] The nearest approach, of practical value, to a relationship of this order is indicated by the fact that a smooth curve may be constructed to represent the viscosities at any two selected temperatures for the series of fractions derived from any given crude. Fig. 7 illustrates this possibility and shows curves obtained by plotting Saybolt Universal viscosities at 210° F. against Saybolt Universal viscosities at 100° F. for the series of products obtained from the Pennsylvania and California crudes. Table VIII includes a series of Saybolt viscosity equivalents for the commonly used temperature points, 100° F., 130° F., and 210° F. This table may prove of practical use in

[1] The conclusions of Oelschlager ("The Viscosity of Liquids," *Z. Verein. deut. Ing.,* **62** (1918), 422, *Science Abstracts,* **21-B** (1918), 320) are obviously untenable, at least in part, in view of the experimental evidence included in the present paper. The logarithmic relationship developed by this investigator (p. 424) is undoubtedly of considerable value, but his constants are not applicable to lubricating oils from all types of crude petroleum.

Values of the three constants, K, A, and B, have been determined for the products from the Pennsylvania and California crudes. An interesting similarity in form may be noted in the curves obtained by plotting values of these constants against the upper distillation limits of the respective cuts from the two types of crude.

7—Present results have failed to indicate any reliable general method of calculating viscosity-temperature curves of oils for which less than three experimentally determined points are available.

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The Effect of Chemical Reagents on the Microstructure of Wood [1,2]

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In connection with research work on paper being carried by this laboratory for the Mead Research Company of Dayton, Ohio, it became desirable to secure an insight into the changes occurring in the structure of wood during various chemical treatments. Consequently, an investigation was undertaken, as a result of which a method was developed and made use of in carrying out such treatments. A number of reagents have been studied, and while the results here presented must be regarded as preliminary and incomplete, it is hoped that they may stimulate further work along similar lines by other investigators.

The most obvious method for studying the effects of reagents on the microstructure of wood would be to treat blocks of the wood with these reagents at the desired temperatures and pressures for specified lengths of time. The wood might then be sectioned and studied either under the microscope or by means of photomicrographs. Unfortunately, however, the mechanical difficulties of sectioning such wood are so great that, even with the most skilful technique, it is apparently impossible to make sections without altering the anatomical structure. For this reason it has been necessary to develop a new procedure, which consists essentially in first making thin sections of wood and treating these with reagents under the proper conditions.

In order that the changes produced by these chemical treatments may be comprehended, it is first desirable to note the three planes in which wood may be sectioned—a *cross* or *transverse* section is one cut perpendicular to the axis of the trunk; a *radial* section is one cut longitudinally along the radius of the trunk; a *tangential* section is one cut longitudinally, tangent to the rings of growth and therefore, perpendicular to the radius of the trunk. Figs. 1, 2, 3 are, respectively, cross, tangential, and radial sections of pine.

Cell Structure

The process of plant growth is essentially that of cell division whereby each cell in the growing region (the "cambium") is split into two daughter cells. The partition separating these cells is known as the "middle lamella" (Fig. 4). As growth continues, other walls are laid down adjacent to the middle lamella and nearer the hollow interior ("lumen") of the cell.

The complete facts connected with cell growth are extremely complicated. To the paper-maker, however, the important fact is that any chemical process for making paper should have for its primary object the separation of individual cells by dissolving out the middle lamella with as little effect as possible on the remainder of the cell wall. To be sure, another very important action is that of decomposing compound celluloses, such as lignocellulose, and thus producing a pure cellulose.

The history of the cell walls and the study of their chemical structure have been the subjects of extensive research, conducted usually, however, by men with botanical rather than chemical training. The results of these investigations[3] show that the middle lamella should be regarded as the primary partition wall, serving to bind the tracheids together; but at the same time, it must be understood that this layer has a complicated history in which it undergoes changes in form, mass and chemical composition.

Allen[1] is certain that the middle lamella differs chemically from the later walls. He believes that the first formed cellular wall consists essentially of pectin-like substances

1 C. E. Allen, *Bot. Ga ..* 32 (1901), 1.

which are plastic, and therefore undergo such changes in form as are necessary to adapt the layer readily to alterations occurring in the cells during growth. As the cells grow older, the middle lamella becomes more rigid and inflexible, until finally it assumes a hard, insoluble form. This process is believed to consist in a transformation of the pectic acid originally present into an insoluble material, probably calcium pectate.

Aside from the mineral constituents of the cell wall, the most important substances are compounds (probably of an adsorption type) of cellulose, such as lignocelluloses and pectocelluloses. Cross and Bevan[1] compare the lignocellulose structure to an alloy of a base and a noble metal, in which the more reactive base metal may be dissolved out by suitable methods, leaving the comparatively inert noble metal. In a similar way, cellulose is comparatively resistant to the action of reagents such as chlorine, alkalies, or bisulfites, all of which tend to remove the lignin groups. König and Rump,[2] after an extensive chemical and microscopic study, conclude that there are no true compounds of cellulose and other substances in the cell, but that these materials exist here intimately mixed.

Spaulding[3] has made an extensive study of cellulose and lignin in various woods. From this he concludes that, whereas cellulose and lignin are generally intimately mixed in the cell wall, yet in some woods a ring of pure cellulose lines the cell lumen. Moreover, this cellulose is found especially in those cells which do not contain starch, and Spaulding concurs with Sablon's[4] previous work on willow, in which Sablon had been led to believe that starch was converted into cellulose.

While there is considerable controversy over the subject, it seems probable that the formation of lignocellulose is a process of thickening by incrustation: colloidal, hydrated celluloses are first formed, and they then take up lignin held in colloidal solution in the sap.[5] These changes follow quite closely upon one another, since heart wood and sap wood give about the same yields of cellulose and lignocellulose.[6]

For the purpose of these considerations, it may then be assumed that the cellular structure is composed largely of intimate mixtures of loose or adsorption compounds of cellulose with lignin and pectin, and the hemicelluloses. The cell walls are largely made up of compounds of lignin and cellulose, while the middle lamella is probably composed largely of pectocelluloses and hemicelluloses.

On account of the fact that these substances are present in a colloidal condition, changes in the individual units cannot be followed by the ordinary microscopic methods. It is only where such changes are expressed in the more extensive structural alterations that the microscope is of value.

Staining with dyes which affect only certain portions of the woody structure has long been the subject of controversy, since some observers advance evidence to show that staining distinguishes mere physical changes in the degree of colloidal dispersion rather than chemical differences in the structure, while other observers take the opposite view. As a matter of fact, it is comparatively unimportant which view we adopt when staining is used in following the

changes produced by reagents on a given structure. It is not unreasonable to believe that such chemical and physical changes go hand in hand and that they are both distinguished by staining.

From all the available information it would appear that in cooking wood with various chemicals in aqueous solution, one or more of the following changes is likely to take place:

1—Hydration of the constituents, naturally accompanied by swelling.
2—Depolymerization, or an increase in the degree of colloidal dispersion, of the various woody substances.
Both of these effects are slow and progressive and both are accelerated toward complete peptization or colloidal solution of the constituents as the time, temperature or concentration of the solution is increased.
3—Actual hydrolysis of the constituents, accompanied generally by true solution.
4—Other fairly definite chemical reactions, such as chlorination, oxidation or sulfonation of constituents, followed by colloidal or true solution.

The reagents used in analytical or practical work on cellulose and lignin are naturally chosen because of a more or less selective action on one of these substances. In such cases a knowledge of the changes in microstructure which accompany these reactions should throw some light on what is taking place.

METHOD OF MAKING WOOD SECTIONS

Starting with the tree itself, small blocks of wood (1 in. $\times$ 0.5 in . $\times$0.5 in.) are cut from the portions of the trunk to be studied. These blocks are boiled vigorously in water for about an hour, or until they sink. The air is thus driven out of the tracheids and is replaced by water.

With the Thomson microtome these blocks may be cut at once; but with other microtomes it is generally necessary to soften the blocks several days in cold 50 per cent hydrofluoric acid to dissolve out mineral constituents such as silica. According to Jeffrey,[1] hydrofluoric acid does and attack the middle lamella. On the other hand, its use should be dispensed with wherever possible, as it undoubtedly hydrolyzes some constituents of the wood. (All wood sections used in these experiments were made after acid treatment.)

Following the acid treatment, the block is washed thoroughly in water and is transferred to a mixture of equal parts of ethyl alcohol and glycerol. Sections of from 20 to 40 microns in thickness are made from these blocks. Thinner sections are difficult to handle during later treatments, while thicker sections are unsatisfactory for visual purposes. These sections are transferred to 50 per cent ethyl alcohol until ready for use.

Many staining reactions for cellulose and lignocellulose are described in the literature, but the combination which has proved most satisfactory for this work is Haidenhain's hematoxylin and safranin. Hematoxylin is commonly supposed to stain cellulose deep purple, and similarly, safranin to stain lignocellulose red. Safranin withstands acid and alkaline treatments satisfactorily, but hematoxylin is acted upon by both; consequently sections may be stained with safranin before such treatments, but not with hematoxylin.

After staining with this combination, the following structures are purplish: the resin ducts, cells of the medullary rays, tori of the bordered pits, and in some instances a thin layer of the cell wall next the lumen. The middle lamella is deep red, while the remainder of the cell wall is of a lighter red color. There is also a marked difference in the refractive indices of these structures.

1 "Wood Pulp and Its Uses," 1911, 30.
2 *Nahr. Genussm.*, **28** (1914), 4.
3 Missouri Botanical Garden, *Report* 1906, 41.
4 *Rev. Gen. Bot.*, **16** (1904), 362.
5 Wislicenus, *Wochbl. Ppierfab*, **41** (1910), 803.
6 Statement, Forest Products Laboratory.

1 "Anatomy of Woody Plants," 1917, 447.
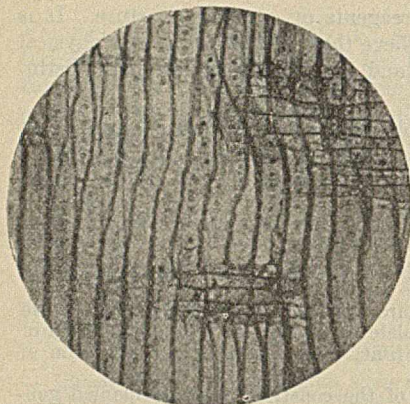
Fig. 1—Cross section of pine, 76, showing tracheids (cells or "fibers") of spring and summer growth, resin duct, and medullarly rays (heavy black lines)
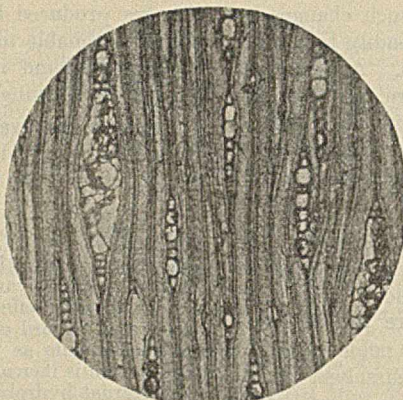
Fig. 2—Tangential section of pine, 76, showing tracheids ("fibers") and medullary rays (the latter in cross section)
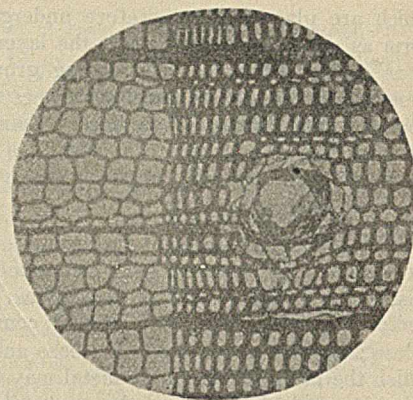
Fig. 3—Radial section of pine, 76, showing medullary rays and tracheids ("fibers") dotted with circular "bordered pits"
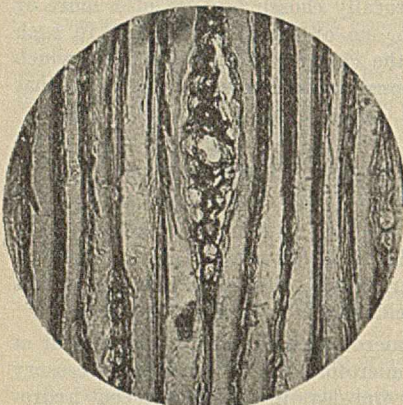
Fig. 4—Cross section of pine, 435, showing tracheids ("fibers") of spring wood; (1) "lumen" or hollow interior of cell, (2) "middle lamella" or primary cell wall, (3) later growth of cell wall
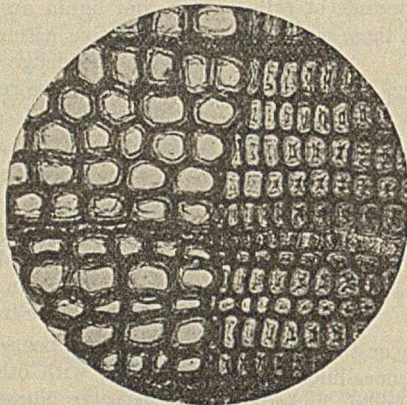
Fig. 5—Cross section of pine, 156, treated with 12N hydrochloric acid for 28 hrs. at 250 C.
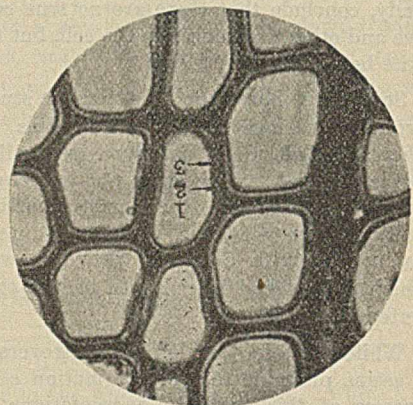
Fig. 6—Tangential section of pine, 156, threated with 12N hydrochloric acid for 28 hrs. at 250 C.

CHEMICAL TREATMENT OF SECTIONS

The sections were placed in the depressions of a microscope cell slide. The cells of the slide were filled with the reagent to be studied, and a plain microscope slide was laid over the cell slide, but separated from it about 0.1 mm. by pieces of thin cover glass. The two slides were wired together and were placed in an autoclave containing a considerable quantity of the reagent. In those cases, where the reagent attacks iron considerably (e. g., sodium bisulfite solution), the slides were sealed into glass tubes with the reagent. The tube containing the slide was then placed in the autoclave and was surrounded with water as the heating liquor.

This method allowed access of the reagent to the section and yet prevented destructive mechanical action. In order to follow the course of the treatment, several slides were introduced into the autoclave simultaneously. The autoclave was bolted shut and heated over a gas flame for various lengths of time at predetermined temperatures and pressures, measured respectively by a thermometer in a well and by a steam gage.

At stated intervals the autoclave was removed from the flame, cooled quickly and opened, and a slide was removed. The autoclave was again closed and heated for another interval of time.

The treated sections were washed carefully to remove adhering liquor and dirt. They were then stained and mounted in balsam for microscopic examination and measurement. Photomicrographs of these sections were made with a metallurgical microscope and camera arranged for use with transmitted light.

In some cases sections took the stains so poorly after treatment, or were so badly decomposed, that satisfactory photographs could not be obtained, although visual observations were reasonably satisfactory. Misleading optical effects due to unsatisfactory lighting sometimes occur, and must always be guarded against. In this investigation observations and measurements were made directly on the sections rather than on photomicrographs.

Measurements have been made on the cell wall, the middle lamella, and the lumen of five representative cells in both the spring and summer wood of each section. These measurements were made in a radial direction and by the use of a filar micrometer. Averages of the five readings were taken and compiled for study. While these results serve to interpret the action of various reagents, they are not sufficiently comprehensive to be taken as quantitative Measurements of the middle lamella are considerably less accurate than the others because of the comparatively slight breadth of this structure.

The effects of various reagents have been studied under different conditions of concentration, time of heating, temperature and pressure.

It must be borne in mind that the results of such experimental treatments, especially as far as the rate of action
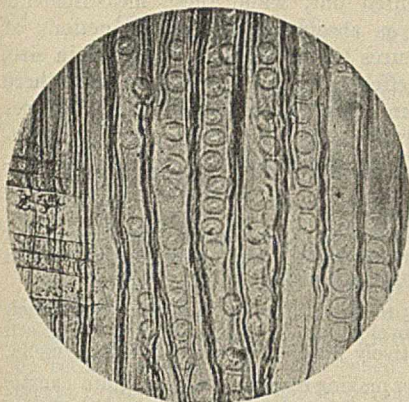
Fig. 7

Fig. 7—Radial section of pine, 156, treated with 12N hydrochloric acid for 28 hrs, at 250 C.
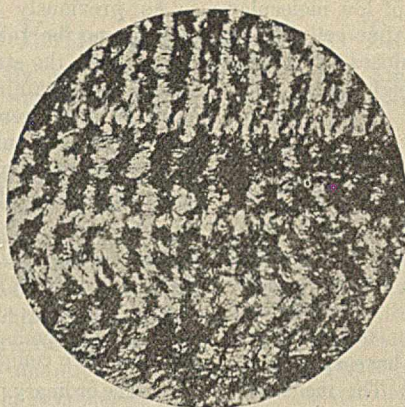
Fig. 8

Fig. 8—Cross section of pine, 156, treated with 50 per cent chromic acid for 1 min. at 250 C.
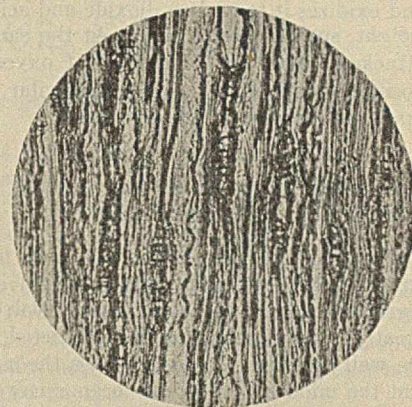
Fig. 9

Fig. 9—Tangential section of pine, 156, treated with 50 per cent chromic acid for 1 min. at 250 C.
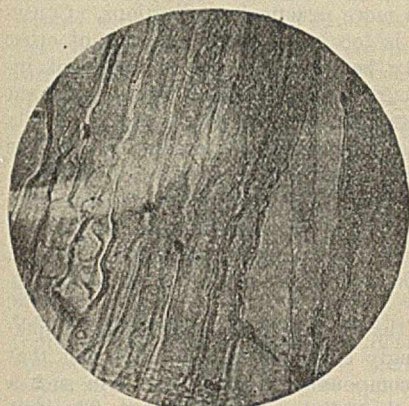
Fig. 10

Fig. 10—Radial section of pine, 156 treated with 50 per cent chromic acid for 1 min. at 250 C.
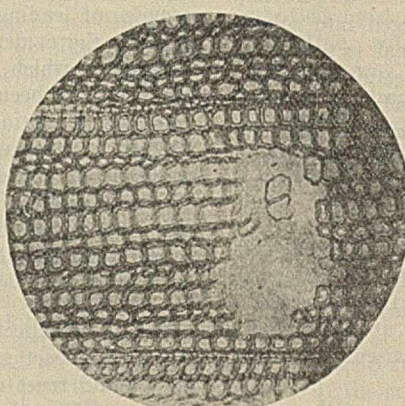
Fig. 11

Fig. 11—Cross section of pine, 90, treated with 4 per cent caustic soda solution for 8 hrs. at 1500 C .
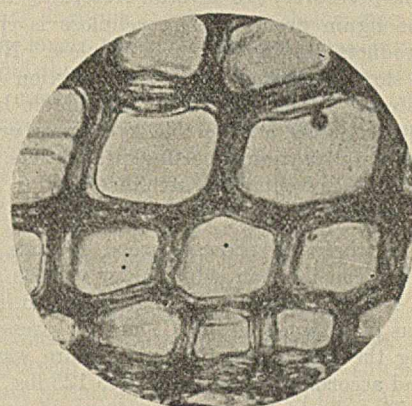
Fig. 12

Fig. 12—Cross section of pine, 465, treated with 4 per cent caustic soda solution for 8 hrs. at 1500 C.

is concerned, cannot be applied directly to large-scale treatments because of the differences in such factors as penetration and quantites of material involved.

The heart wood of *Pinus Virginiana* (Jersey Pine; scrub pine) was generally used for study. The following reagents have been used in these treatments:

Distilled water	Mangin's reagent (ethyl alcohol, 4 conc. HCl, 1)
Copper ammonium reagent	
10 per cent sodium chloride	50 per cent chromic acid
72 per cent sulfuric acid	Lime bleach
Concentrated hydrochloric acid	1.0 N caustic soda solution
Phenol	12.0 N caustic soda solution
Concentrated nitric acid plus potassium chlorate	10 per cent sodium bisulfite
	Saturated sodium bisulfite
	Saturated sulfurous acid
	10 per cent sodium sulfide

DISCUSSION OF PHOTOMICROGRAPHS

In all, about seventy sections have been made and examined. Photomicrographs have also been made of many of these sections. A detailed description of these results would obviously be out of place here; hence the discussion will be confined primarily to the following treatments as typical of the results which may be obtained by this method:

Untreated sections.
Concentrated (12 N) hydrochloric acid—a cellulose solvent.
50 per cent chromic acid—a strong, oxidizing agent.
1.0 caustic soda—a paper-making reagent.

UNTREATED SECTIONS (Figs. 1, 2, 3, 4)—The cross section shows the dividing line between spring and summer growth, the well-marked medullary rays, and a longitudinal resin duct, surrounded by epithelial tissue. The middle lamella

and bordered pits are brought out more clearly in Fig. 4.

Figs. 2 and 3 show the well-defined, overlapping tracheids (or "fibers") having the radial walls dotted with bordered pits; the numerous medullary rays and their storage contents.

CONCENTRATED HYDROCHLORIC ACID TREATMENT (Figs. 5, 6, 7)—The action of concentrated hydrochloric acid is to dissolve cellulose, probably in a more or less depolymerized and esterified form. On standing, particularly when diluted, the action on the dissolved material is largely one of hydrolsyis, with dextrose as the principal product. The lignin of coniferous wood is for the most part undissolved by this treatment, although the residue from treatments by such solvents is thought by Dore[1] to be dehydrated form of the original lignin.

In these experiments sections of wood were allowed to stand in concentrated hydrochloric acid at room temperature for 28 hrs. They were washed thoroughly and stained.

The effects of the treatment are pronounced. The cell walls are greatly swollen, particularly in the summer wood, where they have filled the lumen; the walls bulge in the middle, but are constricted at the corners. In places the cells have split away from the middle lamella, but the middle lamella itself is apparently unchanged. The medullary rays have withstood the treatment, except that some of the central cells have been removed.

FIFTY PER CENT CHROMIC ACID TREATMENT (Figs. 8, 9, 10) —Chromic acid attacks the lignin complex of lignocellulose

[1] THIS JOURNAL, 11 (1919), 556.

and oxidizes it to carbon dioxide and acids of low molecular weight, such as acetic acid.[1] At the same time cellulose is attacked,[2] with the formation of oxycelluloses or decomposition products of lower molecular weight, depending upon the severity of the treatment.

In these experiments wood sections were treated for 1 min. in 50 per cent chromic acid at room temperature, washed thoroughly, and stained.

The action in these sections is very marked. The entire structure has evidently been attacked and partially disintegrated even in the short time involved. Cell walls are greatly swollen, the corners restricted, but the center of the wall bulging. In some places the cells have split apart and the middle lamella has been removed. The medullary rays persist, but have been distinctly attacked by the acid.

1.0 N CAUSTIC SODA TREATMENT (Figs. 11, 12)—The reactions of dilute caustic soda on wood, at high temperatures and pressures, are several. According to Cross and Bevan,[3] the lignin group of lignocellulose is changed into soluble products, leaving insoluble cellulose. Normal (α) cellulose is slowly attacked, but a small portion (β-cellulose) is dissolved. Pectocelluloses of the middle lamella are resolved into cellulose and soluble hydrolysis products of the noncellulose portion (pectin, pectic acid, metapectic acid), while hemicelluloses are dissolved even by cold dilute alkalies.

In these experiments wood sections were treated with 1.0 N caustic soda solution for various lengths of time (2, 3, 4, 6, 8, 11 hrs.). During the first 8 hrs. the temperature was maintained at 150°C. and the pressure at 65 lbs.; during the last 3 hrs. the temperature was raised to 180°C., and accordingly the pressure to 125 lbs.

The effects of the early stages of cooking on these sections will not be described as they appear more markedly in the sections treated for a longer time.

During the cooking, the cell walls swell considerably and striations appear. The resin ducts are attacked in the early stages, while the rays are acted upon gradually, and as in most other treatments retain their form after the other structures have been attacked.

The middle lamella gradually dissolves and, at the same time, splits away from the cell wall in some places. With the exception of the thickened intercellular substance at the corners of the cells (which substance persists even through the most drastic treatment), a clean channeling away of the middle lamella occurs, and consequently the tracheids are separated one from another. In the later stages of treatment the sections are badly decomposed and fall apart readily.

Discussion of Treatments

One method of studying the effects produced by these reagents is by a comparison of the measurements made on treated and untreated cells. While swelling or absence of swelling in such structures does not necessarily measure the extent of the reactions which are taking place, yet they serve to indicate the comparative effects of reagents on different portions of the structure. If, for example, a sponge were thoroughly impregnated with rubber, benzene would swell and eventually dissolve out the rubber and not affect the structure of the sponge; on the other hand, water would swell the sponge but have no effect on the rubber.

1 Cross and Bevan, "Paper Making," 1916. 42.
2 Tromp. deHaas and Tollens, Ann., 286 (1895), 296.
3 "Paper Making," 1916. 60.

As previously pointed out, while these measurements should not be taken as absolute, the selective actions of reagents on the structures (as evidenced by changes in size, shape, and staining effects) indicate definitely that there must be a difference in composition between the structures which, for the purposes of this discussion, may be distinguished as the "middle lamella" and "cell wall." Furthermore, they show that:

1—Cellulose solvents (such as copper ammonium reagent and 72 per cent sulfuric acid) act strongly and about equally on both the middle lamella and the cell wall.

2—Strongly oxidizing solutions (such as chromic acid, bleach solutions and potassium chlorate in nitric acid) act on the cell wall but have comparatively little effect on the middle lamella.

3—The ordinary paper making reagents (such as dilute caustic soda and sodium bisulfite solutions) act strongly on the middle lamella and, relatively, have very much less effect on the cell wall.

Unfortunately it has been necessary to discontinue this investigation, at least temporarily, at a time when it gave promise of leading to more practical applications. Consequently, the evidence is too incomplete to permit of other deductions which may be allowable when additional information has been secured. For example, it is a significant fact that the ratio between the thickness of middle lamella and cell wall remains constant during treatment by cellulose solvents but varies greatly with other classes of reagents. This may argue for similarity in the amounts of cellulose in these structures, but for the presence in the cell wall of larger quantities of readily oxidizable substances than in the middle lamella.

It is to be expected that the chemicals used in paper making would react strongly on the middle lamella, but that they would react on compounds of the cell wall in such a manner as to attack the cellulose but slightly. The fact that this method brings out the evidence clearly is of great interest, because it points out the way for a systematic study of reagents which might be used in paper making.

During the progress of this work it has become increasingly evident that it would be desirable to separate the middle lamella and various portions of the cell wall, and to submit them individually to chemical analysis. This would clear up many uncertainties with regard to the structure of wood. Unfortunately, however, the individual units are so small that mechanical separation is out of the question.

The most promising method now in sight is the use of microörganisms which act only on certain parts of the cell structure. By the use of pure cultures it might be possible to treat thin sections of wood and then analyze the residual constituents. Microscopic studies should be of great assistance in such investigations, and it is not unlikely that such an investigation may open up the way for fundamentally different methods of making paper. Certainly it is becoming increasingly apparent that basic improvements in this industry can be realized only by some such a comprehensive study.

Summary

A new procedure has been developed whereby the action of chemical reagents on the microstructure of wood may be followed readily either by the microscope or by photomicrographs. This method has been used in investigating the effects of various electrolytes on pine wood. A number of typical treatments are described and discussed. The results have been studied with the microscope, photomicrographs, and by measurements with a filar micrometer.

The Detection and Estimation of Coal-Tar Oils in Turpentine[1]

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The detection of small quantities of coal-tar oils, such as toluene, xylene, and commercial solvent naphtha, in turpentine, and the estimation of the quantity of such adulterants present are considerably more difficult than the detection and estimation of mineral oil adulterants.

Marcusson[2] and Krieger[3] have published methods for such analyses, but these have not, in the hands of the authors, when followed most carefully, given concordant or reliable results, especially when the quantity of adulterant present was less than 10 per cent, as is frequently the case when coal-tar oils are used to adulterate turpentine fraudulently. Authentic pure gum turpentines have given results when treated according to the above methods which indicated adulteration, and samples of turpentine adulterated with as much as 2.5 and 5 per cent of solvent naphtha gave results quite similar to those obtained on pure turpentine. A brief outline of the methods referred to above may not be out of place.

Marcusson adds 10 cc. of the turpentine, drop by drop, to 30 cc. of fuming nitric acid which has previously been cooled to —10° C. by placing the flask in a freezing mixture to prevent explosion or ignition of the mixture, as the reaction is extremely violent. After standing at room temperature for about 15 min., 75 cc. of ordinary concentrated nitric acid are added, and the mixture is poured into 150 cc. of water in a flask having a narrow, graduated neck and allowed to stand on the steam bath for 15 min. The insoluble nitration product, which settles to the bottom, is then floated into the neck of the flask by adding concentrated sulfuric acid to increase the density of the liquid. The volume of the nitration product, multiplied by an empirical factor, represents the quantity of coal-tar oil present in the turpentine. Pure turpentine, according to the author, yields nitration products which go into solution in the water almost completely when heated on the steam bath, leaving only a negligibly small quantity of light resinous residue, which cannot be confounded with the heavy oily liquid nitration product obtained from the coal-tar oils.

These results are at variance with our observations. We have repeatedly obtained a considerable quantity of a viscous, gummy nitration residue from pure gum turpentine, which was insoluble in hot water, and the residues obtained in the case of authentic turpentine adulterated with commercial solvent naphtha to the extent of 3, 5, and 10 per cent, respectively, were all of very nearly the same volume as that obtained from pure turpentine, the only difference being a diminution of viscosity as the percentage of adulterant present increased. The 10 per cent residue was not free-flowing, and could not be called liquid.

Krieger shakes 20 cc. of the turpentine with 100 cc. of diluted sulfuric acid (4: 1, sp. gr. 1.76) in a flask, dilutes with 200 cc. of water, and distils with steam. This is repeated, and the oily portion of the final distillate, which is supposed to represent total aromatic and paraffin hydrocarbons, is treated with 10 to 15 cc. of fuming sulfuric acid containing 8 per cent free SO_3, to sulfonate the benzene hydrocarbons. The oily portion of the final distillate, which is supposed to which separates is considered as mineral oil, and the difference between the volume of this oil and the volume of the oily distillate obtained by the last steam distillation is calculated as benzene or coal-tar hydrocarbons.

As shown by Veitch and Donk,[4] it requires a fuming sulfuric acid, containing approximately 4 per cent free SO_3, in the proportion of 4 parts acid to 1 part turpentine, to-

gether with heating and frequent agitation at 60° to 65° C. for 10 min. to polymerize pure turpentine completely. Even then, on addition of ordinary concentrated sulfuric acid and steam distillation of the mixture, a small percentage (below 5 per cent) of a dark volatile oil with unpleasant odor, is often recovered, having a refractive index above 1.500. It is thus evident that turpentine cannot be completely polymerized by Krieger's method, and that the steam distillate will contain more or less terpene hydrocarbons. Such was found to be the case.

In order to be able to detect with certainty small percentages of coal tar oils, *i. e.*, 1 or 2 per cent, it was deemed necessary first to concentrate these oils from a large volume of sample. Fractionation was not feasible, as most solvent naphthas have initial distilling temperatures below that of turpentine, with a much wider distillation temperature range. It was found that the reaction between turpentine and dry hydrogen chloride gas offered a solution to this phase of the problem. The pinene hydrochloride crystallizes out on standing in the cold, and the non-crystallizable products have much higher boiling points, while both coal-tar oil and mineral oil are unaffected. On filtering off the crystalline pinene hydrochloride and distilling the filtrate under reduced pressure, the coal-tar oils are all concentrated in the first portions of the distillate.

By sulfonating this distillate with fuming sulfuric acid, the terpenes are polymerized into soluble, nonvolatile bodies, and the benzene hydrocarbons are converted into sulfonic acids. If the mixture is then subjected to steam distillation, a very small percentage of volatile oil, having a dark yellow color, disagreeable odor, and a refractive index at 20° C. slightly above 1.500, is recovered in the case of pure turpentine. If any mineral oil is present, it is recovered at this stage as a limpid, almost colorless oil, having the characteristic mineral oil odor and a refractive index below 1.500, usually below 1.480. Pure toluene, xylene, and solvent naphtha give no oily distillate when the sulfonation mixture is steam distilled. The coal-tar oils which are recovered, after the steam distillation no longer give any oily distillate, by the reaction first pointed out by Armstrong and Miller,[1] who showed that if the sulfonic acids of the benzene hydrocarbons, dissolved in an excess of sulfuric acid, are heated in the presence of steam to temperatures above 100° C., depending on the hydrocarbon derivative used, decomposition takes place with liberation of the free hydrocarbon. The operation is carried out by adding water, drop by drop, to the boiling acid mixture. The oils recovered in this step have always had practically the same odor and refractive index as the original coal-tar oil used as the adulterant. The recovery of any appreciable quantity of oil at this stage is an indication of the presence of coal-tar oils in the turpentine under examination.

The results obtained by the proposed method are given in Table I. It will be noted from this table that traces of oil are usually recovered in the case of pure gum turpentine. However, the small quantity of such oil recovered from pure turpentine, its odor, and the resinous gummy product obtained upon nitration, as outlined more fully below, serve to distinguish between this oil and that obtained when even small quantities of coal-tar oils are present.

It was impossible to recover the theoretical quantity of coal-tar oil which was added to the turpentine in the ex-

[1] Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *Chem.-Ztg.*, 36 (1912), 413, 421.

[3] *Ibid.*, 40 (1916), 972; *J. Soc. Chem. Ind.*, 35 (1916), 746a.

[4] U. S. Bureau of Chemistry. Circular 85.

[1] *J. Chem. Soc.*, 45 (1884), 150.

TABLE I—RESULTS OBTAINED ON KNOWN MIXTURES OF GUM TURPENTINES AND COAL-TAR OILS

Sample No.	Nature of Sample	Adulterant Present		Recovered on Steam Distillation Cc.	Recovered on Direct Distillation Cc.	Proportion of Total Coal-Tar Adulterant Recovered Per cent
		Per cent	Kind	Trace	Trace	
1	Pure turpentine, No. 1	None	Solv. naphtha, 1	0.2	2.2	44
2	No. 1, adulterated	5	" " 2	0.2	2.0	44.4
3	" "	4.5	" " 2	0.25	2.0	50
4	" "	10	" " 3	0.2	1.25	50
5	" "	2.5	" " 3	0.25	0.2	...
6	Pure turpentine, No. 2	None	" " 3	0.35	3.2	40
7	No. 2, adulterated	8	Mineral spirits	7.5	0.2	...
8	" "	10		0.3	0.2	...
9	Pure turpentine, No. 3	None	C. P. xylene	0.3	5.5	55
10	No. 3, adulterated	10	C. P toluene	0.3	0.9	41
11	" "	2		0.3	Trace	...
12	Pure turpentine, No. 4	None	Solv. naphtha, 1	0.3	0.8	40
13	No. 4, adulterated	2	C. P xylene	0.2	0.8	40
14	" "	2	Solv. naphtha, 2	4.0	2.2	44
15	" "	5	Mineral spirits,			
16	" "	5				Mean, 44.8
						Factor, 2.2

periments. Hydrolysis of the sulfonic acids takes place very slowly at the temperature of initial hydrolysis, and requires a constantly rising temperature to bring about anything approaching a complete recovery of the hydrocarbons in a reasonable length of time. The reaction being a reversible one, it was found that the recovery of the hydrocarbons was better, the more rapidly the operation was carried out. However, when the temperature of the acid mixture rose to about 170° C., frothing set in, due to the resinous and carbonaceous matter formed by the action of the sulfuric acid on the terpene compounds. When the frothing became excessive, it was necessary to discontinue the distillation. The use of paraffin to prevent frothing did not prove feasible, since some of it was carried over into the distillate, introducing a corresponding error in the results. An empirical factor of 2.2, by which to multiply the quantity of oil recovered to show the true quantity present, was determined by experiment, as shown in Table I. One hundred-cc. samples were used in each experiment.

RECOMMENDED PROCEDURE

Place 100 cc. of the turpentine in a wide-mouth, 8-oz. bottle fitted with a 2-hole stopper carrying glass tubes arranged as in a gas-washing bottle. Allow to stand in a mixture of ice and salt for a short time, and then pass into the turpentine a gentle stream of hydrogen chloride gas, dried by passing through two gas-washing bottles containing concentrated sulfuric acid. A sufficient quantity of gas may be conveniently generated by gently warming 100 g. of common salt with 100 cc. of sulfuric acid made up by diluting 85 to 90 cc. of the concentrated acid. The acid is added to the salt from a dropping funnel in portions of about 20 cc. during the course of the absorption. A 3-way stopcock is placed between the generator and the first wash bottle, so that when the absorption of HCl by the turpentine is complete, the gas still being generated can be diverted readily into a bottle containing sodium hydroxide solution. The tube should not extend into the solution but just into the neck of the bottle. An ordinary 2-way stopcock is also placed between the second wash bottle and the absorption bottle, so that the former may be closed from the air while not in use. An exit tube from the absorption bottle leads into the neck of a bottle containing a little water. When the absorption of gas is complete, the excess passes on through the turpentine into this bottle, and can be seen dissolving in the water.

After the absorption is complete, disconnect the absorption bottle and allow to stand, corked, in a freezing mixture for about an hour, to obtain maximum crystallization of the pinene hydrochloride. This compound is very soluble in both mineral and coal-tar oils, so that with increasing percentages of adulteration the quantity of crystals formed becomes smaller, and scarcely any are formed at 10 per cent

adulteration. Filter off the crystals on a small Hirsch funnel, with suction, and distil the filtrate under a reduced pressure equivalent to 10 in. of mercury, until crystals separate out in the condenser (which indicates complete distillation of the oils) or until 25 cc. of distillate are obtained. If the quantity of adulterant is quite large, *i.e.*, 10 per cent or more, as shown by the odor of the original sample, it will be well to collect a second 25-cc. portion of distillate and treat in the same way as the first, adding the results together. Add the distillate slowly with occasional shaking, to four times its volume of fuming sulfuric acid containing 3 to 4 per cent free SO_3, in an Erlenmeyer flask, keeping cool by holding under the water tap. Acid of 4 per cent free SO_3 content is that regularly used for testing turpentine for mineral oil, and contains 82.38 per cent total SO_3, equivalent to 100.92 per cent total H_2SO_4.[1] After the distillate has all been added to the acid, the flask is heated on the steam bath at about 70° C., for about 20 min., with frequent thorough shaking, in order to sulfonate the oils completely.

It was found that pinene hydrochloride is not readily sulfonated, and after cooling the sulfonation mixture, crystals will sometimes appear, especially when the turpentine is pure or only slightly adulterated. If the quantity is appreciable, it is advantageous to filter off these crystals on a small Hirsch funnel before proceeding. No filtering medium is needed. Dilute the sulfonation mixture cautiously with an equal volume of cold water and pass steam through it, collecting the distillate. In the case of pure turpentine, only a very small quantity (not over 0.5 cc.) of a disagreeably smelling, yellow, and rapidly darkening oil is recovered, having a refractive index at 20° C. above 1.500. If mineral oil is present, it is recovered at this point, and can be identified by its characteristic odor and refractive index, which is usually below 1.400.

When oil ceases to come over with the steam, disconnect the steam line and distil with direct heat, fitting the cork of the flask with a dropping funnel and a thermometer which extends into the liquid. After the mixture starts to boil, and when the condensate starts to show an oily portion, allow warm water to flow from the dropping funnel down the side of the flask, at a slightly slower rate than that at which it is being distilled off, to obtain a gradually increasing boiling temperature. Run the distillation at the rate of about 3 drops per sec., or about 7 to 8 cc. per min. In the case of adulteration with solvent naphtha hydrolysis starts at about 115° C. Discontinue the distillation when frothing becomes excessive, to prevent contamination of the distillate with the acid mixture. Note the quantity of oil recovered and multiply by the factor 2.2. The result will be the percentage of coal-tar oil present in the turpentine.

[1] A convenient method for preparing this acid is described in U. S. Department of Agriculture, *Bulletin* 898.

If the oil recovered is less than 0.5 cc., it may be neglected, as the quantity of adulterant, if any, is probably less than 1 per cent.

Further to identify the oil as consisting of benzene hydrocarbons, nitrate a little of it by dropping cautiously into three times its volume of fuming nitric acid, previously cooled in ice water. After warming slightly and standing aside until the action ceases, pour the mixture into cold water. A heavy, yellow to light brown, aromatic smelling oil separates out which, after washing away the excess acid, has a refractive index between 1.550 and 1.555 at 20° C. The odor is characteristic of nitrobenzene and its homologs. To carry the test still further, it may be reduced with a little zinc and hydrochloric acid, and, after neutralizing with sodium hydroxide, the amines may be recovered by steam distillation and extraction of the distillate with ether. Evaporate off the ether, acidifying with hydrochloric acid, diazotize with sodium nitrite solution, and after neutralizing with a little sodium hydroxide solution, convert into a bright scarlet azo dye by adding a few cc. of a solution of the dye intermediate known as F-acid, 2,7-β-naphtholsulfonic acid. A piece of washed wool boiled in the solution after making slightly acid with acetic acid will be dyed a bright scarlet, fast to light. Other intermediates of the general nature of F-acid may be used, if the latter is not available, but F-acid gives the brightest solution.

Wood turpentines, both steam and destructively distilled, do not give reliable results when tested by the above procedure, probably because the high temperatures to which the wood and the resinous constituents thereof are exposed in present methods of manufacture partly break down the terpenes and resins to simple ring hydrocarbons. Both toluene[1] and *m*-isopropyltoluene, or *m*-isocymene [2] have been identified in rosin spirits, the low-boiling fraction from the destructive distillation of rosin. The destructively distilled wood turpentines, as was to be expected, gave considerably higher yields of oil from the distillation of the sulfonation mixture than the steam distilled wood turpentines. The wood in the steam distillation process, being treated with superheated steam, is not subjected to such high temperatures as to decompose the rosin materially, as in the destructive distillation process. This is being studied further.

Summary

A method has been devised for detecting and estimating the percentage of coal-tar oils in gum turpentine adulterated therewith. The method will also serve to detect the presence of mineral oils if any be present.

As a result of certain causes not fully understood, the recovery of coal-tar oils is, on the average, about 45 per cent of the theoretical, requiring that the quantity of oil recovered be multiplied by the factor 2.2.

In order to obtain concordant results, the strength of the sulfuric acid used to decompose the turpentine must be definite, varying between 3 and 4 per cent free SO_3.

A method for further identifying the oils obtained in the last step of the analysis has also been described.

The method is not strictly applicable to wood turpentine, because small quantities of the coal-tar oils are often found as normal constituents of this kind of turpentine. However, any considerable recovery of oil from the sulfonation mixture, *i.e.*, 4 per cent or more, even in the case of destructively distilled wood turpentine, will serve to throw suspicion on the purity of the turpentine.

A Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose[1]

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One of the most interesting sugars from a chemical and analytical standpoint is the trisaccharide, raffinose. This sugar, first indicated by Johnston[2] in *Eucalyptus manna* in 1843, was afterwards investigated in 1856 by Berthelot,[3] who gave it the name melitose. In 1876 Loiseau[4] discovered in the impure molasses of a beet-sugar refinery an unknown high polarizing sugar to which he gave, from the place of its occurrence, the name raffinose. In 1884 Böhm[5] announced the discovery in cottonseeds of a new sugar to which he gave the name gossypose. Tollens[6] in 1886 proved melitose and gossypose to be identical with Loiseau's raffinose. This identification was important, for it established the wide occurrence of raffinose in the vegetable kingdom. The sugar has been found also in young wheat sprouts, in barley, and in other plant substances; careful investigation would no doubt show it to be widely distributed.

Raffinose is almost always associated in nature with sucrose, and the importance of devising a method for estimating these two sugars when they occur together was quickly recognized, especially in the analysis of beet sugars, where the presence of only a slight amount of raffinose may cause the polarization of a sugar to exceed 100.

Owing to the fact that raffinose is hydrolyzed by the ordinary methods of acid inversion and undergoes a decrease in polarizing power, the customary Clerget method for determining sucrose was found to be no longer applicable to sucrose-raffinose mixtures. Creydt,[3] however, found that when a separate formula for estimating raffinose is united with the familiar Clerget formula, a combined equation can be derived which permits the estimation of the two sugars with a fair degree of accuracy.

With the later substitution of the Herzfeld modification in place of the old Clerget process of inversion, the Creydt formulas for estimating sucrose and raffinose were revised in order to conform to the new conditions. These revised formulas, as given by Herzfeld,[4] are

$$S = \frac{0.5124\,P - P'}{0.839} \quad \text{and} \quad R = \frac{0.3266\,P + P'}{1.554}$$

in which S and R are respectively the percentages of sucrose and raffinose, and P and P', respectively, the direct and invert polarizations at 20°C.

[1] Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] *J. prakt. Chem.*, [1] 29 (1843), 485.

[3] *Ann. Chim.*, [3] 46 (1856), 66.

[4] *Compt. rend.*, 82 (1876), 1058.

[5] *J. prakt. Chem.*, [2] 30 (1884), 37.

[6] *Ann.*, 232 (1886), 169.

1 Pelletier and Walter, *Ann. chim. phys.*, [2], 67 (——), 278; Kelbe, *Ann.*, 210 (1881), 14.

2 Kelbe, *Loc. cit.*

3 *Z. Ver. deut. Zuckerind.*, 37 (1887), 153.

4 *Z. Ver. deut. Zuckerind.*, 40 (1890), 194.

Purpose of Investigation

Previous to 1910 considerable doubt began to be expressed among chemists as to the accuracy of the Herzfeld divisor 142.66 in the Clerget formula, and in 1912 a committee was appointed by the International Commission for Uniform Methods of Sugar Analysis to determine the exact value of this factor. The outbreak of the war prevented the International Commission from meeting again, and for general purposes the Herzfeld divisor 142.66 still continues in common use. Langguth-Steuerwald[1] in 1913 determined the Clerget divisor for Herzfeld's process of inversion to be 143.05. Schrefeld,[2] in a posthumous paper published in September 1920, of a research conducted in Herzfeld's laboratory in 1910, found the Clerget divisor to be exactly 143, and stated that the erroneous value 142.66 was probably due to its having been established for a preparation of sucrose that contained raffinose as an impurity. The writers of the present paper also find a value of 143, which corresponds to a Clerget divisor of 133 with a negative constituent of —33 at 20°C., when following the process of inversion recommended by Schrefeld. This correction in the inversion constant for pure sucrose obviously necessitates another revision of the modified Creydt formulas for analyzing mixtures of raffinose and sucrose, and this was one of the purposes which the writers had in mind when beginning the present investigation.

A second purpose in connection with this research was the redetermination of the inversion constant of pure raffinose. For this purpose two preparations of chemically pure raffinose were used, one of foreign and the other of domestic manufacture. The foreign product, manufactured by Kahlbaum, consisted of fine white crystals of raffinose hydrate, which on drying in a vacuum, first at 70°C. and afterwards at 100°C., lost 15.18 per cent water; the theoretical loss for $C_{18}H_{32}O_{16}.5H_2O$ is 15.16 per cent water. The crystals of the hydrate dissolved in water to a perfectly colorless solution and gave a specific rotation upon a quartz wedge saccharimeter corresponding to $[\alpha]_{D}^{20°} = +104.42$. The average value for the specific rotation of raffinose hydrate according to Landolt, Tollens, Lippmann, and other authorities is $[\alpha]_{D}^{20°} = +104.5$.

The raffinose of domestic manufacture was a preparation of the anhydrous sugar, which, either from imperfect dehydration or from reabsorption of atmospheric moisture, contained considerable raffinose hydrate. The product gave a specific rotation upon the saccharimeter corresponding to $[\alpha]_{D}^{20°} = +119.8$, which would correspond to a mixture of about 82 per cent anhydride and 18 per cent hydrate. It lost upon drying in vacuo over sulfuric acid, first at 60°C. and then at 95°C., 2.71 per cent moisture. The specific rotation when corrected for this amount of moisture, is $[\alpha]_{D}^{20°} = +123.14$, which agrees very closely with the generally accepted value of +123.2.

Determination of Inversion Coefficient of Raffinose

For determining the inversion coefficient of raffinose, the process recommended by Schrefeld for the inversion of sucrose was followed. Several solutions of different concentration were polarized at exactly 20°C., 50 cc. of these solutions were measured into 100-cc. flasks, water was added to bring the total amount of water in each flask to 75 cc., 5 cc. of HCl (sp. gr. 1.19) were added, and the flasks were immersed in a large water bath kept at exactly 70°C. A thermometer was placed in each flask, which was gently rotated. In about 3 min. the temperature of the

solutions in the flasks reached 67°C., from which point the heating was continued exactly 5 min. longer. The temperature at the end of the heating was 69.5°C. The flasks were quickly cooled, and after rinsing off the thermometers the solutions were made up to 100 cc. at 20°C., mixed, and polarized at this temperature in a quartz wedge saccharimeter, using a 400-mm. tube. The results obtained with six solutions of raffinose are recorded in Table I. The saccharimeter readings were taken by four observers on two different instruments, and the average values recorded.

Table I—Ratio of Direct to Invert Polarization of Raffinose Solutions

Raffinose Preparation	Direct Polarization (P) 200-mm. Tube, 20° C.	Invert Polarization (P') 400-mm. Tube, 20° C.	Ratio $\frac{P'}{P}$
Kahlbaum	+99.69	+51.21	0.5137
Kahlbaum	+99.63	+51.22	0.5141
Domestic	+57.20	+29.46	0.5150
Kahlbaum	+26.95	+13.86	0.5143
Domestic	+12.80	+ 6.59	0.5148
Kahlbaum	+ 7.44	+ 3.82	0.5134
Average			0.5142

In the present paper the rounded three-decimal value 0.514 is taken as the basis of calculation. This is a little higher than the value used in the Herzfeld formula, which is 0.5124. The values reported by other observers for different methods of inversion are 0.5070 by Creydt,[1] 0.5182 by Dammüller,[2] 0.5188 by Lippmann,[3] and 0.5094 by Beythien and Tollens.[4] Variations in the concentration of raffinose seem to have but little influence upon the ratio.

Evaluation of Formulas for Estimation of Sucrose and Raffinose

The evaluation of the formulas for estimating sucrose and raffinose, on the basis of the invert factor —0.33 for sucrose and + 0.514 for raffinose, is made as follows:

The generally accepted ratio of the specific rotation of sucrose to that of raffinose anhydride is $\frac{+123.2}{+66.5} = 1.852$.

If the sucrose normal weight of a product be taken, the direct polarization (P) of S per cent sucrose and R per cent raffinose, upon a saccharimeter, would be represented by the equation

$$P = S + 1.852 R \qquad (1)$$
$$\text{whence } R = \frac{P - S}{1.852} \qquad (2)$$
$$\text{and } S = P - 1.852 R \qquad (3)$$

The polarization of S per cent sucrose at 20°C. after inversion (disregarding the influence of concentration) would be — 0.33 S, and the polarization of R per cent raffinose at 20°C. after inversion would be $1.852R \times 0.514$. The total invert polarization (P') at 20°C. of the mixture of sugars is then

$$P' = -0.33 S + (1.852 R \times 0.514) \qquad (4)$$

Substituting for R in Equation 4 its value from Equation 2 we obtain

$$P' = -0.33 S + 0.514 (P - S) \qquad (5)$$
$$\text{whence } S = \frac{0.514 P - P'}{0.844} \text{at } 20° \text{ C.} \qquad (6)$$

Substituting for S in Equation 4 its value from Equation 3 we obtain

$$P' = -0.33 (P - 1.852 R) + (1.852 R \times 0.514) \qquad (7)$$
$$\text{whence } R = \frac{0.33 P + P'}{1.563} \text{at } 20° \text{ C.} \qquad (8)$$

Formulas 6 and 8 are valid only when the solutions are made up and polarized at exactly 20°C., and a third pur-

1 Arch. Suikerind., 21 (1913), 1383.
2 Z. Ver. deut. Zuckerind., 70 (1920), 402.

1 Ber., 19 (1886), 3115.
2 Z. Ver. deut. Zuckerind., 38 (1888), 748.
3 Z. Ver. deut. Zuckerind., 38 (1888), 1232.
4 Z. Ver. deut. Zuckerind., 39 (1889), 917.

pose of the present investigation was the evaluation of a general formula that would be applicable at all temperatures.

EVALUATION OF GENERAL FORMULA APPLICABLE AT ALL TEMPERATURES

TEMPERATURE COEFFICIENT FOR SUCROSE—The influences of changes in temperature upon the direct and invert polarization of sucrose upon quartz-wedge saccharimeters have been very thoroughly investigated, and are expressed by the general equation

$$P = S [1 - 0.0003 (T - 20)] = S (1.006 - 0.0003 T)$$

for the direct polarization (P) and

$$P' = S [-0.33 + 0.005 (t - 20)] = S (-0.43 + 0.005t)$$

for the invert polarization (P'), S being the percentage of sucrose, T the temperature of the direct polarization, and t the temperature of the invert polarization.

TEMPERATURE COEFFICIENT FOR RAFFINOSE—There is very little information in the chemical literature as to the influence of temperature changes upon the direct polarization of raffinose. Creydt[1] states that the rotation of raffinose undergoes a slight decrease with increase in temperature. Other authorities state the influence of temperature changes to be imperceptible or negligible. The writers, from measurements of the polarization of raffinose solutions made up and polarized at 10°C. and of similar solutions made up and polarized at 32°C., observed a decrease in polarization with increase in temperature, this decrease amounting to 0.00034 for each degree of the saccharimeter scale for 1°C. increase in temperature. This value differs by only 0.00004 from that obtained for sucrose. The temperature correction for sucrose may, therefore, be applied to the direct polarization of raffinose on quartz-wedge saccharimeters without sensible error. Equation 1 for the direct polarization at temperature T of a sucrose normal weight of product containing S per cent sucrose and R per cent raffinose would then be

$$P = S (1.006 - 0.0003 T) + 1.852 R (1.006 - 0.0003 T) \quad (9)$$

Several formulas have been worked out for correcting the invert polarization of raffinose for changes in temperature. Herles[2] found a solution of raffinose, which polarized $+100$ at 20°C. upon the saccharimeter before inversion, to read, after inversion by Herzfeld's method, $+51.24$ when the inverted solution was made up and polarized at 20°C., and to read $+47.24$ when the inverted solution was made up and polarized at 0°C., which corresponds to a loss of 0.2 in polarization for 1°C. decrease in temperature.

The writers found a solution of raffinose, which polarized $+100$ at 20°C. before inversion, to read, after inversion by Schrefeld's modification, $+53.54$ when the inverted solution was made up and polarized at 32°C., and to read $+49.61$ when the inverted solution was made up and polarized at 10°C., which corresponds to a loss of 0.18 in polarization for 1°C. decrease in temperature. The temperature correction for the invert polarization of a solution of raffinose, polarizing $+100$ at 20°C. before inversion upon a quartz-wedge saccharimeter, is therefore $+51.4 + 0.18 (t - 20) = +47.8 + 0.18t$, which, calculated to a solution of raffinose having a direct polarization of $+1$, would be $+0.478 + 0.0018t$. The temperature correction for the invert polarization of sucrose, employing Schrefeld's modification of Herzfeld's process, is $-33.0 + 0.5(t - 20) = -43.0 + 0.5t$, which, divided by 100, equals $-0.43 + 0.005t$ for a direct polarization of $+1$ at 20°C. Equation

1 *Z. Zuckerind. Böhmen*, 13 (   ), 559; 15 (   ), 528.
2 *Z. Ver. deut. Zuckerind.*, 37 (1887), 153.

4 for the invert polarization at temperature t of a sucrose normal weight of product containing S per cent sucrose and R per cent raffinose would then be

$$P' = S (-0.43 + 0.005t) + 1.852 R (+0.478 + 0.0018t) \quad (10)$$

Substituting in (10) the value of R from Equation 9 we obtain

$$S = \frac{P(0.478 \times 0.0018t) - P'(1.006 - 0.0003\,T)}{(0.908 - 0.0032t)(1.006 - 0.0003\,T)} \quad (11)$$

Substituting in (10) the value of S from Equation 9 we obtain

$$R = \frac{P(0.43 - 0.005t) + P'(1.006 - 0.0003\,T)}{(1.681 - 0.0059t)(1.006 - 0.0003\,T)} \quad (12)$$

When T and t are each 20°C., Equations 11 and 12 become necessarily the same as (6) and (8).

Applications of the preceding formulas to the analysis of several mixtures containing known amounts of sucrose and raffinose are given in Table II.

TABLE II—ANALYSIS OF KNOWN MIXTURES OF SUCROSE AND RAFFINOSE

TAKEN		OBSERVED					CALCULATED	
Sucrose Per Cent	Raffinose Per Cent	P	T °C.	P'	t °C.		Sucrose Per Cent	Raffinose Per Cent
96.06	3.25	+102.00	20	−28.68	20		96.09	3.19
92.22	6.51	+104.30	20	−24.30	20		92.31	6.48
76.85	7.47	+ 90.72	20	−18.25	20		76.87	7.48
76.85	7.47	+ 90.50	30	−14.26	30		76.90	7.46

In making the analyses of Table II, only the most carefully graduated flasks and observation tubes were employed, and the measured volumes of solution used for inversion were checked by weighing. The work was performed in an insulated constant temperature room, and the average readings of two observers were taken as the recorded values of P and P'.

With mixtures containing low percentages of sucrose, the negative constituent −33 of the Clerget divisor requires a slight modification for changes in concentration, and this necessitates a small correction of the revised formulas given in this paper. This correction is most easily applied by the method of approximation. For pure sucrose the negative constituent of the Clerget divisor for the Schrefeld-Herzfeld formula varies according to the equation

$$N = -(32.1 \times 0.07g)$$

in which g is the grams of sucrose in the half normal weight of substance taken for inversion. After determining the approximate percentage of sucrose by means of Formulas 6 or 11, the value of g is found, and from this the calculated value of the negative constituent (N) is determined. The value of 0.01 N is then substituted for −0.33 in Formula 5, and the corrected formulas for S and R are evaluated as previously described.

Thus, for a beet molasses containing 50 per cent sucrose, $g = 6.5$, whence $N = -(32.1 + 0.07 \times 6.5) = -32.6$ and $0.01 N = -0.326$. Formula 5 as thus corrected would give

$$S = \frac{0.514\,P - P'}{0.84} \text{ and } R = \frac{0.326\,P \times P'}{1.556} \quad (13)$$

In mixtures containing low percentages of sucrose and high percentages of raffinose the concentration of the inverted sucrose solution is affected so that this method of correction is no longer strictly valid. The products met with in commercial analysis contain, however, for the most part only small percentages of raffinose, so that the question of high raffinose mixtures has nit a wide practical significance. In mixtures of sucrose with other sugars the negative constituent of the Clerget divisor varies with the total carbohydrate concentration and not with the concentraion of sucrose alone.

THE INFLUENCE OF IMPURITIES UPON THE ESTIMATION OF SUCROSE AND RAFFINOSE BY THE OPTICAL METHOD

While the results of Table II indicate that the optical method may give concordant results in the analysis of pure

mixtures of sucrose and raffinose, no conclusion can be drawn as to the relative accuracy of this method in the analysis of mixtures of these sugars with the salts, nitrogenous substances, and other impurities that are found in natural and commercial products. The question of impurities and of their influence upon the accuracy of the method introduces so many complications that only a few simple instances can be considered in the present paper. The following cases are taken: (1) Influence of optically inactive salts, (2) influence of optically active amino compounds, and (3) influence of clarifying agents. In this connection the analysis of such a product as sugar-beet molasses is chiefly considered.

INFLUENCE OF OPTICALLY INACTIVE SALTS—Ordinary beet molasses contains about 8 per cent of various organic and inorganic salts of potassium, about 1 per cent of the chloride and other salts of sodium, and a small remainder consisting principally of calcium salts. Potassium and sodium salts are the principal disturbing factors. Organic and inorganic salts of the alkalies, according to the results of different investigators, produce generally a pronounced decrease in the polarization of sucrose. The results in the case of raffinose are less marked, there being either no change or else a slight increase in polarization. Washburn[1] obtained an increase in the polarization of raffinose on the addition of potassium and sodium chlorides. The writers selected potassium oxalate as a convenient salt for experiments, and, with the proportion of 3 g. $K_2C_2O_4.H_2O$ in 100 cc., obtained the following results for the direct and invert polarization of sucrose and raffinose.

| | P | | P' | |
	Without Oxalate	With Oxalate	Without Oxalate	With Oxalate
Sucrose	+50.00	+49.75	−16.40	−16.50
Raffinose	+17.13	+17.20	+ 8.85	+ 8.93

A decrease of 0.25 is observed in the direct polarization of sucrose, an increase of 0.07 in the direct polarization of raffinose, an increase of 0.10 in the invert polarization of sucrose, and an increase of + 0.08 in the invert polarization of raffinose. The effect of these influences in the analysis of a mixture of sucrose and raffinose is partly compensating. A normal weight of a mixture containing 50 per cent sucrose, 9.25 per cent raffinose, and 11.54 per cent $K_2C_2O_4.H_2O$, dissolved to 100 cc., gave a value of + 66.95 for P and −7.57 for P'. The percentages, as calculated by Formula 13, would then be 49.98 per cent sucrose and 9.16 per cent raffinose. We may, therefore, conclude that the presence of optically inactive salts of potassium and sodium in such amounts as occur in sugar-beet molasses will not produce errors exceeding 0.1 or 0.2 per cent.

INFLUENCE OF OPTICALLY ACTIVE AMINO COMPOUNDS.— Among the optically active amino compounds which have been detected in sugar-beet products are asparagine and glutamine, and the corresponding derivatives of these, aspartic and glutaminic acids. The presence of any foreign, optically active substance introduces an error in the estimation of sucrose and raffinose by the optical method. Thus a foreign substance affecting the determination of P and P' to the extent of + 0.1 would make the calculated percentage of sucrose 0.06 too low and the calculated percentage of raffinose 0.09 too high. When, however, the foreign, optically active substance has a different polarization in neutral and acid solution, as is the case with the optically active amino compounds, these errors of method are greatly increased. The following approximate specific rotations are given for several amino substances in water and in the presence of hydrochloric acid:

1 J. Am. Chem. Soc., 31 (1909), 338.

	WATER	IN PRESENCE OF HCl
Asparagine	− 6	+34
Aspartic acid	+ 4	+34
Glutamine	0	+30
Glutaminic acid	+10	+30

The marked increase in dextrorotation of these substances in the acid inverted solution causes a pronounced diminution in the calculated percentage of sucrose and a pronounced increase in the calculated percentage of raffinose. Thus, a mixture of amino substances having an influence of —0.1 upon P and of +0.5 upon P' would make the calculated percentage of sucrose 0.66 too low and the calculated percentage of raffinose 0.30 too high. In other words, application of the method to a mixture of sucrose and asparagine would indicate the presence of raffinose when this sugar was entirely absent, as may be seen from the following example. A mixture containing 50 per cent sucrose and 3.85 per cent asparagine gave a value of + 49.65 for P and of — 14.8 for P'. Application of Formulas 13 indicate 48.00 per cent sucrose and 0.86 per cent raffinose.

Ehrlich,[1] Andrlik and Stanek,[2] Smolenski,[3] and other chemists have called attention to the errors which may result from the presence of optically active amino compounds in the analysis of beet products, and for a more detailed account of such errors the original papers of these investigators should be consulted.

INFLUENCE OF CLARIFYING AGENTS—In this connection the influence of basic acetate of lead as a clarifying agent is alone considered. The errors due to the use of this reagent are of two kinds, first the error due to the volume of the lead precipitate, and second, the error due to the effect of any excess of lead subacetate upon the polarization of optically active substances.

The error due to the volume of the lead precipitate produces an increase in the percentages of sucrose and raffinose as calculated from the direct and invert polarizations. For a normal weight of 26 g. of beet molasses the volume of lead precipitate may equal 1 cc., which, for a product containing 50 per cent sucrose and 5 per cent raffinose, would produce an increase of 0.50 in the percentage of sucrose and of 0.05 in that of raffinose

The action of dissolved lead subacetate upon the polarization of optically active substances is variable. In the case of sucrose, the results of Bates and Blake[4] show a slight decrease for amounts of lead solution not exceeding 6 cc. For volumes of lead solution exceeding 6 cc. a gradual increase in polarization was noted. In the case of raffinose small amounts of lead subacetate produce no change in polarization; larger amounts, according to Weisberg[5] and to Svoboda,[6] cause a decrease. An experiment of the writers showed that a solution of raffinose made up to 100 cc. with water and 10 cc. of lead subacetate solution of 1.26 sp.gr. underwent a decrease in polarization from +34.25 (the reading for a pure aqueous solution) to +32.90.

Lead subacetate causes the polarizations of asparagine and aspartic acid to deviate strongly to the right, and those of glutamine and glutaminic acid to deviate slightly to the left. Experiments by Smolenski,[7] upon the mixture of amino substances in the waste saccharate liquor of a beet sugar factory, showed that 5 cc. of lead subacetate in

1 Z. Ver. deut. Zuckerind., 53 (1903), 809.

2 Z. Zuckerind. Bohmen, 31 (1906-7), 417.

3 Z. Ver. deut. Zuckerind., 60 (1910), 1215; 62 (1912), 791.

4 U. S. Bureau of Standards Bulletin 3, 105.

5 Bull. assoc. chim. sucr. dist., 9 (1891), 498.

6 Z. Ver. deut. Zuckerind., 46 (1896), 107.

7 Z. Ver. deut. Zuckerind., 62 (1912), 804.

100 cc. of solution caused the direct polarization to decrease from $+1.50$ to $+1.25$ and that 5 cc. of hydrochloric acid in 100 cc. of solution caused the invert polarization to increase from $+1.50$ to $+2.70$. The effect of lead subacetate, according to the nature of the amino compounds present, might therefore cause an increase as well as a diminution in the errors which these foreign optically active substances produce. The sum of all the influences of lead subacetate upon the errors of the optical method for analyzing sucrose-raffinose mixtures would seem, however, generally to be compensating, the errors being usually less with than without its use. This is shown by Table III, which gives a general summary of the results obtained in the analysis of mixtures of sucrose and raffinose with potassium oxalate and asparagine, both in presence and in absence of lead subacetate.

TABLE III—Showing Influence of Impurities Upon the Estimation of Sucrose and Raffinose

	TAKEN				OBSERVED		CALCULATED	
No.	Sucrose Per cent	Raffinose Per cent	Potassium Oxalate Per cent	Asparagine Per cent	Lead Subacetate	P	P′	Sucrose	Raffinose
1	50.00	9.25	....	....	.....	+67.13	−7.55	50.06	9.21
2	50.00	9.25	11.54	....	.....	+66.95	−7.57	49.98	9.16
3	50.00	9.25	.....	3.85	.....	+66.78	−5.85	47.83	10.23
4	50.00	9.25	11.54	3.85	.....	+66.80	−5.90	47.89	10.20
5	50.00	9.25	11.54	3.85	10c.c.	+67.18	−6.20	48.49	10.09

There are two possibilities for improving the accuracy of the inversion methods for estimating sucrose and raffinose—one by the use of an inverting agent, such as invertase, which avoids the disturbances produced by free acid in polarization of the amino substances, and the other by use of precipitating agents which remove the acid after inversion from solution.[1] Both of these possibilities are being examined by the writers, who hope to report upon them at a later time.

SUMMARY

The change in the Herzfeld divisor of the Clerget formula for estimating sucrose from 142.66 to 143 has necessitated a revision of the Creydt formula for analyzing mixtures of sucrose and raffinose. In the course of this revision, the inversion constant of raffinose and the temperature coefficient for the polarization of raffinose before and after inversion have been redetermined.

The relative accuracy of this revised formula is illustrated in the case of known mixtures of sucrose and raffinose and in the case of known mixtures of these sugars with potassium oxalate and asparagine when lead subacetate is used as a clarifying agent. Possibilities of improving the optical method for analyzing mixtures of sucrose and raffinose are also indicated.

[1] R. F. Jackson and C. L. Gillis (Bureau of Standards *Scientific Paper* 375, 177) suggest a modification of the Creydt method, which consists in neutralizing the inverted solution with ammonium hydroxide and adding the equivalent amount of ammonium chloride to the solution for the direct polarization, in order to secure equality of conditions before and after inversion. This suggestion, which has not been worked out in detail, deserves consideration.

Shortening: Its Definition and Measurement[1,2]

By Clark E. Davis

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The term "shortening" has never been satisfactorily defined. Still less satisfactory have been the attempts to measure it.

The term is used throughout this paper as related to crackers, biscuits, or cakes. The average baker tests the shortness of a cracker in two ways: (1) by its resistance to breaking, and (2) by its resistance to crushing. This is natural in view of the fact that in eating a cracker the shortness is first apparent when it is broken, either by the aid of the hands or by the teeth. It is even more apparent in the chewing operation, which is really one of grinding or crushing. Consequently if some method could be devised which would measure either the breaking strength or the crushing strength, or both, it might lead to a definition of the term "shortening."

With this idea in mind, a machine has been devised which will measure either the breaking strength or the crushing strength with a high degree of accuracy. This machine is similar to the forms of cement testing machines commonly in use. These machines, however, are designed for measuring heavy loads, and their sensitiveness need not be of the highest order of accuracy. The force required to break or crush any food product, such as those with which we are working, is necessarily very small. This requires that the measuring machine be extremely sensitive in order to obtain great accuracy. In a cement briquet a force of six, seven, or eight hundred pounds is required, while for a cracker a force of two, three, or four pounds is necessary.

APPARATUS

The machine[3] described in this paper has been devised for measuring breaking strength and crushing strength. It will be hereafter referred to as a "shortometer."

In the drawing, Fig. 1 represents a side elevation of one

form of the testing device. Fig. 2 is a horizontal section taken upon line 2—2 of Fig. 1, size of base 4.5 in. $\times$ 6 in. Fig. 3 is an end elevation of the lower portion of the ap-

Fig. 1.

Fig. 2.

Fig. 3   Fig. 4

Fig. 5

```
196 lbs. flour, medium winter
 35 lbs. shortening
 80 lbs. sugar
 43.8 lbs. water
  0.5 lbs. salt
  0.5 lbs. ammonium bicarbonate
  0.3 lbs. monocalcium acid phosphate
  1.5 lbs. sodium bicarbonate
```

All the experimental batches were 1 per cent of the original formula. This produced 3.5 lbs. of dough.

In order to arrive at some definite method of procedure several hundred batches of cakes, made with the various shortening agents, were tested for their shortness.

Standardized conditions must be established. In the manufacture of a cake there are many variables, e. g., exact amount of material used, method of mixing,[1] temperature of dough while mixing, time of mixing, the pressure exerted by the brake, temperature of baking oven, conditioning of the cake after baking, etc.

In the experimental work these conditions have all been so standardized that each cake gets the same treatment as every other one. The materials are all accurately weighed, the mixing is done by machine, the doughs are all made as near the same temperature as possible, which is 80° F., the time of mixing is 7 min., the brake treatment gives all green cakes the same thickness, three-thirty-seconds of an inch, and the cakes are always cut of the same diameter, two and five-sixteenths inches.

The temperature of baking is 465° F., and in the reel oven used this was controlled to ± 2.5° by means of an electric control of the gas supply. The oven temperature is undoubtedly not uniform throughout, but this irregularity is obviated by the use of the reel oven which takes the cake through the relatively hot and cold zones, thereby giving all uniform treatment. Each batch is baked for the same length of time (8.25 min.), determined by the number of revolutions (6).

The product is cooled in the absence of drafts to prevent checking. It is then conditioned for at least 48 hrs. in a closed cabinet where the temperature and humidity remain practically constant. At the end of this time the cake is broken in the shortometer. All cakes are of approximately the same diameter and are always placed in the same relative position.

Several hundred cakes were used in testing some shortenings, while in some cases as many as three thousand were used in the standardization of this apparatus.

A few results are given, showing the method of recording and the breaking strength of each individual cake in various batches:

paratus shown in Fig. 1, engaged in breaking a test cake. Fig. 4 is similar to Fig. 3, showing the test of a sample cake for its resistance to crushing. Fig. 5 is a side elevation of a modified form of testing apparatus.

In the apparatus shown in Figs. 1 to 4, inclusive, a table, 1, is supported on 3 by means of adjustable screws, 2.

A pair of parallel rails, 4, extend upward from table 1 to support the cake, 5, when tested for breaking strength. A vertical hardened steel rod, 6, 5 in. long is mounted in vertical hardened steel bearings, 7, formed on a lateral extension, 8, of a vertical standard, 9, which is mounted on table 1. Spindle 6 carries a horizontal support, 10, at its upper end, on which a shot container, 11, is stationed. The striking member, 12, elongated, in socket 13 with set-screw 14 is detachable from spindle 6 and is preferably rounded and comparatively narrow (See 15, Fig. 3). 16 is a guideway for the striking member.

When a cake is to be broken it is positioned across the rails 4, and member 12 is placed thereon, while shot is run into container 11 until the point of rupture occurs. The container and contents are then weighed.

A modified form of apparatus is shown in Fig. 5 in which the spindle, 6', is pivotally connected to an arm, 17, which is pivoted at 18 to the standard 9'. Arm 17 carries a graduated scale as indicated at 19 and a sliding weight, 20.

When it is desired to test the crushing strength a portion of the cake, as indicated at 5' in Fig. 4, may be placed on table 1 between the rails, 4, so that the cake rests firmly on the table. Striking member 12 is removed from spindle 6 by unscrewing set-screw 14. The lower portion, 6_a, of spindle 6 has a horizontal bottom surface of comparatively small diameter. Shot is allowed to flow into the container 11 until the spindle crushes or pulverizes that portion of the cake against which it rests. The container with contents is then weighed.

Experimental

In searching for a type of goods upon which the experiments were to be made it was decided to use a variety of sugar cooky, because the amount of shortening used is a fair average and the cake is easily made.

The following formula was used:

TABLE I			
Kind of fat	No. 1 Lard	No. 2 Lard	No. 3 Lard	No. 4 Lard
Date of baking	July 10	July 17	July 24	July 26
Date of test	July 12	July 19	July 26	July 28
Temp. of dough, °F.	79	81	80	81
Temp. of room, °F.	77	80	84	91
Temp. of oven, °F.	465	465	465	465
Humidity, per cent	83	79	66	62
	Breaking strength, Lbs.			
	2.63	2.63	3.06	2.63
	2.75	2.88	2.69	3.38
	2.75	3.06	2.94	2.94
	3.13	2.88	2.94	2.75
	2.88	2.94	2.94	2.63
	3.06	2.94	2.56	2.94
	2.88	2.63	3.00	2.94
	2.88	3.25	2.88	2.69
	2.69	2.88	3.06	2.88
	2.94	3.50	2.81	2.94
	2.56	2.75	2.94	2.56
	2.81	2.81	2.88	3.19
	2.81	2.56	3.06	3.06
	3.06	3.13	2.81	3.38
	3.19	3.06	2.94	2.88
	3.06	2.69	2.69	2.94
	2.94	2.94	3.19	2.63
	2.75	2.94	2.63	3.25
Average	2.88	2.91	2.89	2.92

[1] It was found impossible to obtain consistent results using hand mixing for the reason that it is never mixed twice alike, the gluten being unequally developed. The machine, No. 7223, of 10 to 12 lbs. capacity, was made by The J. H. Day Co., Cincinnati, Ohio.

Table II

Kind of Fat	UNHYDROGENATED OIL			HYDROGENATED OIL		
Date of baking	Dec. 31	Dec. 31	Dec. 10	Dec. 12	Dec. 13	Dec. 17
Date of test	Jan. 2	Jan. 2	Dec. 13	Dec. 14	Dec. 16	Dec. 19
Temp. of dough, °F.	70	70	68	80	81	80
Temp. of room, °F.	76	72	80	80	78	76
Temp. of oven, °F.	465	465	465	465	465	465
Humidity, per cent	35	48	38	45	55	59
	Breaking strength, Lbs.					
	(14 tests)	(14 tests)	(14 tests)	(18 tests)	(18 tests)	(17 tests)
High	3.88	3.94	4.13	3.75	3.75	3.69
Low	3.50	3.13	3.13	2.94	2.88	2.88
Average	3.71	3.64	3.72	3.26	3.21	3.28

It is obvious that there are no great differences in the individual cakes. The general averages check very closely. An accuracy of 1 to 2 per cent is readily attainable.

After the conditions have been standardized it is not necessary to use more than thirty cakes for each test.

Similar series with other oils, unhydrogenated and hydrogenated, seem to show that hydrogenation results in greater shortening power. Measurements have been made of the shortening power of the following oils and fats:

Lard	Corozo (cohune nut) oil
Lard compound	Corn oil
Butter	Olive oil
Cottonseed oil	Peanut oil
Cottonseed oil, hydrogenated	Peanut oil, hydrogenated
Coconut oil	Rapeseed oil
Coconut oil, hydrogenated	Soy-bean oil

In all the comparative breaking tests made on various oils and fats, lard is the best shortening agent; hence it is used as the standard. Its breaking strength will vary according to the conditions of standardization, and each operator must determine the value to be used as a standard.

The shortometer value in pounds is arbitrarily taken as 100 per cent. All other oils and fats having less shortening power will have a greater shortometer value. This weight in pounds of the standard divided by the weight in pounds of any other oil or fat will give its relative shortening value.

Experiments determining the crushing strength are not included in this article, but the same relationship holds.

CLASSIFICATION OF FLOURS

By holding all other ingredients constant and varying the flour used it is possible to arrive at a satisfactory classification of flours.[1]

A few results on flour are shown:

CLASSIFICATION OF FLOUR	BREAKING STRENGTH
	Lbs.
Soft winter	2.49
Soft winter	2.33
Soft winter	2.48
Soft winter	2.42
Medium winter	2.69
Medium winter	2.79
Medium winter	2.78
Strong winter	3.01
Strong winter	3.04
Strong winter	3.07
Spring	3.39
Spring	3.39
Spring	3.09

DEFINITION OF SHORTENING

That cake which requires the least load to measure its breaking strength is the shortest, that which requires the heaviest load is the least short.

The best shortening is that material which when baked in a dough gives to the product a minimum breaking strength and a minimum crushing strength.

SUMMARY

1—Apparatus has been devised which will measure the shortening value of different oils and fats and mixtures of them.

2—Shortening has been defined in terms of measurable units.

3—Lard has been found to be the best shortening agent.

4—Partial hydrogenation of an oil increases its shortening power.

5—A method has been suggested whereby flours may be classified.

[1] Further work is being done along this line.

A Process for Producing Palatable Sirup From Sugar Beets[1]

By Sidney F. Sherwood

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The *Sugar Beet* (October 1906) refers to the very objectionable flavor and odor of sirup prepared from sugar beets and states that during the preceding fifty years numerous experiments had been made to eliminate this, but that all of the processes suggested were worthless. The same journal (January 1908) contains a brief note stating that "excellent" sirup is made from beets in Belgium and Germany by cooking the beets in water for several hours, pressing out the juice and evaporating directly to sirup of about 75 per cent solids; the statement is made also that about 70 g. of sulfuric acid are added to the extract from 100 k. of beets.

In 1917, C. O. Townsend and H. C. Gore[2] described a process, the essentials of which consisted in reducing the beet roots to thin slices, extracting the sugar by means of hot water, drawing off the sugar solution from the beet chips, and subjecting it to slow and long continued boiling and constant removal of scums during the process of evaporation. Acceptable sirup could be produced by the process recommended, but in a great many cases the odor and flavor was highly objectionable, while the sirup was always very dark in color. In January 1919, the writer suggested improvements in the process, the use of which

[1] Received June 6, 1921.
[2] "Sugar Beet Sirup," U. S. Department of Agriculture, *Farmers' Bulletin*, 823 (1917).

resulted in marked improvement in the quality of the sirup produced. These suggestions were attached in printed form to copies of the bulletin sent out thereafter, and included thorough ripeness of the beet, removal of the top and upper green colored portions, removal of the skin, permitting the slices to fall directly into water of sufficient depth to prevent access of air and consequent oxidation and darkening of the slices, and direct evaporation to sirup.

John M. Ort and James R. Withrow, who investigated the preparation of beet sirup, were unacquainted with the fact that this improved process had been offered at the time they presented the results of their investigations before the Division of Industrial and Engineering Chemistry at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919, but refer to it in their published article,[1] and state that the precautions used are similar to those used by them and that the results obtained should be better than in the case of the original method. They tried many chemical and mechanical processes for clarification and removal of objectionable odor and flavor and state that none of them resulted in marked improvement in flavor. Identical results have been obtained by the writer in using many similar processes, and it is concluded that it is not advisable to suggest chemical processes at all for use where the sirup is to be produced upon a small

[1] THIS JOURNAL, 12 (1920), 154.

scale, and that any mechanical processes suggested should be of the simplest sort. Ort and Withrow conclude that various published processes for making palatable sugar beet sirup do not consistently fulfil all claims made for them, that the sirup should not be evaporated in copper kettles, that, in the case of immature beets, the flavor will be improved by preliminary storage, etc.

Improved Process

The frequently occurring unpleasant and objectionable odor and flavor of beet sirup made by the original process is quite similar to that of beet molasses, though, of course, very much less pronounced. While the use of the modifications noted above resulted in marked improvement in the characteristics of the sirup, the objectionable odor and flavor was not always entirely absent and the work has been continued at intervals. Noting that beet molasses is a product resulting from the evaporation of juices and sirup under reduced pressure, it was considered that the characteristics of the sirup might be improved by some process of heating under pressure, and many experiments were made relative to processes of blowing air, steam, and superheated steam through juice, semi-sirup, and finished sirup; heating juice, semi-sirup, and finished sirup under pressure and at temperatures greater than the normal boiling point of finished sirup (105.5° to 106.5° C.), etc. As a result, the following process, for which a government patent[1] has been issued and the use of which is free to any citizen of the United States, was developed early in 1920, and is suggested as one affording the production of a satisfactory sirup from sugar beets: The beets are washed and the tops, upper green portions, and skin or peel removed. The beets are sliced, permitting the slices to fall directly into warm water of sufficient depth (an excess is avoided) to prevent access of air to the slices, heated to about 80° C. for about an hour, and the extract drained off and strained to remove fine particles, etc. This extract, or a similar extract prepared in any other manner, is placed in an autoclave—or other container which may be sealed—provided with a controlled outlet for blowing off steam and ordinarily with a pressure gage and thermometer, heated to 108° to 110° C. —corresponding to a pressure of approximately 21 lbs. to the sq. in.—and maintained at this temperature for 1 hr., blowing off a considerable quantity of steam at approximately 15-min. intervals. The extract is strained to remove the slight quantity of coagulated material and evaporated directly to sirup, removing the very slight amount of scum that forms.

Ordinarily this treatment serves to remove the objectionable odor and flavor, though the temperature, length of time of heating, and intervals for blowing off steam are not necessarily confined to the ones mentioned, but may be varied. Thus, in a number of instances, successful results have been obtained by heating to 110° to 112° C. for 0.5 hr. with constant blowing off of steam, the sirup in every instance being of a lighter color than those from a heating period of 1 hr. Sirups from a second extraction of the slices were quite acceptable, though they possessed a somewhat stronger flavor and their appearance was somewhat inferior.

Numerous lots of sirup have been prepared by the process from beets grown in southern Michigan and in each case the characteristics were satisfactory in that they were of an amber color, the unpleasant odor and flavor were absent, and the cloudiness was no greater than in average cane or sorghum sirup. (In several cases the sirup was perfectly clear.) Sirups such as cane, sorghum, maple,

1 U. S. Patent 1,370,372 (March 1, 1921), Sidney F. Sherwood.

etc., possess characteristic flavors, and the after-taste of any one of them may be disagreeable to a person who is accustomed to any other one. Beet sirup possesses a flavor quite distinct from any other sirup, the first taste being agreeable and very sweet, while the after-taste is faintly similar to that of hoarhound, and expressions of opinion from numerous persons indicate that, as in the case with other sirups, it is agreeable to some persons and not agreeable to others.

Yield and Composition of Sirup

The yield of sirup varies, depending upon the sugar content of the beets. In the experimental work, the yield from 100 lbs. of beets averaged slightly over 2 qts. for a single extraction, and 1 qt. for a second, or a total of slightly over 3 qts. The beets were sliced with a large knife, and a somewhat larger yield would undoubtedly have been obtained with a slicing machine affording thinner slices. The debris (top, peelings, etc.) amounted to 40 to 50 per cent of the weight of beets. This material, and also the extracted slices, affords a valuable food for cattle, chickens, etc. The evaporation was continued until the boiling point reached 105.5° to 106.5° C., the thermometer not being permitted to touch the bottom of the evaporating vessel. The following is the composition of a number of sirups:

COMPOSITION OF BEET SIRUP

Sample No.	Sucrose Clerget HCl Cold Per cent	Reducing Sugars (As Invert Sugar) Per cent	Ash Direct (Not as Carbonate or Sulfate) Per cent	Total Solids (Refractometer) Per cent	Undetermined Per cent
1	61.53	3.43	1.39	69.92	3.57
2	61.07	3.32	1.54	68.87	2.94
3	62.38	2.43	1.20	68.37	2.36
4	63.68	3.10	1.13	70.87	2.96
5	63.98	3.01	1.52	71.82	3.31
6	63.06	2.60	1.56	70.87	3.65
7	65.28	2.39	1.33	71.77	2.77
8	64.60	1.54	1.25	69.82	2.43
Average	63.20	2.73	1.37	70.29	3.00

Application to Home Production of Sirup

The object of these investigations has been directed entirely to processes for the production of palatable sirup from sugar beets on a small scale, as in the home, and the heating may be carried on in a very satisfactory manner in the ordinary pressure cookers used in a great number of homes. In fact, one of these cookers was used frequently for preparing the experimental sirup. With beets at $7 per ton, the cost of 100 lbs. would amount to only 35 cents, and sirup could be produced at small cost if, as in the case in the home, the value of time and labor were not included. It is considered not improbable that at some time beet sirup may be produced profitably on a factory scale—utilizing the by-products as cattle feeding material—especially in certain sections of the West, admirably suited for the production of beets but situated far from a beet-sugar factory and in which the available agricultural land is insufficient to support such a factory. In this connection it is worthy of note that the consumption of beet sirup in Germany in 1916 to 1917 amounted to 20,000 tons (probably metric).[1]

Decolorizing

In connection with the study of the process, experiments were made to ascertain the effect of infusorial earth and decolorizing carbon. The treatment of hot semi-sirup containing 45 to 50 per cent solids with 3 per cent of its weight of infusorial earth, filtration under pressure, and direct evaporation to sirup resulted in sirup of an improved degree of clearness as compared with untreated sirups. Treatment of the filtrate with decolorizing carbon resulted in sirup of somewhat lighter color, but the differ-

1 Berthold Block, "Beet Sirup," Through J. fabr. sucre., 61 (1920), 282.

ences between these sirups and sirups from treatment with infusorial earth alone were not great. Obviously such processes would not be practical for use in small-scale operations, though they would probably prove advantageous in the case of factory production.

The writer has not had an opportunity to consult the book by Berthold Block on beet sirup manufacture and use, but a review of it makes no mention of superheating processes, though a brief reference[1] to the manufacture in Germany of sirup from beets states that coarse pieces of beets are treated with steam at 100° to 104°C. for 3 hrs., resulting in removal of bad odor and flavor and the development of a flavor of vanilla. Subsequent to working out the above process, the writer became acquainted with a patent issued to H. S. Alexander[2] covering a process for producing an "edible" sirup from sugar beets in which the beets are cooked before pulping for 0.75 to 1.5 hrs., preferably by steam under pressure and at a temperature of 110° to 130° C., shredded, pressed, and the juice filtered and evaporated to sirup; and also one issued to P. Kestner[3] covering a process for evaporating beet juice in an evaporator until sirup of the desired concentration has been produced and then heating under pressure for a very brief period to remove objectionable odor and flavor. As an example, he states that sirup that would boil at 120° C. under atmospheric pressure is heated under pressure until the temperature reaches 130° C., more or less, and the sirup is then cooled at once by releasing the pressure. He states that it can be maintained at this high temperature for a few seconds only or the sirup will be caramelized (burned). The writer's process is believed to be more satisfactory than either of these, in that the introduction into the extract of semi-soluble and suspended material from cooked and pulped beets is avoided and actual filtration is rendered unnecessary, while the danger of scorching is eliminated.

CONCLUSIONS

1—A simple and satisfactory process is described whereby the objectionable odor and flavor of beet sirup is eliminated and a palatable sirup produced.

2—The composition of several sirups is given.

A Study on the Oil Bromide Test of Linseed Oil [1]

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The valuation of linseed oil as a drying oil is still carried out by indirect methods. The iodine value test estimates constituents of a nondrying nature, as well as those imparting drying properties to the oil. The hexabromide test applied to the oil, as described by Hehner and Mitchell,[5] would seem to have fallen into desuetude, whereas renewed attention has from time to time been given to the test as applied to the separated fatty acids. Lewkowitsch[6] would appear to have set the fashion by stating that after "very extensive practice it is preferable to apply this test to the isolated fatty acids."

The drying properties of linseed oil are due to the glycerides of linolenic acid, and not to linolenic acid itself.

The attention given to the hexabromide test upon the isolated fatty acids has no doubt been due to the assumption that linolenic acid was present in linseed oil as the simple glyceride, trilinolenin, to which it bears a simple relationship. There is good reason for doubting that linolenic acid is present as a simple glyceride, as the evidence which the author has to put forward suggests that it exists in linseed oil as a mixed glyceride. On this account, and until the composition of the linolenic glycerides has been placed beyond doubt, it is desirable that the test be applied to the oil direct, and not to the isolated fatty acids. After considerable work on the insoluble bromoglycerides, the author is satisfied that the chief reason for comparative disuse of the hexabromide test since Hehner and Mitchell's paper appeared has been the difficulty of obtaining the bromo derivative as a clean, free powder, when dried.

To differentiate between the two tests it is proposed to use the term "oil bromide" for the insoluble brominated glycerides, and "hexabromides" for the insoluble brominated acid, hexabromostearic acid.

While it is desirable that the oil bromide test should give the full theoretical yield of the linolenic glyceride derivative, such a result—depending as it does on differential solubilities—appears so far to be impracticable.

It is of greater importance that the test, carried out under specified conditions, should be capable of giving consistent results in the hands of different workers and have only a small experimental error; and that the precipitate be of reasonably constant composition. The test proposed here should satisfy these conditions, and has the advantage of a considerable saving of time over the hexabromide test on the isolated fatty acids. It should not take much longer to carry out than the determination of the iodine value, but its results should prove of considerably greater value as an indication of drying power.

The oil bromide yields in this test are higher than any in the literature, and undoubtedly the proposed method applied to the poorer drying oils, such as hempseed and poppy-seed oils, will give higher results than any so far recorded for them.

The investigation whose results are now being presented was carried out in the intervals of routine work and other research work from 1907 to 1910, and is not as complete as the author would wish. Since that time, no opportunity of completing the investigation has offered itself, and the author considers it desirable, without delaying further, to place on record his results, which, giving an improved method of preparation, go far enough to point out the road to complete success for any further investigation.

PURPOSE OF INVESTIGATION

The purposes of the investigation where:

1—To find out what was wrong with the test as described by Hehner and Mitchell,[1] and the causes of the large experimental error.

2—To ascertain the most convenient method of separating the oil bromides from the reaction mixture.

3—To discover a means of separating the oil bromides as a loose, dry, granular powder.

4—To determine the most reliable and convenient method for the estimation of bromine in the oil bromides.

5—To gain some information as to their properties and composition.

6—To formulate the most suitable working conditions to insure maximum yield and maximum purity.

[1] J. fab. sucre., 61 (1920), 25.1.
[2] Brit. Patent 133,744 (October 13, 1919).
[3] Brit. Patent 135,235 (November 27, 1919).
[4] Received January 11, 1921.
[5] ANALYST, 23 (1898), 310.
[6] Chemical Technology of Oils, Fats and Waxes, 1909, I, 384.

PRELIMINARY EXPERIMENTS

In preliminary work on varnish linseed oils, Hehner and Mitchell's method was used.

From 1 to 2 g. of oil were dissolved in 40 cc. of ether, and 5 cc. of glacial acetic acid were added. The mixture was cooled in an ice bath to 0° C., and carefully brominated, using enough excess bromine to give a distinct reddish color. After 3 hrs. at 0° C. the precipitate was separated, washed with three 10-cc. lots of ether, and dried to constant weight.

Whereas Hehner and Mitchell obtained yields of only about 24 per cent, with a single instance of 42 per cent, the yields obtained by the present writer were generally over 50 per cent. Great difficulty was experienced in separating the precipitate and washing it satisfactorily because of the volatility of the ether. Filtration through a Gooch crucible with slight suction was first tried, but it was found that the oil crept to the top of the crucible; that the resulting washed product dried hard and horny, although the precipitate had been granular and that it was difficult to dry to constant weight. Filtration through an inverted thistle funnel covered with chamois leather offered no advantage. Following the experience of L. M. Tolman,[4] a centrifuge was tried for the separation and washing of the precipitate. The resulting manipulation proved much simpler, and this method was finally adopted. The most suitable form of apparatus proved to be as shown in the figure: a is a thin, round, flat-bottomed glass tube 6 in. long by 1 in. in diameter, fitted with a sound cork, b, through which passes a thin glass rod, c, which can be used for stirring the oil solution during bromination, and for breaking up the precipitate for washing. The complete apparatus need not weigh more than 25 to 30 g. Any type of centrifuge taking these tubes may be used. In the present experiments a geared-up, hand-driven model was used. To minimize breakage of tubes, a thin slice of cork is fitted at the bottom of each metal tube in the centrifuge, for the bottom of the glass tube to bear against. Glass tubes, corks, and rods should be carefully selected of practically equal weight, so that the weights in centrifuge tubes are equally balanced.

A summary of the results of these experiments is given in Tables I, II, and III. In all cases the amount of oil stated in the tables was dissolved in 40 cc. ether, with or without acetic acid. It was cooled before and during bromination, and was finally washed three times with 10 cc. each of ether or the solvent used in test, unless otherwise stated. The use of acetic acid was recommended by Hehner and Mitchell as yielding a more granular precipitate.

CONCLUSIONS FROM EXPERIMENTS—(1) Acetic acid in the solvent results in a reduced yield, as is indicated by a comparison of Tests 1 to 4 with Tests 5 and 6 in Table I, and of Tests 6 to 12 with Test 14 in Table III.

(2) An increased ratio of oil to solvent gives an increased yield, as is seen by comparing Tests 2 and 3 in Table III with Tests 4 to 12 and 14, and with Tests 15 and 16 in the same table.

In seeking for the causes of the large experimental error, the condition of the dried oil bromide was held partly responsible. It was observed that although the oil bromide was in a granular condition during precipitation and washing, it was obtained as a horny mass, hard and tough, and of slightly softer consistency below the surface. This suggested that the oil bromide was soluble in the ether, which on evaporation deposited the solute as a varnish film, cementing all the particles together.

Table I—Oil Bromides from La Plata Linseed Oil

No.	Ref. No. of Oil	Oil to 40 Cc. Solvent, Grams	Yield Oil Bromides Found Per ct.	Average Per ct.	Containing Br. Per ct.	Remarks
1	233	1.006	39.35	39.77	56.24	Solvent ether + 7.5 per cent acetic acid
2	233	1.022	41.68			
3	233	1.026	39.47		57.45	Solvent ether + 7.5 per cent acetic acid
4	233	1.001	38.56			
5	233	1.018	42.93	43.04	58.16	Solvent ether only
6	233	1.015	43.15			
Average		40.86		57.28		

Table II—Oil Bromides from Calcutta Linseed Oils

No.	Ref. No. of Oil	Oil to 40 Cc. Solvent, Grams	Yield Oil Bromides Per cent	Containing Br. Found, Per cent	Average, Per cent	Remarks
1	176	1.976	49.12			
2	176	1.822	49.00			
3	31	1.741	54.65			
4	226	2.138	53.24	57.37		
5	226	2.144	53.31	57.50	57.43	
6	202	1.006	46.82			
7	202	1.009	47.47			
8	202	1.015	46.80	57.94		
9	202	1.898	55.90	57.83	57.89	
10	202	2.373	49.90			
Average		50.85		57.66		

Table III.—Oil Bromides from Baltic Linseed Oils

No.	Ref. No. of Oil	Oil to 40 Cc. Solvent Gms.	Bromides Found	Yield Oil Aver. Per cent	Aver. Per cent	Containing Br. Found Aver. Per cwt.	Remarks
1	144	2,273	60.0				Svy. ether 40 cc. + acetic acid 3 cc.
2	50	0.515	49.3	49.8	57.50		Washings 1, acetic acid 5 cc.
3	50	0.543	50.3				Washings 2, alcohol 5 cc.
							Washings 3, ether 5 cc.
4	50	0.992	61.7	61.7			Do., do.
5	50	1.000	61.7				
6	50	1.012	50.3				Syt. ether (0.717) + 7.5% acetic acid 40 cc.
7	50	1.010	49.5	50.2			
8	50	1.038	50.9				Washings 1, solvent; Washings 2, ether (0.717); Washings 3, ether
9	50	0.999	51.8			58.69	Svt. ether (0.725) + 7.5% acetic acid 40 cc
10	50	1.001	52.7	52.5	58.50	Over 58.55	Washings 1, solvent
11	50	1.007	51.1				Washings 2 (0.725)
12	50	1.021	54.6				Washings 3, ether (0.725)
13	50	1.245	59.6				Svt. ether + 7.5 acetic acid 40 cc.
14	50	1.003	56.9			58.60	Ether alone; Svt. ether
15	50	2.008	66.5	65.6			Washings, 3 × 15 cc. ether
16	50	2.011	64.6				
17	293	2.007	67.7	67.5			Svt. ether (0.725) + 0.2% acetic acid
18	293	2.009	67.3				Washings, 3 × 10 cc. ether (0.725)
19	293	2.012	72.3	72.3			Svt. ether (0.717) + 0.2% cetic acid
20	293	2.015	72.3				Washings, 3 × 10 cc. ether (0.717)
21	297	2.025	72.4	72.2			Svt. ether (0.725) + 0.2% acetic acid
22	297	2.011	72.4				Washings, 3 × 10 cc. ether (0.725)
23	297	2.023	73.7	73.6			Svt. ether (0.717) + 0.2% acetic acid
24	297	1.995	73.4				Washings, 3 × 10 cc. ether (0.717)
Average		60.9			58.30		

SOLUBILITY TESTS

Saturated solutions were made by warming together 2 g. of an average sample of crude oil bromides with 50 cc. of solvent, keeping the corked flasks immersed in a bath of water at 60° F. for 1 day, and filtering through paper. Twenty cc. of filtrate were evaporated in small aluminium basins to constant weight. The following results were obtained:

Solvent	Wt. Residue Grams	Grams per Liter
Ether (sp. gr. 0.717 at 15.5°C.)	1.133	6.8
Ether (sp. gr. 0.725 at 15.5°C.)[1]	0.134	6.7
Industrial alcohol (sp. gr. 0.820 at 15.5°C.[2]	0.002	0.10
Ether (0.717) + alcohol (90:10)	0.143	7.15
Ether (0.725) + alcohol (90:10)	0.117	5.85

[1] Commercial product, containing some alcohol.
[2] Grain alcohol, 90 per cent; wood naphtha, 10 per cent.

The insolubles left on the filter paper from the ether had set to horny masses; those from ether and alcohol mixtures were not quite so hard; while those from alcohol alone were quite a free powder. This latter fact, coupled with the low solubility of the oil bromides in alcohol (1 part in 10,000), at once suggested the use of alcohol as a final wash liquor to remove the ether from the washed oil bromide. A marked improvement was the result. The bromide was obtained as a nice, free powder, and it was felt that the experimental error due to differences in drying had been overcome.

ESTIMATION OF BROMINE

Before the bromine in the oil bromides can be estimated it is necessary to convert it into a soluble form which will react with silver nitrate to form the insoluble silver bromide, after which its treatment may be either gravimetric or volumetric. The following methods were tried:

(1) IGNITION WITH LIME—The oil bromide was intimately mixed with lime in a platinum crucible and covered with a good layer of lime. This was heated gently at first, then more strongly. After cooling, the mass was dissolved in a slight excess of nitric acid, and filtered. In gravimetric determinations, the silver bromide precipitate should be allowed to stand in the dark overnight; otherwise results tend to be high. If filtered off soon after precipitation, the silver bromide retains traces of calcium salts.

(2) IGNITION WITH LIME AND CARBONATE OF SODA—The comment on Method 1 applies also to this case.

(3) IGNITION WITH LIME AND SODIUM PEROXIDE, according to Parr.[1] The reaction in this case was too vigorous, and there was risk of loss.

(4) SAPONIFICATION WITH ALCOHOLIC POTASH—This could be made a satisfactory method if saponification were complete and definite, but as shown under the heading " saponification " this is questionable.

(5) SAPONIFICATION WITH SODIUM ETHOXIDE, prepared *in* sity.[2],[3],[4] This was the most reliable and rapid method of all. Careful attention must be given to maintaining constant the ratio of oil bromide to alcohol and to sodium. The ratio employed in the present work was:

W =grams oil bromide (0.2 to 0.3 g.)
68 W =Cc. alcohol (not under 98 per cent)
8.5 W =grams fresh metallic sodium

This mixture was heated under a reflux condenser, and over a very tiny flame for 1 hr. Treated in this manner, the reaction product was very thick when cold. There was no spitting. The product was practically colorless, and on addition of dilute nitric acid a very peculiar, hardly pleasant odor was noticeable. There was only a very small separation of solid fatty bodies. Volhard's method[5] was used for the volumetric estimation. A known excess of $0.1N$ silver nitrate was added, and the excess was titrated back with $0.3N$ ammonium thiocyanate in the presence of a ferric salt. An accuracy of 0.1 per cent was possible.

COMPARATIVE TESTS OF METHODS—A comparison of Methods 1, 4, and 5 was made upon a sample of crude oil bromides prepared from a Baltic linseed oil. Its melting point was low, about 116° C.

	DETERMINATION	PER CENT BROMINE
Method 1	Gravimetric	56.69
	Volumetric	55.92
Method 4	Gravimetric	56.25
	Volumetric	56.00
Method 5	Volumetric	57.02

1 *J. Am. Chem. Soc.*, 30 (1908), 168; *C. A.*, 2 (1908), 1802.
2 Stephanow, *Ber.*, 39 (1906), 4056.
3 Rosanoff and Hill, *J. Am. Chem. Soc.*, 29 (1907), 269.
4 Bacon, *J. Am. Chem. Soc.*, 31 (1909), 49.
5 Treadwell and Hall, "Analytical Chemistry," 1909, II, 545

After considerable experiment, the last-named method was considered the most reliable, giving total conversion of bromine into a soluble form without any possible loss during conversion. Consistently higher results were always obtained with Method 5 than with Method 1, and it was questioned whether Method 1 gave absolutely accurate results. It is of interest to compare the bromine content as found by Hehner and Mitchell. Their results varied from 55.55 to 56.38 per cent, an average of 56.12 per cent. The present writer's results by the lime method generally ran from 56.2 to 57.5 per cent, whereas by the Stepanow-Bacon method they were generally over 57.5 per cent. The variations cannot be entirely due to variations in composition. Most of the figures for bromine content in Tables I, II, and III were determined by the lime method, and the results are not considered so accurate as those in Tables VI and VII, which were determined by the Stepanow-Bacon method. In a private communication Mr. C. A. Mitchell informs the author that the method of ignition with lime in a combustion tube was used in their determinations of bromine. As tending to confirm the unreliability of the lime ignition method, reference may again be made to Hehner and Mitchell's paper. Purified samples of hexabromostearic acid of melting point 180° to 181° C. were found to contain 61.38 to 61.80 per cent bromine (theory 63.31 per cent Br). Again, a several times recrystallized sample of tetrabromostearic acid of melting point 113.4° C. was found to contain only 51.97 per cent bromine (theory 53.32 per cent). These differences from theory equal 2.7 and 2.4 per cent, respectively.

ACTION OF ALCOHOLIC POTASH

Alcoholic potash acts not only by saponifying the glyceride, but by abstracting the bromine from the molecule, forming potassium bromide. The following experiments were originally undertaken in the hope that the saponification value would serve as a substitute for the bromine determination, as a check on the composition of the oil bromides. Half-normal alcoholic potash was first tried. The salts produced being insoluble in alcohol, the reaction mixture was very liable to spit up during heating. Long-necked Kjehdahl flasks were used, tilted, and connected to upright condensers by means of bent adapter tubes, so that any salts spitting up would remain within the flask. Spitting was so bad that it was found advisable to add a few cubic centimeters of water to dissolve the salts. Normal alcoholic potash made up in 90 per cent alcohol was next tried. This gave higher saponification values, but, as can be seen from Table IV, the figures were indefinite. The maximum value, 482.7, was reduced on further heating to 469.0. Blank tests were run alongside the regular tests for the same times.

TABLE IV—SAPONIFICATION VALUES OF OIL BROMIDES

Time of Heating Hours	Saponification Value 0.5 N Alc.KOH	Saponification Value 1.0 N Alc.KOH	Time of Heating Hours	Saponification Value 0.5 N Alc.KOH	Saponification Value 1.0 N Alc.KOH
0.5	411.6	....	2.5	....	482.7
1	416.2	464.3	3	....	470.7
2	....	471.5	4	....	469.0

The figures given in Table IV are the average of a large number of tests. In Table V will be found the saponification values of each of the possible unsaturated glycerides up to linolenin. The values are calculated on the assumption that for saponification with complete removal of bromine, the number of molecules of potassium hydroxide required equals the number of atoms of bromine in the molecule of oil bromide plus 3 (for saponification).

ACTION OF SODIUM ETHOXIDE PREPARED *in situ*

Sodium ethoxide, prepared *in situ*, removes the bromine

TABLE V—POSSIBLE BROMINATED GLYCERIDES OF THE UNSATURATED ACIDS PRESENT IN LINSEED OIL

NAME	FORMULA	Mol. Wt.	Sap. Value	\u2014PERCENTAGE COMPOSITION\u2014			
				C	H	O	Br
Trilinolenin bromide or hexabromostearin	$(C_{17}H_{29}Br_6COO)_3$ C_3H_5	2312	509.5	29.58	3.98	4.15	62.28
Dilinolenin-linolin bromide	$(C_{17}H_{29}Br_6COO)_2$ $(C_{17}H_{31}Br_4COO)$ $>C_3H_5$	2154	494.9	31.76	4.36	4.46	59.4
Dilinolenin-olein bromide	$(C_{17}H_{29}Br_6COO)_2$ $(C_{17}H_{33}Br_2COO)$ $>C_3H_5$	1996	477.8	34.27	4.81	4.81	56.11
Linolenin-dilinolin bromide	$(C_{17}H_{29}Br_6COO)$ $(C_{17}H_{31}Br_4COO)_2$ C_3H_5	1996	477.8	34.27	4.81	4.81	56.11
Linolenin-linolin-olein bromide	$(C_{17}H_{29}Br_6COO)$ $(C_{17}H_{31}Br_4COO)$ $(C_{17}H_{33}Br_2COO)$ $-C_3H_5$	1838	457.8	37.21	5.33	5.23	52.23
Trilinolin bromide or tetrabromostearin	$(C_{17}H_{31}Br_4COO)_3$ C_3H_5	1838	457.8	37.21	5.33	5.23	52.23
Linolenin-diolein bromide	$(C_{17}H_{29}Br_6COO)$ $(C_{17}H_{33}Br_2COO)_2$ C_3H_5	1680	434.1	40.72	5.95	5.71	47.62
Dilinolin-olein bromide	$(C_{17}H_{31}Br_4COO)$ $(C_{17}H_{33}Br_2COO)_2$ $>C_3H_5$	1680	434.1	40.72	5.95	5.71	47.62
Linolin-diolein bromide	$(C_{17}H_{31}Br_4COO)$ $(C_{17}H_{33}Br_2COO)_2$ C_3H_5	1522	405.5	44.94	6.70	6.31	42.05
Triolein bromide or dibromostearin	$(C_{17}H_{33}Br_2COO)_3$ C_3H_5	1364	370.2	50.15	7.62	7.04	35.19

easily and completely. Oil bromides treated by the Stepanow-Bacon method formed a thick reaction product, and there was no loss of material by spitting. When acidified, it was observed that the fatty bodies which separated were solid, not liquid. It is presumed that the nascent hydrogen not only removed bromine, but reduced the unsaturated acids to stearic acid. No experiments were carried out to verify this, though only an iodine value determination of the separated fatty acids would be required. It is probable that the following reactions take place at the same time:

$$(C_{11}H_{29}Br_1.COO)_2 = C_3H_5 + 32\ H = (C_{17}H_{35}.COO)_3C_3H_5 + 16HBr$$
$$(C_{17}H_{31}Br_4\ COO) \u2014 \qquad\qquad Stearin \qquad\qquad (1)$$
Dilinolenin-linolin Bromide
$$EtONa + HBr = NaBr + EtOH \qquad (2)$$
$$(C_{17}H_{35}COO)_3.\ C_3H_5 + 3\ EtONa = 3\ C_{17}H_{35}.COO\ Na + C_3H_5$$
$$(OEt)_3 \qquad\qquad\qquad\qquad (3)$$
Stearin   Sodium Stearate Triethylin
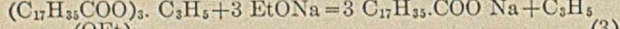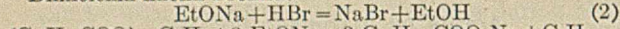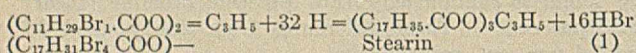
MELTING POINT OF OIL BROMIDES

A number of determinations showed that the melting point was not sharp, which indicated that the oil bromide was not a pure substance. It softened at 130°C., liquefied about 140° to 145°C., and darkened at higher temperatures. A sample recrystallized from carbon tetrachloride melted at 151° (corr.). Hehner and Mitchell give the melting point of their oil bromides as 143.5° to 144°C.

PROPERTIES OF THE CRUDE OIL BROMIDE

Crude oil bromide is an amorphous solid of faintly yellow color, odorless, stable at moderate temperatures, melts at 140° to 145° C., hardening to a waxy solid on cooling, and decomposes on stronger heating. It contains approximately 57 to 58 per cent bromine, and, when moist, decomposes readily in contact with iron (e. g., a spatula) with liberation of bromine. It is moderately soluble in chloroform, carbon tetrachloride, acetone, and acetic acid, slightly soluble in benzene, petroleum ether, and ether, and practically insoluble in alcohol. It is saponified by sodium ethoxide with removal of bromine, and is also saponified by alcoholic potash with removal of bromine, but much less easily. The oil bromide is not a pure substance, but appears to be of fairly uniform composition, depending upon the conditions of preparation.

PURIFICATION OF CRUDE OIL BROMIDES, CONTAINING 57.10 PER CENT BROMINE

Several attempts were made to purify the oil bromide by crystallization. In all the solvents tried, there seemed to be only a slight difference in solubility between the higher bromide and its accompanying lower bromide.

ETHER—The ether-soluble portion had a melting point below 100°C. and contained 55.36 per cent bromine.

CARBON TETRACHLORIDE—A saturated solution of crude oil bromides in hot carbon tetrachloride was filtered hot and allowed to crystallize. The separated precipitate was whirled and washed several times with a mixture of ether and alcohol (2:1), and finally washed with alcohol alone and dried. The crystallized product was almost pure white in color, melting point 151°C., and contained 59.24 per cent bromine. The substance separated from the mother liquor was waxy and tough, but not hard. It contained 55.62 per cent bromine.

ACETONE—Five grams of crude oil bromide were heated with 250 cc. of acetone and filtered. A portion (0.36 g.) which remained undissolved was washed with alcohol and dried. It tested 58.09 per cent bromine. The filtrate was slowly cooled by immersing the flask containing it in a bulk of water at 99°C., which was allowed to cool gradually. The crystalline precipitate was washed in succession with acetone and alcohol and dried. The yield was 1.63 g., and the bromine content was 58.04 per cent. (These recrystallization experiments were interrupted and unfortunately were never completed.)

Various solvents were tried, and the bromine content of the first crop of crystals was estimated, as summarized in the following results:

	Per cent Br.		Per cent Br.
Carbon tetrachloride	59.24	Benzene and ether (1:1)	58.17
Benzene and alcohol (1:1)	58.43	Benzene	57.74
Acetone	58.04	Acetic acid	57.38

COMPOSITION OF OIL BROMIDE

Table V contains a list of the possible glycerides of the unsaturated acids up to linolenic acid, with their calculated percentage composition. It will be observed that the bromine content is likely to give quite as much information as the estimation of carbon and hydrogen.

Hehner and Mitchell suggested tentatively that the composition was dilinolenin-olein bromide, basing their conclusion upon an ultimate analysis, and an average of a number of bromine estimations, 56.12 per cent. They seem to have overlooked the fact that linolenin-dilinolin bromide has also exactly the same percentage composition and also contains 56.11 per cent bromine.

Gemmell[1] considers the composition to be a varying mixture (according to conditions of preparation) of tetrabromostearin and hexabromostearin.

Tetrabromostearin is very easily soluble in ether, so that it is unlikely to be precipitated from an ether solution of oil. It ought also to be comparatively easy to separate the tetra- and hexabromostearins by the action of solvents. In the present recrystallization experiments the maximum.

Analyst, 39 (1914), 297 S; C. A., (1914), 3303.

bromine percentage obtained (on a sample recrystallized from carbon tetrachloride) was 59.24 per cent bromine. Both these figures are a good way removed from hexa-bromostearin (theory 62.28 per cent) and tetrabromostearin (theory 52.23 per cent).

In the writer's opinion it is unlikely that the composition is that of a mere mixture of hexabromostearin and tetra-bromostearin. It seems more probable that the composition is mainly dilinolenin-linolin bromide (theory 59.42 per cent

$$(C_{17}H_{29}Br_6.COO)_2 \atop (C_{17}H_{31}Br_4.COO) {\Large>} C_3H_5$$
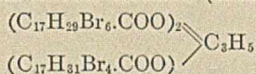
bromine), admixed with some (unidentified) brominated glyceride of lower bromine content. It is not improbable that any mucilage in the raw oil is also carried down by the precipitated oil bromides. In the crystallization experiments, the solutions were generally hazy and required filtration.

The glycerides from which the bromo derivatives in Table V are formed are practically unknown compounds. It would be very interesting to know the comparative drying value of all the glycerides containing linolenic acid. Future investigation on these lines is very desirable.

⁂ Further Experimental Work

Profiting by the experience just recorded, a further series of tests were carried out on Baltic linseed oil, of iodine value 198.5 (Wijs, 2 hrs., 23°C.), varying the ratio of oil to solvent, using 40 cc. of chilled ether (sp. gr. 0.717) as solvent, washing the precipitate twice with 10 cc. of ether, and once with 10 cc. of alcohol. The results are given in Table VI. Bromine was estimated by the Stepanow-Bacon method. It can be seen that as the ratio of oil to solvent increases, the yield of oil bromide increases, and also that the bromine content remains fairly constant. If a graph be made from Table VII, of oil bromide yield and amount of oil taken, it will be found that the points do not form a smooth curve, which fact appears to indicate some differences in the solubility factor.

The mean experimental errors in the oil bromide yields in Table VI are respectively (from 1 to 5 g.) 0.55, 5.16, 1.22, 0.51, and 4.66 per cent. This variable error was considered to be due to the heating up of the tubes by the hand when the precipitate was broken up with ether for washing, thereby increasing the solubility factor of the oil bromide in ether. For this reason it is desirable to cool the tubes in the ice bath after breaking up the precipitate with the wash liquors.

There is just a possibility that some substitution of bromine may have taken place with the greater concentration (12.5 per cent) of the 5-g. tests. It is also possible that an additional ether wash would have given more agreement in the yields. The fact that the bromine content is so close to those of the other tests is compatible only with a greater amount of lower bromides in the precipitate, provided a certain amount of substitution had taken place.

These considerations were borne in mind in framing the proposed method of preparation.

Table VI—Effect of Oil Concentration on Yield of Oil Bromides

Nominal Wt. Oil Grams	Oil Used Grams	Found Per cent	Average Per cent	Found Per cent	Average Per cent	Color of Oil Bromide
1	0.996	63.25	63.6			Nearly white
	1.005	63.86				
2	2.000	65.30	65.1	57.80	57.98	Nearly white
	2.002	63.99		58.03		
	2.007	68.46		58.25		
	2.010	62.77		57.26		
3	3.009	71.02	71.9			Nearly white
	3.013	72.69				
4	4.014	70.70	71.1	57.91	57.93	Nearly white
	4.016	71.46		57.95		
5	4.991	78.08	81.9	57.22	57.30	Yellow
	5.005	85.71		57.37		

Effect of Heating Upon the Constants of Linseed Oil

It is considered of interest to include Table VII, which shows the effect of heat upon the oil bromide yield and other constants of the same No. 50 Baltic linseed oil. Sample L863 was cooked in an open copper pot (i. e., exposed to air) for 1 hr. at 260°C. (Loss, 1.43 per cent.) Sample L903 was cooked in a closed glass flask in an atmosphere of hydrogen for 4 hrs. at 260°C. (Loss, 0.83 per cent.) Expt. L863 was selected from a range of experiments because in specific gravity and refractive index it so closely resembled L903. It will be noted from the figures that the chemical reactions involved are markedly different, according as the heating takes place in the presence or absence of air.

Table VII—Effect of Heat Upon Constants of Baltic Linseed Oil

Oil	Sp. Gr. 15.6° —C. 15.6°	Oil Bromides G. Oil Used	Yield Per cent	Acid Value	Saponification Value	I. V. Wijs 2 Hrs., 23°C.	Refractive Index 20.0°C.	Viscosity "Redwood" sec., 21.1°C.
Raw	0.9373	2.008	66.5	5.1	190.4	198.5	1.4822	206
		2.011	64.6					
		1.003	56.9					
L863	0.9413	0.998	20.2	3.3	190.5	187.7	1.4841	345
		1.006	20.5					
		1.008	19.5					
		1.014	20.5					
L903	0.9414	1.003	2.7	6.0	185.8	184.2	1.4842	428
		2.000	4.4					
		2.011	4.4					

Suggested Method for Oil Bromide Estimation

The method finally proposed is as follows: For the separation use centrifuge and corked tubes and rods, as described above. For solvent and washing use ether (sp. gr. 0.717) which has been saturated at 0°C. with a purified sample of oil bromide (obtained from preliminary experiments). Measure ether and alcohol (sp. gr. 0.820) at 0° to 5°C.

Dissolve 4.00 g. of linseed or other oil in 35 cc. of ether. Cool in an ice bath to 0°C. Add 1.0 cc. of bromine slowly from a 10-cc. stoppered buret, divided into 0.1 cc. and with the orifice constructed so that bromine is delivered slowly when tap is turned full on. While adding the bromine, stir the reaction mixture so as to avoid local rise of temperature. Wash down the top of the tube with 5 cc. of ether. Cork and let stand at 0° C. for 2 hrs. to insure complete bromination. There should be an excess of bromine present after 2 hrs. Whirl the tubes in the centrifuge for 3 min. at 2000 r.p.m. Decant liquor from precipitate. Wash down the tube and rod with 10 cc. of ether, break up precipitate with rod thoroughly, and cool in ice bath for a few minutes. Whirl as before for 3 min. at 2000 r.p.m. Decant liquid. Repeat washing with 10 cc. of ether as before. Cool, whirl, and decant. Give a final washing with 10 cc. alcohol, breaking up precipitate as before, cool, and whirl for 3 min. at 1600 r.p.m. Decant as before, and dry first in air, then in a hot-water oven for 0.5 hr.

precautions—The following precautions should be observed:

1—Keep all temperatures low.
2—Make all measurements carefully, especially of the ether, and weigh the oil to within 1 per cent of quantity stated.
3—Use ether saturated at 0° C. with oil bromide.
4—After breaking up the precipitate in wash liquor, always cool in ice bath before whirling.
5—After the alcohol wash, do not whirl at a greater speed than 1600 r.p.m. If a higher speed be used, the precipitate will pack together and be difficult to dry properly.
6—Avoid the use of acetic acid.

Summary

1—The centrifuge was found to be the most satisfactory

means of separating oil bromides from the reaction mixture, and the volatility of ether proved no drawback.

2—Alcohol (sp. gr. 0.820) used as a final wash liquor removes ether, and yields oil bromides as a loose granular powder when dried.

3—The Stepanow-Bacon method was found to the most satisfactory and accurate of the methods tried for the estimation of bromine in oil bromides.

4—The properties of the crude oil bromide are summarized, and its composition is suggested to be mainly dilinolenin-linolin bromide

$$\begin{matrix} (C_{17}H_{29}Br_6.COO)_2 \\ (C_{17}H_{31}Br_4COO) \end{matrix} \Big\rangle C_3H_5$$
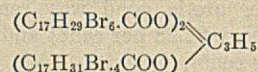
5—A method is given, based on the results of this investigation, which should ensure a maximum yield of oil bromide of maximum purity, and with small experimental error.

The Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution[1]

By E. Twitchell
Wyoming, Ohio

If a hot alcoholic solution of a mixture of fatty acids, such as is obtained from an ordinary fat or oil, is treated with an alcoholic lead acetate solution, also hot, there is no precipitation at first; but on cooling, the lead salts of the solid acids precipitate in a crystalline form, which can be filtered with great rapidity and ease. This simple method of direct precipitation of solid fatty acids, was long ago employed by Jean to separate a portion of the liquid acids and to obtain their iodine value in the examination of lard. It does not seem to be commonly used to separate and estimate the solid fatty acids. The present author, however, much prefers it to the well-known lead-salt-ether method, and has briefly referred to it in some previous publications.

Solubilities of Lead Palmitate and Myristate

The following experiments were made to test the accuracy of the results obtained by this method:

A solution of pure palmitic acid in hot 95 per cent alcohol was treated with an excess of lead acetate dissolved in hot alcohol. This precipitated on cooling and was allowed to cool further over night to a temperature of $16.5°C$. It was then filtered and washed with 95 per cent alcohol. From the precipitate 98.8 per cent of the palmitic acid was recovered.

One hundred cc. of the filtrate, on decomposing with dilute nitric acid and collecting with ether, yielded 0.010 g. of palmitic acid; and 100 cc. of the washings, 0.004 g. of palmitic acid. This shows a sufficient insolubility of lead palmitate, for analytical purposes, in the filtrate, which contains lead acetate and acetic acid, and in the washings, which consist of 95 per cent alcohol.

The same experiment with pure myristic acid showed a solubility of lead myristate at $12°C$., corresponding to 0.0175 g. of myristic acid in 100 cc. of the filtrate, and of 0.0110 g. in 100 cc. of the washings.

A slight impurity of the palmitic and myristic acid would have a considerable effect on the above results, so the solubility found in this way must be considered as a maximum.

The solubilities of lead laurate, eruceate, or iso-oleate have not been determined in this manner; but in most fats and oils palmitic acid would be the solid acid forming the most soluble lead salt, those of the higher saturated acids being less soluble.

Effect of Liquid Fatty Acids

As it seemed possible that the solubility of lead palmitate might be considerably increased by the presence in the solution of the liquid acids found in most fatty acid mixtures, and as the author knew of no way to prove directly the presence or absence of small quantities of solid fatty acids in the liquid acids of the filtrates, the following indirect method was used:

The fatty acids of cottonseed oil contain about 25 per cent of a solid acid, which is almost pure palmitic acid. A hot alcoholic solution of the cottonseed oil fatty acids was precipitated as above with lead acetate *insufficient* to combine with all the palmitic acid. On cooling to $22°$, filtering, and adding to the filtrate a few drops of a dilute alcoholic solution of sulfuric acid, a mere trace of lead was found, while the filtrate obtained after cooling the liquid to $16°$ contained no lead that could be detected with alcoholic sulfuric acid, showing that, with palmitic acid in excess, lead palmitate is practically insoluble at $16°$ in 95 per cent alcohol containing liquid fatty acids, palmitic acid, and a small amount of acetic acid; and it seems probable that, with lead acetate in excess, the lead palmitate would be equally insoluble.

The same experiment was performed with fatty acids containing iso-oleic acid. Sufficient lead acetate was used to combine with all the stearic and palmitic acids, but not enough to combine with all the iso-oleic acid. At $13°$ the filtrate contained the merest trace of lead, showing that lead iso-oleate is practically insoluble under these conditions.

Though the liquid fatty acids can be separated fairly free from solid acids, it has hitherto been found impossible to obtain the solid acids free from liquid acids, either by the method herein described or by the old lead-salt-ether method. Lewkowitsch[1] states that the iodine value of the solid fatty acids obtained by the latter method will, as a rule, be in the neighborhood of 10, provided there is no erucic acid, etc., present, and he quotes a table of Tortelli and Fortini, in which the solid acids of cottonseed oil are given as having an iodine value of 19! If our object were only to determine the amount of solid acids in a mixture, a rough correction might be made for this iodine value; but it is generally very desirable to obtain the solid acids in a pure state so that, for instance, their neutralization value (mean combining weight) can be exactly determined, also their melting points, etc., and finally so that if they have an iodine value this shall indicate not an imperfect separation of liquid acids, but shall prove the presence of *unsaturated solid* fatty acids.

It has been found in using the method described in this paper that the solid acids separated from the lead salt precipitate will have an iodine value generally ranging from 3 to 10 per cent, and no amount of washing of the precipitate will lower this figure. Even ether, in which lead oleate, linolate, etc., are soluble, will wash practically nothing from the precipitate which has been exhausted with alcohol. Evidently there is formed a lead salt containing liquid fatty acid which is quite insoluble in alcohol containing acetic acid and in ether.

[1] "Chemical Technology and Analysis of Oils, Fats and Waxes," 5th Ed., 1, 552.

This residue of liquid acids can, however, be removed from the solid acids by dissolving the latter in alcohol and reprecipitating with lead acetate; or more simply by removing the washed first precipitate from the filter, dissolving in boiling alcohol containing about 0.5 per cent of acetic acid and allowing this to cool, and precipitating again. Two precipitations in all are generally sufficient to reduce the iodine value of the solid fatty acids to 1 per cent or under, a trifling figure.

ANALYTICAL PROCESS IN DETAIL

Weigh in a beaker as much of the fatty acid as is estimated to contain 1 to 1.5 g. of solid acids. In the case of a very liquid oil this amount will be about 10 g., while in the case of tallow it will be only 2 or 3 g. Dissolve in 95 per cent alcohol. Dissolve 1.5 g. of lead acetate in 95 per cent alcohol. The total alcohol for the two solutions should be about 100 cc. Heat both solutions to boiling and pour the lead acetate solution into the solution of fatty acid. Allow to cool slowly to room temperature, and then for several hours, preferably over night, to about 15°C. Filter and test the filtrate for lead with a few drops of an alcoholic solution of sulfuric acid. If there is no precipitate, showing that lead is not in excess, the analysis must be repeated, using less fatty acid or more lead acetate. Wash the precipitate with 95 per cent alcohol until a sample of the washings diluted with water remains clear. Transfer and wash the precipitate from the filter back into the beaker, using about 100 cc. of 95 per cent alcohol. Add 0.5 g. of acetic acid and heat to boiling. The precipitate will slowly dissolve. Allow to cool to room temperature and then to 15°C. as before. Filter and wash with 95 per cent alcohol as before. Transfer the precipitate by washing the filter paper with ether into the beaker. Add sufficient dilute nitric acid to decompose the lead salts. Pour and wash the whole mixture into a separatory funnel and shake. Wash with water until the washings are no longer acid to methyl orange. If a trace of nitric acid should remain with the ethereal solution it will act on the fatty acids in the subsequent drying. Transfer the ethereal solution to an evaporating dish, evaporate, dry, and weigh.

If desired larger quantities of material than those given above can easily be handled.

RESULTS OBTAINED BY METHOD

The figures of the following table are in accordance with the above directions. In each case two precipitations were made as described.

Sample Oils No.	Weight Fatty Acid Grams	Lead Acetate Grams	Alcohol for Each Precip Cc.	Weight Solid Fatty Acids Grams	Per Cent	Iodine Value of Solid Fatty Acids
1. Cottonseed	5	1.5	100	1.1565	23.13	0.72
2. Soy-bean	10	1.5	100	1.7010	17.01	0.85
3. Olive	10	1	100	1.0935	10.93	1.75
4. Peanut	20	3.5	300	3.3165	16.58	0.80
5. Cottonseed	20	4	200	4.8680	24.34	0.56
6. Lard	3	1.25	100	1.2005	40.02	0.58
7. Partly hydrogenated cottonseed	2.5	1.5	100	1.2655	50.62	42.21
8. Tallow	3	1.5	100	1.6085	53.62	4.38

The solid fatty acids of most of the fats and oils in this table have iodine values below 1 per cent.

Sample 7 is a partly hydrogenated cottonseed oil which would contain iso-oleic acid.[1] The iodine value of its solid fatty acids, 42.21, shows a large amount, $\frac{100 \times 42.21}{90} = 46.9$

[1] Moore, *J. Soc. Chem. Ind.*, **38**, (1919), 320t.

per cent of an unsaturated solid fatty acid (iso-oleic acid). To confirm this figure, the solid acids were redissolved in alcohol and reprecipitated with lead acetate as before. The iodine value of the resulting solid acids was 40.07, only slightly below the value found above.

Sample 8 is a sample of beef tallow, the solid fatty acids of which have the comparatively high iodine value of 4.38. On redissolving these solid fatty acids in alcohol and reprecipitating, their iodine value was reduced only to 3.89. This would indicate the presence in tallow of a small amount of an unsaturated solid acid, of which, however, we have no other proof.

If in the above process insufficient lead acetate is used to precipitate all of the solid acids, the precipitation is fractional, and the solid saturated fatty acids of higher molecular weight come down first. In this case liquid acids are not carried down with the solid and a second precipitation is not required. For example:

Thirty g. of peanut-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 12°, yielded 1.6935 g. of solid acids having a mean combining weight of 317.

Thirty g. of olive-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 11°, yielded 1.3770 g. of solid acids having a mean combining weight of 266 and an iodine value of 0.79.

ORGANIZATION OF CHEMICAL SALESMEN

A movement to organize a national association of chemical salesmen was started at a recent meeting of sales representatives of every branch of the chemical industries held at the Chemists' Club. It was felt that there is a broad field for service for an organization composed of members of the sales and advertising staffs, manufacturer's sales agents and executive sales officers of companies in every branch of the chemical industry. It was the unanimous opinion of those present that such an organization should concern itself with the broad commercial problems whose solution would react to the benefit of the entire industry, and that the questions of prices or sales policies of individual companies should not be included. An Organization Committee was appointed, to arrange for a general meeting at the time of the Exposition. This committee was composed of the following: Fred E. Signer, chairman, Butterworth-Judson Corporation; William Haynes, secretary, Drug & Chemical Markets; C. F. Abbott, National Aniline & Chemical Co.;

The Technical Committee on Standardization of Petroleum Specifications held a meeting at the Bureau of Mines in Washington recently to consider a number of changes in the specifications used by the Government for the purchase of kerosene, gasoline, fuel and lubricating oils. Dr. N. A. C. Smith of the Bureau of Mines was chairman of the meeting, and Dr. T. G. Delbridge of the American Society for Testing Materials and the American Petroleum Institute represented the several engineering societies constituting the Advisory Board. It was decided to give further study to the new methods which have been approved by the American Society for Testing Materials before deciding upon their adoption. The methods include the following tests: corrosion, flash, distillation, sulfur, cloud and pour, saponification in place of fatty oil, water and sediment, precipitation, viscosity, and melting point.

Determination of Metallic Aluminium and of Aluminium Oxide in Commercial Metal[1,2]

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One of the most vexatious problems confronting the aluminium industries is the question of determining the oxygen content of aluminium. Considerable evidence is at hand to indicate that this impurity may be present in surprisingly large amounts and that it may exert profound influences on the properties of the metal. But no really dependable and trustworthy method has been developed for its quantitative determination.

A number of methods are in use. Of these the method of Rhodin[3] has been more widely accepted than any other. This is based on the assumption that 10 per cent caustic soda solution dissolves metallic aluminium quantitatively without attacking the oxide which is present. The laboratories of a metallurgical company have proposed a method employing iodine as a reagent for the same kind of a selective attack, and another laboratory recommends 50:50 hydrochloric acid for the purpose. This last method may be modified by adding potassium chlorate.

These four methods were tried out on a large sample of small millings from an ingot of secondary No. 12 alloy (8 per cent copper). This metal was procured from melting down clean borings and was thought to contain a rather high percentage of aluminium oxide. Five-gram samples were exposed for different, specified lengths of time to the action of the reagents.

The results of these determinations, expressed as per cent oxide in terms of Al_2O_3 weighed, are shown in Table I. No agreement among methods is evident here. The length of time of exposure to the reagents appears to exert no definite influence.

TABLE I

REAGENTS	TIME OF ACTION			
	1 Hr.	24 Hrs.	7 Days	35 Days
NaOH	1.9	2.21	2.28	1.68
Iodine	0.09	0.05	0.05	0.06
HCl	0.36	0.15	0.41	None (no ppt.)
HCl + KClO₃	0.05	2.15 (?)	Impossible to filter	0.09

This alloy contained, according to separate analyses:

	Per cent
Fe	1.33
Si	0.59
Cu	8.06
Al_2O_3 plus Al	90.02 (By difference)

Another quite different method developed for the evaluation of aluminium powder[4] makes use of the reducing property of aluminium in a thermite reaction. Lead oxide is reduced by the sample at high temperature, under a flux of borax. Accuracy within 1 per cent is claimed for this method, but the present author has had no success in attempts to put it into practice.

A certain amount of evidence has been cited indicating the existence of an oxide or oxides of aluminium other than Al_2O_3. Rhodin[5] produces evidence of the existence of a compound Al_3O_4. M. Pionchon,[6] in 1893, concluded that aluminium, oxidized directly, produces a compound Al_2O. Duboin[7] believes this Al_2O to be a mixture of $4 Al + Al_2O_3$.

Kohn-Abrest[1] saw the effect of temperature on the degree of oxidation of aluminium powder and concluded that AlO was the final product.

It is possible, also, that elemental oxygen may be present, occluded or dissolved as such. The solubilities of gases in aluminium have not been determined. But for the purposes of this investigation, combined oxygen alone is considered. Because of the strong reducing power of aluminium, it is assumed that no oxide other than one of aluminium can be present.

After a long search for a new method of determining this oxide, the results of which will be published in detail in a later paper, an apparatus and procedure have been de-

veloped which at once permit of rapid, direct determination of aluminium (and of oxide, by difference) and avoid certain potential sources of error in the wet methods mentioned above.
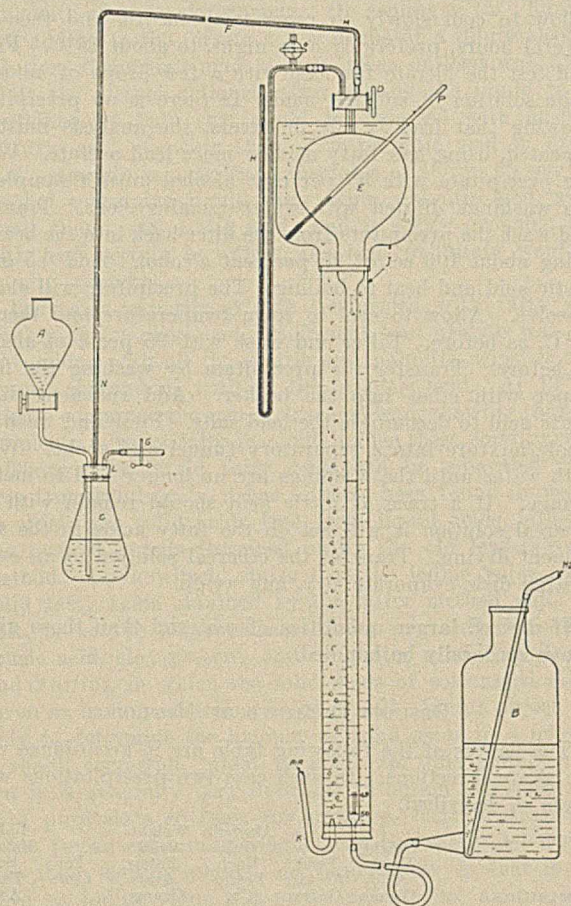
The metal is taken into solution by a reagent, either caustic or acid, under such conditions that all of the hydrogen liberated by the reaction is caught in a measuring buret, where its volume, temperature, and pressure may be read accurately. This gas is equivalent in quantity to the unoxidized aluminium, together with whatever iron is present when an acid reagent is used, or with the silicon, when caustic is used. Whether or not oxide of aluminum

1 Received May 25, 1921.
2 Published by permission of the Director of the Bureau of Mines
3 Trans. Faraday Soc., 14 (1919), 134.
4 H. B. Faber and W. B. Stoddard, THIS JOURNAL, 12 (1920), 576.
5 Loc. cit.
6 Compt. rend., 117 (1893), 328.
7 Compt. rend., 132 (1901), 826.

1 Compt. rend., 141 (1905), 323.

goes into solution is immaterial. If this be Al_2O_3, no gas will result from its solution; if Al_2O_4, for example, it is thought that enough gas will be evolved in its dissolution to correspond with the passage of this "lower oxide" to a compound of the trivalent Al_2O_3.

Apparatus

The apparatus, shown in Fig. 1, consists essentially of a reaction flask, C, connected to the measuring buret, E. Flask C is equipped with a 3-hole rubber stopper, L, which bears the dropping funnel, A, for the admission of the reagent solution, the outlet tube, G, whose use will be spoken of later, and the capillary tube, F, which leads the gas to E for the necessary measurements.

The buret, E, was made from ordinary laboratory equipment. A 750-cc. glass flask was used for the bulb. Its neck was sealed to the top of an accurate 50-cc. buret, such as is used in ordinary volumetric analytical work. To the base of the flask was sealed a 2-way stopcock to connect E with F and with the water manometer, H. Water was used as the confining liquid in E, and its level was controlled by the bottle, B. The water jacket, J, was made from a length of 2-in. glass tubing joined to the mouth of a large reagent bottle, from which the base had been cut. The water in this was kept stirred by a constant stream of air which bubbled up from K.

The first method of reading buret E was simply to raise B until the level of the water in it coincided with that in the buret. This, however, introduced an almost constant error due to capillarity in the latter. Hence the outfit was equipped with the water manometer, H. In a number of runs the buret was read by both these methods for comparison. It was found that from 0.1 to 0.2 cc. error in volume was made in each reading by the first method. The average error in twenty-three such comparisons was 0.16 cc., which correction was applied. All "old" results were recalculated to the basis of the "manometer" reading.

The calibration of the gas measuring device was accomplished as follows: Set up in its water jacket in the position shown in Fig. 1, with conditions exactly the same as those obtaining when in actual use, the gas container was carefully cleaned with strong caustic soda solution and with chromic acid, and rinsed thoroughly with tap water and with distilled water. It was then filled, including cock D, with distilled water saturated with air. After it had stood thus for a couple of hours and had come to the same temperature as the water in the jacket, it was allowed to run out to some point in the graduated portion, through a specially made tube fitted with a cock, into a tared flask, in which it was carefully weighed. After 15 min. (to allow for drainage from the bulb), the water level in the graduated part was read. The temperature of the water was known from that of the jacket.

The weight of water, divided by the density of air-saturated, distilled water, weighed in air against brass weights, gives the volume occupied at the known temperature. From this, the reading of the buret was subtracted, and the resulting volume represented that of the measuring flask to the first, or "zero" graduation.

Three calibrations made according to this procedure gave 778.74, 778.84, and 778.76 cc. The average, 778.78, is called 778.8 for actual use, since the buret can be read with accuracy to only about 0.05 cc.

In order to make unnecessary the careful reading of the barometer once or twice for each run, a compensator, such as is used in Orsat gas analysis equipments, was installed. It had a volume of about 100 cc., contained a little water, and was immersed in the water jacket along with E. It was satisfactory over periods when changes in the temperature of the jacket and in the atmospheric pressure were small, but not at all satisfactory otherwise. Its strange behavior could not be explained, and lest it prove misleading, it was discarded.

It was feared at first that the rather large solubility of hydrogen in water would introduce an error too large to be neglected, and attempts were made to eliminate this source of possible inaccuracy. A strong solution of potassium carbonate, in which hydrogen is soluble to a very limited extent, and the aqueous vapor pressure of which was plotted over a sufficient range of temperature, was tried as the confining liquid in E. This seemed successful enough, but its use was abandoned because its advantages did not compensate for its disadvantages. Distilled water was found to be the best confining liquid, and, when it was kept saturated with hydrogen by a continuous stream of bubbles in B, no loss from solution of the gas under investigation could well take place. Hydrogen has often been kept over water in E over periods of several days duration without suffering any measurable loss.

Procedure

A sample of the aluminium under investigation is weighed into the Erlenmeyer flask, C, with an accuracy of 0.1 mg., and a little distilled water is introduced and brought to a boil over a burner. This drives out what gases may be dissolved in the water and serves to rid the metal sample of air that may be adsorbed thereon. As soon as this has boiled for a few seconds, the flask is almost filled with cold, distilled water (previously boiled to expel all air), its neck is moistened, and it is connected firmly to the stopper, L. Tube G is open. Now, by raising B, E is filled completely with water to a point, M, in the capillary tube. Cock D is now closed. Flask C is filled completely with water from A until its level reaches the stopper, L, and water runs out through G. G is now closed, and preparations for the determination are complete.

A quantity of reagent is admitted to A and allowed to run into C, displacing an equivalent volume of water through G. When gas evolution commences, G is closed, and the increasing volume of gas collecting in C forces solution back into A. This displacement may be accelerated by heating C. A very small amount of gas may be carried out of C suspended in the reagent liquid. But when the operation is carefully performed, it does not amount to enough to introduce any sensible error. When about half the liquid is displaced from C into A, the "free space" formed is deemed sufficient for more rapid gas evolution. So the cock of A is closed, and D is opened. A fresh supply of new reagent is now admitted and the gas evolution may become violent. As this action slows up, C is kept heated by a burner until all action is complete, when, by admitting more liquid from A, all the gas is forced over into E. The liquid of C now stands in F to about the point N. The small capillary, F, is gas filled after the reaction as well as before, so no appreciable error is introduced here.

Cock O is opened, if necessary, to equalize water levels in the manometer, H. With O closed, cock D is next turned to connect E with H, and the water levels of H are again equalized by adjusting the height of B. Now the pressure upon the confined gas in E is identical with the atmospheric pressure of the room.

The level of the confining water in the graduated part of

E is carefully read and recorded, as are also the temperature of the water jacket and the barometric pressure.

After 10 or 15 min. these same adjustments and readings are repeated. By this time drainage of water from the walls of E will have been more thorough, the gas will more certainly have attained the temperature of the jacket, and any supersaturation of it by water vapor will have become relieved by condensation.

Temperature (t) is read to $0.1°C$., pressure (p) is read to 0.1 mm. of Hg, and volume (v) is read to 0.05 cc. The gas is calculated to standard pressure and temperature by applying the formula

$$v \times \frac{p - \text{vapor pressure of water at } t}{760} \times \frac{273}{273 + t} = V.$$

Calculations were made by the use of a table of five-place logarithms.

PROBABLE ERROR

The accuracy of these gas measurements may be judged by the following:

Error in Reading	Resulting Error of Gas Volume (S.T.P.)	Resulting Error of "Per cent Al"
	Cc.	Per Cent
0.1 mm. in barometer	0.1	0.014
0.1° C. in thermometer	0.24	0.034
0.1 cc. in buret	0.1	0.01
TOTALS................	0.44	0.058

This shows the inherent error of the measurement. Other errors may be introduced from other causes unless care is exercised.

If hydrochloric acid is used to act on the aluminium, an amount of HCl may be carried into E with the hydrogen. This would dissolve in the film of water adhering to the walls of E, lower the aqueous vapor pressure of this film, and cause an inaccurate, low reading of gas volume. By the proper choice of reagents, this source of error can be avoided.

As previously stated, the solubilities of gases in aluminium are not known, but some idea of the gas content of the metal is furnished by Gwyer,[1] who found that cast aluminium which showed exceptionally severe blistering after rolling into sheet and annealing contained one-tenth to one-third of its own volume of occluded gas, that the composition of the gas varied exceedingly, and that its chief constituent was hydrogen.

This severe blistering is the result of unusually large amounts of gas being occluded; more gas, that is, than should be looked for in ordinary primary metal such as the sample used in this investigation. However, if the worst conditions which Gwyer cites should obtain in this sample (gas to the extent of one-third the volume of the metal), they would introduce an error too small to alter the results materially.

Thus, the density of Al is about 2.7 and the sample employed in this work is about 0.564 g. Hence the volume of Al used was only 0.21 cc. One-third of this, or 0.07 cc., is of the order of magnitude of the probable error of reading the buret, and could throw the result of a determination in error by less than 0.01 per cent of the sample weight.

The fact that hydrogen is the chief gaseous impurity in aluminium is confirmed by other investigators, notably Guichard and Jourdain[2] and Dumas,[3] though Sieverts[4] states that aluminium does not dissolve hydrogen.

1 In discussion of papers on "Occlusion of Gases by Metals," *Trans Faraday Soc.*, 14 (1919), 254.

2 *Compt. rend.*, 155 (1912), 160.

3 *Compt. rend.*, 90 (1880), 1027.

4 *Elektrochem.*, 16 (1910), 707.

THEORETICAL

The weight of a liter of dry, pure hydrogen at 760 mm. pressure and 0°C. temperature is taken as 0.08994 g. (the value accepted by the U. S. Bureau of Mines). From this, it follows that 1 g. of "100 per cent pure" aluminium should displace 1.24068 liters of hydrogen (27.1 being the atomic weight of aluminium).

If an acid is used as the reagent, the reaction

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

will take place along with the reaction

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)^3 + 3H_2$$

So the hydrogen collected will represent the iron present, as well as the metallic aluminium. If caustic soda is used, it interacts with silicon according to the reaction

$$4NaOH + Si \longrightarrow Na_4SiO_4 + 2H_2$$

In this case, of course, the H_2 represents Si and Al. The amounts of these impurities must be known from separate analyses of the metal. However, these are the substances which are always determined in ordinary analyses of aluminium and, with copper, which is not acted on by either alkalies or nonoxidizing acids, are the chief impurities present.

1 g. Fe liberates 401.34 cc. H_2 (S.T.P.)
1 g. Si liberates 1584.09 cc. H_2

Hydrogen equivalent to the iron present or to the silicon, depending upon the nature of the reagent, is subtracted from V, the total hydrogen reduced to 0°C. and 760 mm. This corrected volume, divided by 1240.7, gives the weight in g. of metallic Al represented, the ratio of which to the weight of the original sample yields per cent metallic Al.

All other constituents (Cu, Fe, Si, and, if necessary, Zn, Mn and Mg) in the sample are known from separate analysis. The difference between the sum of all these plus metallic aluminium and the total weight of the sample is taken as aluminium oxide. This value may represent actual Al_2O_3 or a larger amount of Al in a lower state of oxidation.

CARBIDE AND NITRIDE—The probable presence of aluminium nitride and carbide is not overlooked, although these have not been considered in this work for the reason that the extent of the contamination of the metal used by these substances is very slight.

The attack of the reagent upon the sample would affect these impurities according to the following reactions:

$$4AlN + 6H_2O = 4NH_3 + 2Al_2O_3 \quad\quad (1)$$
$$Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3 \quad\quad (2)$$
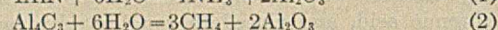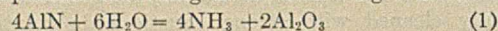
From the former, ammonia would be formed, which, if it passed into the gas measurer, would be readily dissolved in the water, and so would not affect the volume of the hydrogen, unless its amount were too large to be completely dissolved or to leave the aqueous vapor pressure of the water film unaltered. In other words, no gas would be measured from the nitride and this substance would be represented as part of the oxide present.

Reaction 2 shows that carbide will produce methane, which will pass into the measurer and be treated as hydrogen. The amount of aluminium which is in this carbide would, if metallic, produce hydrogen to the extent of just twice the volume of this methane.

Now, since the aluminium in aluminium carbide is roughly seven-tenths of the weight of the carbide, it follows that the error introduced by a given percentage of carbide will be in increasng the apparent percentage of metallic aluminium, and by an amount equal to about one-third of the percentage of carbide in the sample.

Thus, if 3 per cent carbide be present, and gives off, say, 20 cc. of CH_4 (which will be measured as hydrogen with which it is mixed), the same percentage (3) of metallic

aluminium would give 60 cc. So the effect of the carbide will be to increase the apparent metallic aluminium content. The amounts of carbide occurring in commercial metal are so small, however, that this factor may safely be neglected.

DATA

The performance of this apparatus was tried out on a sample of primary aluminium millings from a piece of ingot sent by Mr. J. G. A. Rhodin of H. L. Raphael's Refinery, London, England.

Analysis of this material, made by Mr. Rhodin, showed the following composition:

Per Cent.

Al	98.60
Al₂O₃	0.52 (Rhodin's method)
Fe	0.38
Mn	0.01
Pb	0.02
Cu	0.07
Sn	0.03
Si	0.44
	100.07

Betwen 0.56 and 0.57 g. of this metal were found to furnish enough hydrogen under the conditions of the experiment to fill the measuring device about midway in the graduated section.

A great many runs were made, and some strangely variable results were obtained before it became evident that the treatment of the sample before a determination is an important consideration. Surfaces adsorb quantities of gases. Failure to take this fact into account, or the wrong assumption that such gases are present in or on these millings in amounts too small to introduce an important error, has vitiated a large amount of otherwise good data.

WITH SODIUM HYDROXIDE—The series of results in Table II shows the effect of this adsorbed gas.

The procedure here was to cover the aluminium sample, in its Erlenmeyer flask, with about an inch of cold, air-free (previously boiled), distilled water, and to warm this or boil it over a Bunsen burner as specified below. After a sample had boiled as long as desired, it was immediately chilled by filling the flask with more cold water. Next, the flask was connected in the position of C, shown in Fig. 1, and the determination made as already outlined, caustic soda being used as the reagent.

The average sample, about 0.564 g., contains, according to the analysis, 0.0025 g. Si, which produces 3.93 cc. of hydrogen when oxidized by caustic soda. This volume was subtracted from the total volume of hydrogen produced in each run and the remainder divided by 1241. This result, divided by the weight of the sample, gives the figure (Column 1), which is called "per cent Al."

TABLE II—SODIUM HYDROXIDE AS REAGENT

Run	Sample Wt. Grams	Vol. of H₂ at S.T.P. Cc	I Per cent Al (1241 Value)	Previous Treatment	II Recalculated (1254.1 Value)
104	0.5623	700.85	99.87	Not heated (cold water)	98.83
105	0.5650	704.15	99.86	90 (small amt. of gas)	98.82
106	0.5652	702.83	99.64	90 (vacuum boiled)	98.60
107	0.5672	705.73	99.70	Almost boiled	98.66
108	0.5637	701.13	99.665	Boiled hard 5 sec.	98.63
109	0.5638	701.23	99.66	Boiled hard 15 sec.	98.62
110	0.5666	704.47	99.63	Boiled hard 15 sec.	98.59
111	0.5631	700.15	99.63	Boiled hard 30 sec.	98.59
112	0.5620	698.50	99.59	Boiled hard 1 min.	98.55
113	0.5665	704.49	99.65	Boiled hard 3 min.	98.61
114	0.5621	699.10	99.66	Boiled hard 3 min.	98.62
115	0.5667	704.85	99.67	Boiled hard 15 min.	98.63
116	0.5642	701.57	99.64	Boiled hard 15 min.	98.60
117	0.5650	702.28	99.60	Boiled hard 60 min.	98.56

Numbers 104 and 105 show much higher results than the rest, because the total gas volumes in these runs represent what gas was adsorbed on the sample as well as the hydrogen from the reaction. The average of Runs 108 to 117, inclusive, is close to 99.64 per cent, which is about 0.23 per cent lower than 104 and 105. Thus it would seem that

enough adsorbed gas was present in these two to make an error of 0.23 per cent in a determination. From this it appears that 1 g. of these coarse aluminium millings holds in the neighborhood of 2.9 cc. of gas (air and CO₂) adsorbed.

This is borne out by the chemical analysis of the hydrogen taken from a run in which the sample had not been boiled before treatment. Analysis was made in the gas laboratory of the Pittsburgh Station, Bureau of Mines.

Per Cent.

CO₂	0.16
O₂	0.07
N₂	0.47 (Difference)
H₂	99.3

Total gases other than hydrogen constitute 0.7 per cent of the whole. According to the above figure for adsorbed gas, this sample held 1.65 cc. The volume of the connecting tube, F, which was filled with air before the run, is about 1.5 cc. This total, 3.15, accounts for about 0.45 of the 0.70 per cent impurities. The remaining 0.25 per cent is within the accuracy of the Orsat combustion method, by which the hydrogen was determined in the above gas analysis.

Runs 108 through 117 are taken as indicating the true value of the hydrogen from the main reaction. Their relative constancy over a range of from 5 sec. to 1 hr. of boiling would indicate that no appreciable chemical attack is made upon the metal by boiling water.

Run 106, in which the water was not heated higher than 90°, and in which violent boiling was induced by reducing the air pressure, shows that the simple driving off of gaseous impurities from the metal surface is all that takes place when the sample is treated with boiling water.

The value of 99.64 per cent Al is 1 per cent higher than the actual content as determined directly by Rhodin. Since there is little room for doubt about the volume of the apparatus and about the analysis of the sample, the reason for this discrepancy must be that the wrong value has been used for the volume of hydrogen which will be set free by a unit weight of aluminium.

Calculating back from 99.64 to a basis of 98.60 per cent, it appears that 1 g. of pure aluminium produces 1254.1 cc. of hydrogen, measured at 0° C. and 760 mm. This would indicate 26.81 as the atomic weight of aluminium, a value more than 1 per cent lower than the present accepted value of 27.1. This is as much lower again as is the value (26.963) obtained by Richards and Krepelka,[1] in the latest work on the atomic weight of this element.

Of earlier investigators, Mallet,[2] Thomsen,[3] and Kohn-Abrest[4] used measurements of hydrogen resulting from solution of analyzed aluminium for determining the atomic weight, and all found values close to 27.0. However, none of them took account of the presence of any oxide of aluminium in the samples used. Al was known only by difference. If oxide had really been present in the metal, their results would be too high.

Nicolardot and Robert[5] obtained a value of 1242.89 cc. per g. as the volume given from the reaction of sodium hydroxide on a sample of aluminium of known composition and calculated to a basis of 100 per cent pure metal.

Nicolardot[6] has described an apparatus, somewhat more complicated than the one described herein, by which he

1 J. Am. Chem. Soc., 42 (1920), 2221.
2 Phil. Trans., 181 (1880), 1003.
2 Z. anorg. Chem., 15 (1897), 447.
4 Bull. soc. chim. [3], 33 (1905), 121.
5 Chimie & industrie 2 (1919), 641
6 Bull. soc. chim. [4], 11 (1912), 406.

suggests that aluminium and other metals may be investigated an deven that atomic weights may be determined.

Adopting the figure of 1254.1 cc. as the volume of hydrogen given off by the action of 1 g. of pure aluminium on a reagent, and recalculating the data already shown to this basis, the values in Column II, Table II, are obtained. These are in accord with the careful analysis of Rhodin.

WITH SULFURIC ACID—A series of runs was made with sulfuric acid, which are tabulated in Table III. To the author's surprise, it was found from the hydrogen figures, and also from tests of the filtered reagent solution after the runs, that the acid had dissolved not only the iron, but also the silicon present, oxidizing it to silicic acid. So this "total hydrogen" had to be corrected for the gas from both the iron and the silicon.

Strange to say, these figures vary pretty widely, by 0.5 per cent, but their average is close to that of the runs made with caustic soda. The acid is slow to act on aluminium, and a strong solution must be employed and the temperature kept near boiling by a burner. Even under these conditions a determination is a matter of several hours.

TABLE III—SULFURIC ACID AS REAGENT
(Sample boiled 30 sec. in every case)

Run	Sample Wt. grams	Vol. of H₂ at S.T.P. Cc.	Per cent Al (Corrected for Fe and Si) Basis, 1254. 1Value
137	0.5712	711.20	98.60
138	0.5710	712.60	98.83
139	0.5639	700.27	98.35
140	0.5663	706.18	98.76
141	0.5638	702.70	98.70
142	0.5637	701.67	98.58
143	0.5634	703.25	98.85
144	0.5658	702.73	98.36
145	0.5681	708.13	98.72

AVERAGE........98.64

PRECAUTIONS

This method is by no means "fool proof," but, when operated intelligently and with proper attention to details of manipulation, determinations can be run off at the rate of about two per hour.

Care must be taken to bring the water over the sample to violent boiling before making a determination. This drives off occluded air from the surfaces of the metal particles. It is best to let this boiling continue for perhaps half a minute.

All water used in filling the reaction flask must be boiled before use to free it from all dissolved air.

Close attention must be given during the early stages of a run to prevent any small metal particles from being carried by the reagent solution out of the reaction flask and into the dropping funnel, where its equivalent of hydrogen would be lost to the determination.

The reaction flask must be completely filled with pure water to the exclusion of all air bubbles before the admission of any reagent.

The gas measuring apparatus must be cleaned as often as necessary with strong caustic solution or chromic acid, or both. Otherwise, grease from the stopcock, which is carried into the apparatus, prevents proper drainage of water from the surfaces and interferes with the reading of the meniscus. For such cleaning, the outfit need not be taken apart. A tube may be attached to the lower end of the buret, and through this the cleaning solutions, wash waters, etc., may be taken into the apparatus by suction.

The rubber stopper, L, should be fitted carefully to the reaction flask and tested frequently, lest small leaks develop which would admit air into the flask. When hydrogen is passing into the gas measurer the pressure in the reaction flask is less than atmospheric, so during this time leaks would be inward.

ADVANTAGES OF THIS METHOD

This method and apparatus have the following advantages over other methods which have been used or suggested:

1—RELATIVE SIMPLICITY OF APPARATUS AND MANIPULATION—The entire equipment is assembled from ordinary laboratory glassware and a good glassblower can make the necessary alterations in a couple of hours. When the exercise of proper care in handling becomes habitual, the use of this apparatus is simple and easy.

2—RAPIDITY OF ANALYSIS—When a very active reagent is used, i. e., caustic soda, runs may be made at the rate of about 30 or 40 min. each. With less active reagents, the process is slower.

3—REPRODUCIBILITY OF RESULTS—When metal, reagent, and other factors are kept the same, results will be found to check one another surprisingly closely. The author has made series of runs on a sample of primary metal, with hydrochloric acid, in which as many as ten or twelve consecutive determinations agreed within 0.06 per cent of the total sample weight, which is the probable error of the measurement (see page —). Lack of homogeneity in the metal sample is the most potent cause of wider variations in results.

4—Only one weighing is necessary for a determination. Calculations made with logarithm tables require no more than about 5 min.

5.—The method is applicable over a wide range of metal composition.

DISADVANTAGES

The disadvantages of the method are as follows:

1—It is realized that the accuracy of this method is not subject to rigorous proof. No aluminium of very high purity, known to be free from oxide, is obtainable with which to test it. Also, knowledge of the exact oxide content of the metal at hand and of the composition of such oxide within the metal, is not available further than is shown by Rhodin's own analysis of the metal used, by his own method, a method which is itself based upon assumptions that have never been proved, and for which great accuracy and dependability are not claimed.

2—On account of the peculiar conditions of procedure, this method is not applicable to metal in a fine state of subdivision. The particles should be no smaller than will be retained by a 30-mesh screen; otherwise they are easily carried out of the reaction flask suspended in the reagent solution. Coarse drillings, millings, and turnings are best adapted. The only types of aluminium with which this method could not be used, however, are bronze powder, dust, and grindings. Pig metal, castings, sheet metal and so on, which comprise the vast bulk of the metal of commerce, furnish coarse borings and turnings with ease. So this limitation does not amount to a serious circumscription.

CONCLUSION

Accurate estimation of metallic aluminium (and of oxide, indirectly) in commercial metal may be made by measuring the hydrogen evolved from reaction between it and a reagent.

By the method herein set forth these values can be determined rapidly and easily. There has long been a really great need of such a method, because aluminium is now bought on pecifications based on a "difference" method of analysis, which utterly fails to consider oxide, nitride, carbide, and possibly other impurities which are undoubtedly almost always present. The ordinary analysis calls for determination of copper, iron, and silicon, and the difference is said to be aluminium. As a matter of fact, this ordinary incomplete analysis is inadequate, giving only a superficial idea of metal quality. The present method supplies a long-felt need.

ACKNOWLEDGMENT

A Rapid Method for the Determination of Sodium Chloride in Soap[1]

By H. C. Bennett

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The usual method for the determination of sodium chloride in soap calls for the decomposition of the soap by sulfuric acid, and the volumetric estimation of the sodium chloride by titration with 0.1N silver nitrate, using potassium chromate as an indicator.[2]

When one is called upon to analyze soaps containing a large amount of silicate of soda or insoluble fillers such as silica or talc, this method proves to be somewhat difficult of manipulation. The method described below, however, is not open to this objection and is quick and accurate. For this reason also it is valuable in routine control analyses in soap works laboratories. A complete determination can be easily made in 7 min.

The method depends upon the precipitation of the soap and admixed soluble fillers in a water solution by the addition of magnesium nitrate. The sodium chloride may then be titrated immediately with silver nitrate solution without filtering off the precipitated magnesium soap and other insoluble compounds. The indicator used is potassium chromate.

Magnesium nitrate was selected as the best precipitating agent to use because of the fact that it does not form an insoluble product with the potassium chromate, which is later used as an indicator in the titration. Solubility tables[3] show that magnesium chromate is very soluble in either hot or cold water, whereas calcium chromate is only moderately soluble in cold water, and much less so in hot water. Barium and strontium chromates are insoluble.

The method, in detail, consists of dissolving 5.85 g. of soap in 150 cc. of hot water in a beaker, boiling if necessary to effect solution of all soluble components. The soap and soluble fillers are precipitated out of solution by the addition of 25 cc. of a 20 per cent solution of magnesium nitrate (crystals). Without cooling, the unfiltered mixture is then titrated against 0.1N silver nitrate solution, using a small amount of potassium chromate as an indicator. The appearance of a reddish brown color is the end-point, and the percentage of sodium chloride is read directly from the buret by dividing the number of cubic centimeters by ten (1 cc. = 0.1 per cent).

Results by this method have been checked in this laboratory time after time against the usual standard method and have always agreed to within 0.01 or 0.02 per cent. Cooling the mixture before titrating increases the accuracy of the method. Soaps to which known amounts of sodium chloride were added have also been made in the laboratory, and the analysis by this method gave concordant results.

The author is indebted to Mr. E. L. Northrup, who performed the laboratory work necessary to demonstrate the feasibility of the method.

The Application of the Immersion Refractometer to the Analysis of Aqueus Salt Solutions[1]

By C. A. Clemens

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In the past the immersion refractometer has been little used in the quantitative analysis of inorganic salt solutions, and then largely with solutions containing but a single salt. This fact may be explained by the lack and unreliability of data on refractive indices. Practically all data upon aqueous salt solutions prepared for quantitative work have been worked out and compiled by Wagner.[5] They take the form of tables worked out for definite temperatures, necessitating the accurate control of temperature, which is a serious drawback in ordinary analytical work.

In this paper it is proposed to demonstrate that the immersion refractometer furnishes a very rapid and, at the same time, fairly accurate method for the determination of soluble salts in aqueous solution, both singly and in simple mixtures; and, furthermore, that the use of tables can be avoided by the determination of a constant for each salt, which constant is applicable at ordinary room temperatures.

The Refractive Index Factor

Jones and Getman[6] measured the refractive indices of several solutions, and in every case they found the refractive index to be a linear function of the concentration. Hallwachs[7] and Bender[8] obtained practically a constant value for

$$\frac{n - n_o}{c}$$

where n = refractive index of solution
n_o = refractive index of water at the same temperature
c = grams solute per 100 cc. solution

From the above it is obvious that the value of one division of the immersion refractometer scale expressed in per cent by volume (g. in 100 cc. of solution) is equivalent to the reciprocal of $n - n_o/c$, the values of n and n_o being expressed in terms of the immersion refractometer scale, and that this value is a constant. It should be noted that when p (g. solute per 100 g. solution) is substituted for c, the values obtained increase with increased concentration. Robertson[1] has worked out such a constant for caseinates, while Zwick[2] and Lalin[3] established factors for tannins and starch, respectively. Robertson finds that " the difference between refractive index of the solution and that of water at the same temperature remains appreciably constant." Salt solutions were tested at different temperatures, and it was found that the above statement held true for them as well as for caseinates.

Cheveneau[4] has shown that ionization has no sensible influence on refractive index; Rimbach and Wintgen,[5] that complexes have no measurable effect, while Jones and

[1] Received June 8, 1921.
[2] This Journal, 11 (1919), 785.
[3] Van Nostrand's " Chemical Annual," 4th Ed.
    Received April 2, 1921.
    Über quantitative Bestimmungen wässeriger Lösungen mit dem Zeiss"schen Eintauchrefraktometer," Sonderhausen, 1907.
[6] Am. Chem. J., 31 (194), 303.
[7] Wied. Ann., 47 (1892), 380.
[8] Ibid., 39 (1890), 90.

[1] J. Phys. Chem., 13 (1909), 469.
[2] Chem.-Ztg., 32 (1909), 405.
[3] Z. ges. Brauw., 32 (1910), 231.
[4] Z. physik. Chem., 74 (1910), 233.
[5] Compt. rend., 150 (1910), 866.

TABLE I.—THE EFFECT OF TEMPERATURE CHANGE UPON $n-n_0$

Formula of Salt.	Per cent of Salt.	$n-n_0$ Expressed in Immersion Refractometer Scale Divisions			
		18°C.	20°C.	23°C.	25°C.
NaCl	0.68	3.00	3.04	3.02	3.07
	6.66	29.75	29.68	29.65	29.62
$K_2Cr_2O_7$	2.01	9.38	9.35	9.38	9.39
	10.00	46.70	46.70	46.70	46.67
$Na_2S_2O_3$	1.79	9.37	9.43	9.37	9.31
	11.54	59.98	60.82	60.35	60.45
$MnCl_2$	1.51	8.47	8.39	8.35	8.51
	6.71	37.51	37.50	37.45	37.52
$KClO_3$	1.05	2.20	2.15	2.19	2.18
	5.13	10.69	10.72	10.70	10.68
$AgNO_3$	5.19	14.05	14.07	14.03	14.00
	10.45	28.26	28.21	28.19	28.17
$CaCl_2$	2.23	12.89	12.90	12.93	12.89
	7.06	40.80	40.81	40.79	40.82

Getman[1] find no effect due to hydration. The analytical data which follow later in the present paper tend to confirm the above work.

The foregoing establishes the fact that $c/n - n_0$ is, for all practical purposes, a constant independent of temperature and unaffected by dissociation, hydration, and the formation of complexes. This constant represents the per cent by volume of salt equivalent to one division of the immersion refractometer scale. Several of these constants have been worked out and are shown in the following table:

TABLE II.—REFRACTIVE INDEX FACTORS

NaCl	0.224	$AgNO_3$	0.370
K_2CrO_4	0.183	KNO_3	0.422
KI	0.298	$BaCl_2$	0.264
$Na_2S_2O_3$	0.191	$CaCl_2$	0.173
$MnCl_2$	0.179	$Cu(C_2H_3O_2)_2$	0.264
$K_2Cr_2O_7$	0.214	$HgCl_2$	0.448
NH_4NaHPO_4	0.206	$K_4Fe(CN)_6$	0.191
$KClO_3$	0.479	K_2SO_4	0.321
$MgSO_4$	0.186	$(NH_4)_2C_2O_4$	0.201
$Zn(C_2H_3O_2)_2$	0.242		

TABLE III.—DETERMINATION OF A SINGLE SALT IN AQUEOUS SOLUTION BY THE IMMERSION REFRACTOMETER

Formula of Salt	Refractive Index		Per cent. of Salt.		
	Water	Solution	Present	Found	Difference
NaCl	14.70	17.70	0.68	0.68	0.00
K_2CrO_4	13.98	27.73	2.50	2.52	+0.02
KI	14.20	18.60	1.33	1.31	-0.02
$Na_2S_2O_3$	14.50	50.21	6.84	6.82	-0.02
$MnCl_2$	13.98	51.00	6.71	6.63	-0.08
$K_2Cr_2O_7$	14.10	37.57	5.05	5.02	-0.03
NH_4NaHPO_4	14.34	46.43	6.69	6.67	-0.02
$KClO_3$	13.81	18.11	2.06	2.06	0.00
$Zn(C_2H_3O_2)_2$	14.20	33.30	4.59	4.62	+0.03
$AgNO_3$	14.15	42.41	10.45	10.46	+0.01
KNO_3	14.08	30.60	7.06	6.97	-0.09
$BaCl_2$	14.32	22.61	2.17	2.19	+0.02
$CaCl_2$	14.30	44.25	5.21	5.18	-0.03
$Cu(C_2H_3O_2)_2$	14.21	25.71	3.01	3.04	+0.03
$HgCl_2$	14.13	25.39	5.00	5.04	+0.04
$K_4Fe(CN)_6$	14.33	64.48	9.61	9.58	-0.03
K_2SO_4	14.33	23.95	3.07	3.09	+0.02
$(NH_4)_2C_2O_4$	14.46	30.94	3.34	3.31	-0.03

APPLICATION OF METHOD

SINGLE SALT—The concentration of all solutions used in the following work is expressed as per cent by volume (g. solute per 100 cc. solution). All solutions were made up at 20°C. No temperatures were read while taking the refractive indices; instead, controls of distilled water were kept in the bath at the same temperatures as the solutions. Unless otherwise stated, refractive index refers to the immersion refractometer reading. In all calculations the anhydrous form of the salt was used. It is assumed that the salts are known qualitatively in every case.

Tables may be conveniently used in the methods described in this paper. If the table is prepared for temperature t and it is desired to work at temperature t', the readings may be corrected by subtracting the refractive index of water at t' from the refractive index of the solution at t' and adding the refractive index of water at t, thus obtaining the reading of the solution at the temperature t.

MIXTURES OF TWO SALTS, ONE OF KNOWN AND ONE OF UNKNOWN CONCENTRATION—The percentage of the salt of known concentration divided by its refractive index factor gives in terms of scale divisions the effect on the refractive index due to that salt. When this value is subtracted from the refractive index of the solution containing the two salts, the remainder is equivalent to the refractive index of the salt of unknown concentration in aqueous solution, and the percentage of salt present is determined in the manner explained before. Table IV gives illustrations of this application.

MIXTURE OF TWO SALTS, BOTH OF UNKNOWN CONCENTRATION—The procedure in this case is based upon that used by Leach and Lythgoe[1] in determining methanol in the presence of ethyl alcohol. This involves the use of the specific gravity or density of the solutions, and again we find a great lack of reliable data. However, it was found that a factor similar to the refractive index factor could be worked out. The specific gravities at 20°C./4°C. of various solutions were taken, and the value for water (0.99823) was subtracted. The values thus obtained were then divided by the respective percentages (by volume) of salt in the solutions. This gave the effect of the addition of 1 per cent of salt upon the density of the solution at 20°C. Table V gives several of these constants.

TABLE V.—DENSITY FACTORS FOR 20°C.

NaCl	0.00700	$AgNO_3$	0.00820
K_2CrO_4	0.00782	KNO_3	0.00602
KI	0.00718	$BaCl_2$	0.00606
$Na_2S_2O_3$	0.00791	$CaCl_2$	0.00753
$MnCl_2$	0.00821	$Cu(C_2H_3O_2)_2$	0.00585
$K_2Cr_2O_7$	0.00675	$HgCl_2$	0.00817
NH_4NaHPO_4	0.00773	$K_4Fe(CN)_6$	0.00652
$KClO_3$	0.00613	K_2SO_4	0.00778
$MgSO_4$	0.01055	$(NH_4)_2C_2O_4$	0.00470
$Zn(C_2H_3O_2)_2$	0.00655		

TABLE IV.—DETERMINATION OF ONE SALT IN A MIXTURE OF TWO SALTS BY MEANS OF THE IMMERSION REFRACTOMETER, THE SECOND SALT BEING DETERMINED BY OTHER MEANS

Salt of Known Concentration						Salt of Unknown Concentration.				
Refractive Index				Amount Present,	Calculated Effect on		Effect on Ref. Index	Amount Present,	Amount Found,	
Water.	Mixture.	Diff.	Formula	Per cent	Ref. Index	Formula	Due to	Per cent	Per cent.	Diff.
13.48	60.70	47.22	NaCl	4.67	20.85	K_2CrO_4	26.37	5.00	4.83	-0.17
13.98	38.00	24.02	NaCl	2.33	10.40	K_2CrO_4	13.62	2.50	2.49	-0.01
14.23	28.83	14.60	NaCl	1.40	6.25	K_2CrO_4	8.35	1.50	1.53	+0.03
14.39	33.42	19.03	NaCl	1.17	5.22	K_2CrO_4	13.81	2.50	2.53	+0.03
14.39	39.29	24.90	NaCl	3.74	16.70	K_2CrO_4	8.20	1.50	1.50	0.00
13.91	32.84	18.93	$Na_2S_2O_3$	1.95	10.21	KI	8.72	2.77	2.60	-0.17
13.91	29.27	15.36	$Na_2S_2O_3$	0.99	5.18	KI	10.18	3.09	3.03	-0.06
13.91	39.18	25.27	$Na_2S_2O_3$	3.96	20.73	KI	4.54	1.27	1.35	+0.08
13.88	36.79	22.91	$MnCl_2$	3.35	18.72	KI	4.19	1.27	1.25	-0.02
14.00	29.30	14.70	$MnCl_2$	1.16	6.48	KI	8.22	2.58	2.45	-0.13
14.05	31.18	17.13	$Na_2S_2O_3$	2.04	10.68	$MgSO_4$	6.45	1.20	1.20	0.00
14.05	42.74	28.69	$Na_2S_2O_3$	1.02	5.34	$MgSO_4$	23.35	4.34	4.34	0.00
15.15	25.43	10.28	$AgNO_3$	2.61	7.05	KNO_3	3.23	1.28	1.36	+0.08
15.15	24.75	9.60	$AgNO_3$	1.35	3.65	KNO_3	5.95	2.50	2.51	+0.01
14.40	23.37	8.97	$(NH_4)_2C_2O_4$	0.73	3.64	K_2SO_4	5.33	1.70	1.71	+0.01
14.40	25.00	10.60	$(NH_4)_2C_2O_4$	1.67	8.31	K_2SO_4	2.29	0.77	0.74	-0.03

[1] Loc. cit.

[1] J. Am. Chem. Soc., 27 (1905), 964.

The density of a solution at 20°C. can be calculated by means of these factors by multiplying the factor by the percentage of the salt and adding 0.99823. By reversing this process the percentage of salt can be found from the density.

Knowing the refractive index of the solution and of water at the same temperature and the specific gravity of the solution at 20°C./4°C., the percentage by volume of the two salts can be calculated as the following illustration shows:

CALCULATION OF THE AMOUNT OF POTASSIUM IODIDE AND SODIUM THIOSULFATE IN AN AQUEOUS MIXTURE

OBSERVED DATA:

Specific gravity 20°/4°.......................... 1.02797
Immersion refractometer reading of mixture.........29.27
Immersion refractometer reading of water..........13.91

The observed specific gravity minus the specific gravity of water,

$$1.02729 - 0.99823 = 0.02974,$$

divided by the respective specific gravity factors of the salts (Table V), gives the percentage concentration of single salt solutions having the same specific gravity as the mixture.

0.02974/0.00718 = 4.14 per cent. potassium iodide
0.02974/0.00791 = 3.74 per cent sodium thiosulfate

The per cent. of salt calculated from the specific gravity divided by the appropriate refractive index factor (Table II),

$$4.14/0.298 = 13.90$$
$$3.74/0.191 = 19.56$$

upon the addition of the observed reading for water, gives the refractive index readings of single salt solutions having the same specific gravity as the mixture.

13.90 + 13.91 = 27.81, refractometer reading for KI
19.56 + 13.91 = 33.47, refractometer reading for $Na_2S_2O_3$

The difference in refractometer readings of the respective salts,

$$33.47 - 27.81 = 5.66$$

divided into the difference between the observed refractometer reading and the reading for sodium thiosulfate alone,

$$33.47 - 29.27 = 4.20$$

gives the proportion of potassium iodide in the mixture taken as unity.

4.20/5.66 = 0.742 potassium iodide
1.000 - 0.742 = 0.258 sodium thiosulfate

Referring back to the possible content of each salt calculated from the specific gravity, and multiplying each by their respective proportional parts just found, we have:

4.14 × 0.742 = 3.07 per cent potassium iodide
3.74 × 0.258 = 0.96 per cent sodium thiosulfate
_____
4.03 per cent total salts.

If the products of the refractive index and specific gravity factors lie close together, an error in the determination of refractive index or specific gravity causes a larger error in the final result than if they lie farther apart. The above method offers a rapid means of analyzing some mixtures which cause considerable difficulty when determined by ordinary analytical methods. Table VI gives a summary of a large number of determinations made by the above method. The range of concentration of the components is shown, as well as the maximum and minimum variation of the results from the truth.

TABLE VI

Combinations of Salts Used	Range of Concentration of Components		Difference Between Concentration Found and that Known to be Present	
	Max. Per cent	Min. Per cent	Max. Per cent.	Min. Per cent
K_2CrO_4+NaCl 5.00		1.17	—0.18	+0.01
KI+$Na_2S_2O_3$ 3.96		0.99	—0.21	+0.01
NaCl+KI 2.85		0.94	+0.08	—0.03
K_2CrO_4+$Na_2S_2O_3$ 5.00		0.99	+0.06	0.00
$MnCl_2$+KI 3.35		1.16	+0.11	—0.04
$NaNH_4HPO_4$+$Na_2S_2O_3$ 2.36		0.99	+0.17	+0.01
K_2CrO_4+$K_2Cr_2O_7$ 5.00		1.00	+0.14	+0.07
$KClO_3$+$K_2Cr_2O_7$ 2.56		1.03	—0.04	+0.02
$MgSO_4$+$Na_2S_2O_3$ 4.34		1.02	—0.13	+0.04
$Zn(C_2H_3O_2)_2$+$KClO_3$ ..1.75		0.65	+0.08	—0.02
KNO_3+$AgNO_3$ 2.61		1.28	+0.33	—0.21
$BaCl_2$+$CaCl_2$ 2.61		1.08	+0.6	—0.03
$Cu(C_2H_3O_2)_2$+$HgCl_2$ ...2.50		1.00	+0.02	0.00
$K_4Fe(CN)_6$+K_2SO_4 ....2.41		0.77	+0.06	—0.01
$(NH_4)_2C_2O_4$+K_2SO_4 ....1.70		0.73	—0.04	0.00

MIXTURE OF THREE SALTS, ONE OF KNOWN CONCENTRATION AND TWO OF UNKNOWN CONCENTRATION—The method of calculation is best illustrated by an example.

CALCULATION OF THE AMOUNT OF SODIUM CHLORIDE AND MAGNESIUM SULFATE IN THE PRESENCE OF A KNOWN AMOUNT OF SODIUM THIOSULFATE

OBSERVED DATA:

Specific gravity, 20°/4°.......................... 1.04366
Immersion refractometer reading of mixture........40.92
Immersion refractometer reading of water..........14.49
Concentration of sodium thiosulfate, per cent........ 2.04

The percentage of the salt of known concentration divided by its refractive index factor (Table II),

$$\frac{2.04}{0.191} = 10.68$$

gives in terms of scale divisions the effect on the refractive index due to the salt. This value subtracted from the observed refractive index,

$$40.92 - 10.68 = 30.24$$

yields a value equivalent to the reading of a solution containing only the two unknown salts in the same ratio and concentration as they occur in the above mixture.

The percentage of the salt of known concentration multiplied by its specific gravity factor (Table V),

$$2.04 \times 0.00791 = 0.01624$$

gives its effect upon the specific gravity. This value subtracted from the observed specific gravity,

$$1.04366 - 0.01624 = 1.02742$$

gives the gravity of the mixture as it would be provided the salt of known concentration were not present.

Using the calculated figures (refractive index, 30.24 and sp. gr. 1.02742), the percentage of the two salts of unknown concentration can be calculated in the manner illustrated for a mixture of two salts, both of unknown concentration.

The above method was employed by the author in analyzing the soluble portion of some " egg laying " tablets, which consisted of potassium chromate, sodium chloride, and magnesium sulfate. Another example of the application of this method was a stock tonic which consisted of sodium chloride, sodium thiosulfate, and magnesium sulfate. Table VII gives a summary of several determinations made by the above method. The range of concentration of the components is shown, as well as the maximum and minimum variation of the results from the truth.

TABLE VII

Combinations of Salts Used, the Quantity of the First Salt Named Being Known in Each Case	Range of Concentration of Components		Difference Between Concentration Found and that Known to Be Present	
	Max. Per cent	Min. Per cent	Max. Per cent	Min. Per cent
$Na_2S_2O_3$+NaCl+$MgSO_4$ 2.17		0.92	+0.14	+0.05
$Na_2S_2O_3$+NaCl+KI 2.41		0.61	—0.09	+0.02
NaCl+$MgSO_4$+K_2CrO_4 ......2.30		1.15	—0.15	—0.11
$AgNO_3$+KNO_3+$KClO_3$ 3.00		0.69	+0.14	+0.01
$MnCl_2$+$BaCl_2$+$CaCl_2$ 2.49		1.04	+0.14	+0.04

The statement has been made earlier in this paper that the methods described are very rapid; consequently some statement of the time consumed by an analysis might be of value. A brief statement is given to show the average working time for the methods described in this paper, not including, however, time consumed by any volumetric or gravimetric determinations necessary to determine the concentration of the salt assumed to be known before the methods described are applicable. No account is taken of the time necessary to bring the solutions to constant temperature, as this requires little or no attention from the analyst. The estimation includes time consumed in calculation. In any case where only the refractive index is desired the time consumed should not exceed 10 min. When both the refractive index and specific gravity are to be determined, the time should not exceed 25 min. Both of these estimates are liberal, and the probabilities are that still less time than that stated would be sufficient.

SUMMARY

Methods have been worked out for determining the per

cent by volume (g. per 100 cc. of solution) of salts in aqueous solution by the aid of the immersion refractometer. The methods are applicable to single salts; mixtures of two salts, one of known and one of unknown concentration; mixtures of two salts, both of unknown concentration; mixtures of three salts, one of known and two of unknown concentration.

The per cent by volume of salt in aqueous solution necessary to cause a change of one scale division on the immersion refractometer has been worked out for several salts.

The effect of 1 per cent by volume of salt upon the density of an aqueous solution at 20°C. was determined for several salts.

Influence of Certain Organic Accelerators on Vulcanization of Rubber[1]

By George Stafford Whitby and Osman James Walker

McGill University, Montreal, Canada

The experiments recorded in this paper refer to the influence of 1 per cent of (a) piperidine piperidyl-dithiocarbamate,[2] (b) hexamethylenetetramine, and (c) thiocarbanilide on the rate of vulcanization of a 90:10 rubber-sulfur mix and on the tensile properties, vulcanization coefficients, and aging qualities of the vulcanizates produced.

The rubber employed was pale Hevea crêpe. The stocks were sheeted out to a thickness of about three-sixteenths of an inch.[3] Vulcanization was done in an oil bath provided with suitable stirring arrangements.[4] The rubber was enclosed in a mold consisting of two steel plates, the upper plate being 0.5 in., and the lower one, which contained a cavity for the reception of the rubber slab, being 0.8 in. thick. The upper and lower parts of the mold were fastened together by means of ten bolts and nuts, a thin gasket of lead foil and a small amount of a litharge-glycerol paste being used to secure oil-tightness. In order to allow for the heating up of the mold, the oil was raised, before the mold was introduced, to a temperature 20° above that at which it was desired to carry out the vulcanization.

After vulcanization, two dumb-bell test pieces were cut from each slab. One of these pieces was subjected to a tensile test after 3 days and the other 7 mo. later. For carrying out the tensile tests, sliding steel wedge-shaped grips, short enough to allow of the ends of the test piece projecting beyond the grips, were employed.[1] The dead weight method was used for applying the load. The loading was done in a uniform manner, measurements of elongation being made, on gage lines,[2] at definite intervals. Stress-strain curves were plotted.

The results obtained are shown in the accompanying tables and figures. The main series of vulcanizations on each mix was done at 141° (40 lb. steam). In the case of the control mix and of the mixes containing hexamethylenetetramine and thiocarbanilide, respectively, vulcanizations were also carried out at a higher temperature, viz., 148° (50 lb. steam). In the case of the mix containing the piperidine salt, a second series of vulcanizations was carried out at a lower temperature, viz., 130° (25 lb. steam), the rate of vulcanization being too high to allow of accurate experiments at 148°.

P_B represents the breaking stress in lb. per sq. in.; L^B the percentage length at break; $P_B \times L_B$ /100, the tensile

product divided by 100, i. e., the breaking stress referred to the cross section at failure, on the assumption that the volume remains unchanged; L_{750}, the percentage length at a load of 750 lb. per sq. in.; V. C., the vulcanization coefficient.

The stress-strain curves are shown only from a point corresponding to a length of about 400 per cent, as the later portion of the curve is the portion which can be determined most accurately and is all that is necessary in order to obtain the desired information as to relative rate of curve, breaking points, etc. The curves referring to tensile tests made 3 days after vulcanization are drawn with unbroken lines; those referring to tensile tests made after aging 7 mo. with broken lines. L_{750} forms a convenient reference point, the figures corresponding to which enable the relative positions of curves corresponding to different periods of vulcanization and the shifting of the curves on aging to be read easily.

TABLE I.—CONTROL (90 PARTS RUBBER : 10 PARTS SULFUR).

	TIME, Min.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V. C.		P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V.C
							After Aging 7 mos.					
				At 141°								
A	120	875	970	8487	951	2.27	A¹	1040	930	9672	888	2.56
B	150	1160	930	10788	866	3.27	B'	1285	880	11335	813	3.59
C	180	1290	875	11288	800	4.31	C'	1280	827	10585	754	4.26
D	210	Brittle (broke at 150 lb/sq. in.)				4.97						
				At 148°								
E	75	930	950	8835	913	2.97	E'	1070	895	9576	836	3.23
F	90	1251	880	11008	802	4.41						

TABLE II.—CONTROL + 1 PER CENT PIPERIDINE PIPERIDYL-DITHIO-CARBAMATE)

	Min. TIME,	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V.C.		P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}	V.C.
							After Aging 7 mos.					
				At 141°								
G	10	1125	913	10271	848	1.88	G'	1500	878	13170	779	2.03
H	15	1220	903	11017	827	2.09	H'	1457	853	12428	745	2.43
I	17.5	1315	870	11440	795	2.70	I'	1420	815	11570	730	2.91
J	22.5	1525	836	12760	744	3.65	J'	1803	805	14510	683	4.00
K	25	1870	845	15801	723	3.72	K'	1841	785	14452	661	4.15
L	30	1826	824	15047	702	4.40	L'	1738	751	13053	634	4.73
				At 130°								
M	45	1291	902	11644	830	2.60	M'	1302	872	11353	798	2.89
N	60	1657	874	14481	776	3.00	N'	1672	836	13978	740	3.55
O	75	1687	820	13834	723	3.73	O'	1769	804	14224	690	4.33
P	90	1654	800	13232	706	4.59	P'	2040	803	16381	666	5.10

TABLE III.—(CONTROL + 1 PER CENT. HEXAMETHYLENETETRAMINE)

	TIME, Min.	P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{75}	V. C.		P_B	L_B	$\frac{P_B \times L_B}{100}$	L_{750}
							After Aging 7 mos.				
				At 141°							
Q	30	745	940	7000	940	3.64					
R	60	1148	959	11010	910	4.76					
S	75	1070	928	9929	884	5.28	S'	1292	880	11370	808
T	90	1312	935	12267	873	5.41	T'	1290	880	11352	808
U	105	1330	925	12302	862	5.69	U'	1362	865	11781	786
V	120	1336	910	12158	844	5.79	V'	1440	867	12485	778
				At 148°							
W	30	1087	970	10544	916	4.71					
X	45	1523	960	14621	880	5.32	X'	1500	880	13200	790
Y	60	1413	900	12717	823	6.07	X'	1350	835	11272	749

TABLE IV.—(CONTROL + 1 PER CENT. TH OCARBANILIDE)

						After Aging 7 mos.			
TIME, Min.	P_B	L_B	$\dfrac{P_B \times L_B}{100}$	L_{750}	V. C.	P_B	L_B	$\dfrac{P_B \times L_B}{100}$	L_{750}

At 141°

I	120	680	920	6256	(930)	5.08	1′	686 800	5488(813)	
II	150	1050	937	9839	891	3.98	II′	1243 856	10640 789	
III	180	1274	910	11593	819	4.87	III′	1390 847	11774 754	
IV	195	1270	868	11024	791	5.21	IV′	1126 890	9098 737	
V	210	Brittle (broke at 285 lb/sq.in.)				6.02	V′	Brittle broke at 228 lb/sq.in.		

At 148°

VI	75	940	935	8780	901	3.41	VI′	1119 878	9824 821	
VII	90	1118	890	9950	834	4.53	VII′	1485 860	12740 760	
VIII	105	1270	850	10790	773	5.21	VIII′	1272 770	9563 700	
IX	120					5.58	IX′	Brittle (broke at 240 lb/sq.in.)		

DISCUSSION OF RESULTS

CONTROL—The optimum cure at 141° is obtained at about 180 min. The maximal tensile strength shown by the rubber is lower than that usually shown in tests with first latex rubber, probably owing, in part at least, to the circumstance that the cross section of the test pieces used (½ x 3/16 in.) was greater than usual. On aging the vulcanizates, the breaking points, the position of the stress-strain curves, and the magnitude of the vulcanization coefficients alter in a normal manner. The downward movement of the stress-strain curve on aging appears to be noticeably slower than that found by de Vries and Hellendoorn[1] in aging experiments at tropical temperatures with rubber samples cured, with 7.5 per cent of sulfur, at 148°.

Comparing vulcanization at 148° with vulcanization at 141°, it may be noticed that the curve for F (90 min. at 148°) is almost coincident with that for C (180 min. at 141°), showing that an increase in temperature of 7° roughly doubles the rate of vulcanization.
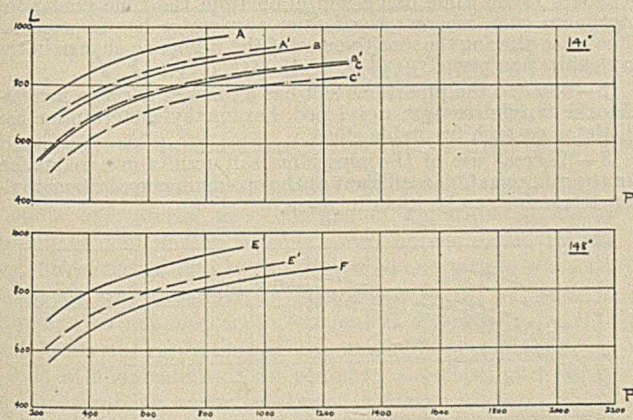
FIG. 1—VULCANIZATION OF CONTROL (90 RUBBER : 10 SULFUR) AT 141° AND AT 148°

PIPERIDINE PIPERIDYL-DITHIOCARBAMATE. *Rate of Cure*— The optimum period of cure at 141° may be considered as being 25 min. Hence the " acceleration factor "[1] of the piperidine salt may be considered as 180/25, *i. e.*, 7. Comparison of the vulcanization results at 130° with the results for the control at 148° shows that 1 per cent of the piperidine salt leads to vulcanization in a shorter period of time at 130° (25 lb. steam) than in its absence is required at 148° (50 lb. steam). (The optimum time at 130° may be taken as 75 min.)

Tensil Properties—The accelerator has an important effect in increasing the tenacity developed by the rubber on vulcanization, the maximal breaking stress developed (1870 lb. per sq. in.) being 45 per cent greater than that developed by the control (1270 lb. per sq. in.). The accelerator, however, reduces the extensibility. It has the further

[1] *Arch. Rubbercultuur*, 4, 1920, 429.
[2] Compare Twiss and Brazier, *J. Soc. Chem. Ind.*, 39, 1920, 125.
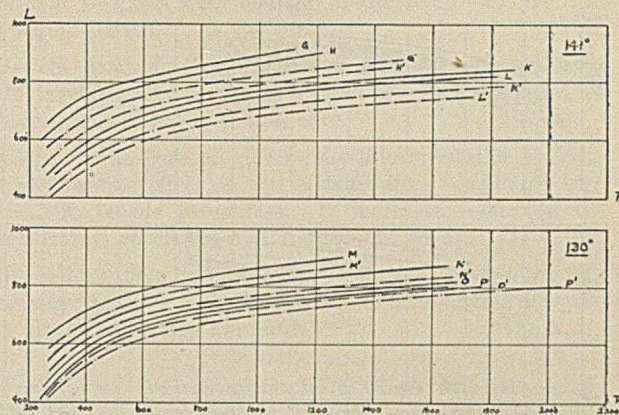
FIG. 2—VULCANIZATION WITH 1 PER CENT PIPERIDINE PIPERIDYL-DITHIO-CARBAMATE AT 141° AND AT 130°

effect of bringing the optimum stress-strain curve into a lower position on the paper, L_{750} being 723 in the presence of the accelerator and 800 in its absence. These noteworthy effects of the accelerator, leading to a lower but longer stress-strain curve, may readily be seen by comparing Curve K, Fig. 2, with Curve C, Fig. 1.

Coefficient of Vulcanization—The vulcanization coefficient at the optimum cure is somewhat reduced by the accelerator (3.72:4.31).

Aging—The aging qualities of vulcanizates prepared with the aid of the accelerator appear to be normal. They do not differ in any essential respect from those of the control or from those of rubber-sulfur vulcanizates in general as studied by deVries and Hellendoorn.[1] There is no evidence of the use of this vigorous accelerator leading to rapid deterioration. The curves move in a normal manner, and, if anything, at a slower rate than in the case of the control. In all cases L_B falls; P_B shows no serious falling off, and, in cures short of the optimum, it rises.

It is of interest to compare the effects of piperidine piperidyl-dithiocarbamate with those of other powerful accelerators for which data have been published. The dithiocarbamate prepared from piperidine, when tested in a mix containing rubber and sulfur only, is by no means as powerful as Cranor's results[2] show the corresponding compound prepared from dimethylamine to be when tested in a mix containing zinc oxide in addition to rubber and sulfur. Quite possibly, however, the piperidine compound would prove to be similar to the dimethylamine compound in its degree of activity if it were tested in the presence of zinc oxide. The results obtained with the piperidine compound in the absence of zinc oxide agree with the results obtained by Cranor with the dimethylamine compound in the presence of zinc oxide in the following respects: In both cases the accelerator raises the maximal breaking stress attainable, and this maximum corresponds to a lower stress-strain curve. They differ in the following respects: (1) According to Cranor's data, the dimethylamine compound does not reduce the ultimate elongation; (2) whereas the vulcanization coefficient at the optimum cure is very greatly reduced by the presence of the dimethylamine compound, it is reduced only to a comparatively small extent by the piperidine compound. This last difference is not unexpected, in view of the much greater degree of activity of the former compound when used in the presence of zinc oxide.

The piperidine salt has almost exactly the same degree

[1] *Loc. cit.*
[2] *India Rubber World*, 1919, 137.
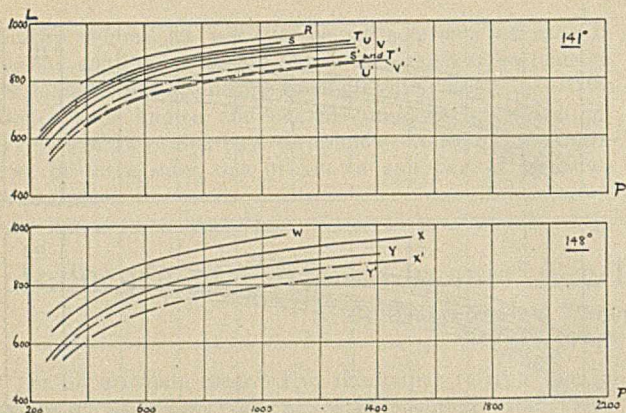
Fig. 3—Vulcanization with 1 per cent Hexamethylenetetramine at 141° and at 148°

of activity as aldehyde ammonia—an accelerator which has been extensively tested in a simple rubber-sulfur mix by Twiss and Brazier.[1] These authors give the "acceleration factor" of aldehyde ammonia as 7.5. A comparison of the effects of the piperidine salt and of aldehyde ammonia shows the following:

1—The effect on the vulcanization coefficient at the optimum cure is of the same order, a reduction, but not a very great one, being noticeable.

2—The effect on the position of the stress-strain curve and on the ultimate elongation at the optimum cure is similar, the curve lying lower and L_B being smaller than with the controls, although the effect of aldehyde ammonia in these respects is not quite so marked as that of the piperidine salt.

3—The piperidine salt appears to have a marked advantage over aldehyde ammonia in regard to the tensile strength of the vulcanizates; for, whereas the former greatly enhances the maximal tensile strength, the latter increases it only a little.

HEXAMETHYLENETETRAMINE. *Rate of Cure*—In these experiments hexamethylenetetramine appears as only a very mild accelerator; the rate of cure at 141° being only a little more than 1.5 times the rate shown by the control (say, 180 : 105–120).

Tensile Properties—The ultimate elongation (L_B) shown by the rubber at the optimum cure is increased. The curve corresponding to the optimum cure is higher in the presence than in the absence of the accelerator by a length of about 50 per cent. The most striking effect of the accelerator on the tensile properties is to be seen in the slowness with which the tensile properties of the vulcanizates change over a rather wide range of curing intervals. The tensile strength, the ultimate elongation, and, as may be seen by a glance at Fig. 3, the position of the stress-strain curve, change only remarkably slowly. Whereas, in the case of the control, a reduction of one-third in the time of cure below the optimum (from 180 to 120 min.) shifts the curve (L_{750}) by 150 per cent, a similar reduction (from 120 to 90 min.) in the case of the mix containing hexamethylenetetramine shifts the curve only 29 per cent. Hence it would appear that the addition of hexamethylenetetramine to a pure gum stock has the effect of enabling the period of vulcanization to be varied over a comparatively wide range without much change occurring in the tensile properties of the resulting vulcanizates.

The maximal tensile strength developed is slightly, but not, as with piperidine piperidyl-dithiocarbamate, strikingly, greater than that developed by the control.

These conclusions as to the effect of hexamethylenetetramine on the tensile properties of rubber-sulfur vulcanizates are in general agreement with conclusions indi-

cated by data published by Twiss and Howson[1] for the same accelerator. These authors, too, find the tensile strength maximum to be flat. They also find the position of the stress-strain curve (indicated by the length at 0.5 kg. per sq. mm.) to change more slowly in the presence than in the absence of the accelerator; although the difference is not so marked as in the present experiments. The results of Twiss and Howson show hexamethylenetetramine to be considerably more active in the presence of zinc oxide than in its absence, 1 per cent in the presence of zinc oxide having an acceleration factor of rather more than 2.[2] They also show that the flatness which is characteristic of the tensile strength maximum when the accelerator is used in the absence of zinc oxide is no longer to be seen when zinc oxide accompanies the accelerator.

Vulcanization Coefficient—Although hexamethylenetetramine accelerates the rate at which the optimum cure (as judged by tensile properties) is reached, it increases the amount of sulfur in combination at this cure. Whether this effect is due to the production of an acetone-insoluble material from the accelerator and sulfur cannot be said.

Aging—The vulcanizates prepared with hexamethylenetetramine behave normally during the aging period.

Comparison of the Effects of Piperidine Piperidyl-dithiocarbamate and Hexamethylenetetramine—The effects of these accelerators present a noteworthy contrast, which shows clearly how different properties may be conferred upon rubber by the use of different accelerators.

1—Whereas the piperidine salt diminishes the extensibility of the rubber, hexamethylenetetramine increases it. Further, the latter accelerator makes the rubber comparatively insensitive to changes in the time of vulcanization from the time giving the optimum cure, whereas the former accelerator has no such influence in altering the sensitiveness of the rubber to change in the vulcanization period.

2—Whereas the piperidine salt has a marked effect in increasing the tensile strength developed, hexamethylenetetramine has little or no such favorable effect.

3—Whereas use of the piperidine salt results in a reduction in the vulcanization coefficient at the optimum cure, hexamethylenetetramine results in an increase.
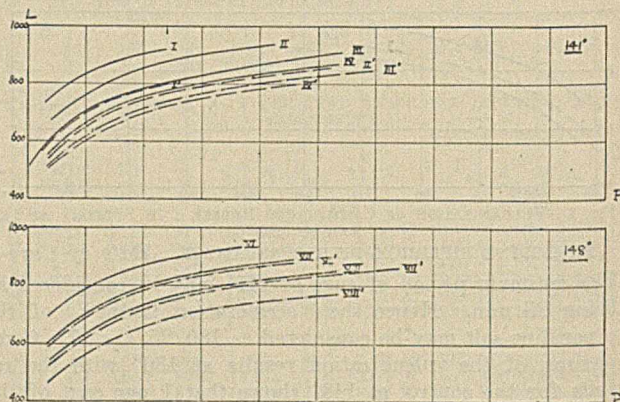
Fig. 4—Vulcanization with 1 per cent Thiocarbanilide at 141° and at 148°

THIOCARBANILIDE—A comparison of the results for the mix containing thiocarbanilide with those for the control shows that, both for vulcanizations at 141° and for those at 148°, the former results are substantially similar to the latter, as regards tensile properties. Hence, with respect

[1] *J. So. Chem. Ind.*, 39 (1920), 287t; Cf. also Twiss and Brazier, *Ibid.*, 131t.

[2] Cf. also Cranor, *Loc. cit.* Cranor's results with hexamethlene-tetramine also show the accelerator to be more active in the presence of zinc oxide than was found by Twiss and Howson or in the present experiments to be in the absence of the oxide. They also indicate that in the presence of zinc oxide the accelerator leads to ceratin irregularities in the manner in which the stress strain curve shifts on continued vulcanization. These irregularities have been examined more closely by Twiss and Howson. (*Loc. cit.*)

[1] *Loc. cit.*

to tensile properties, thiocarbanilide is without accelerating effect. The presence of thiocarbonilide in the pure gum stock in question leads, however, to some increase in the combined sulfur, the vulcanization coefficient at the 180-min. cure being raised from 4.31 to 4.87. This is in accord with results of Kratz, Flower and Shapiro.[1] It is possible that the apparent increase in the vulcanization coefficient is due to the formation of acetone-insoluble products as a result of interaction between sulfur, thiocarbanilide or its decomposition products, and, possibly, caoutchouc.

The thiocarbanilide is without effect on aging.

Summary

1—In a simple rubber-sulfur mix piperidine piperidyl-dithiocarbamate is a comparatively powerful, and hexamethylenetetramine a weak, accelerator, 1 per cent reducing the time of optimum cure to one-seventh and to two-thirds, respectively, of the time required in the absence of the accelerator.

2—These two accelerators present a notable contrast in their effects on the tensile properties of the rubber. The piperidine salt greatly enhances the tensile strength which can be developed; it leads to a smaller ultimate elongation and a lower position of the stress-strain curve (strains as ordinates) at the optimum cure. Hexamethylenetetramine enhances the tensile strength only a little; it leads to a greater ultimate elongation and a higher position of the stress-strain curve at the optimum cure; it also has the effect of causing the tensile properties to change with exceptional slowness with change in the length of the vulcanization period.

3—The piperidine salt reduces somewhat, whereas hexamethylenetetramine increases somewhat, the coefficient of vulcanization at the optimum cure.

4—In the absence of zinc oxide, thiocarbanilide is without accelerating effect on the vulcanization, considered with respect to tensile properties. It increases somewhat the vulcanization coefficient at the optimum cure.

5—In an aging test of 7 mo.' duration, pure gum vulcanizates prepared with the aid of the accelerators in question are found to age normally.

ADDENDUM. Vulcanization tests which Mr. Arnold H. Smith has kindly carried out with material supplied by the authors show that the presence of zinc oxide increases the accelerating activity of piperidine piperidyl-dithiocarbamate very greatly over that found, in the absence of zinc oxide, in the experiments recorded above. In a mixture similar to that used above, but containing in addition 10 per cent of zinc oxide, the acceleration factor for 1 per cent of the piperidine compound is in the neighborhood of 200; 1 mins. heating at 141° giving an over-cure, and a good cure being obtainable by 4 mins. heating at a temperature as low as 105° (3 lb. steam).[1]

[1] It is proposed to record more fully the data relative to these tests in the Correspondence column of a succeeding issue of This Journal.

LABORATORY AND PLANT

A Combined Extractor, Reflux Condenser, Still and Autoclave[2]

By Alfred T. Shohl and Mathilde L. Koch

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A good extraction apparatus to accommodate large amounts of material at a charge, an apparatus to make absolute alcohol, and an autoclave were needed in the laboratory. Because of limited funds available a single piece of apparatus was designed to meet these needs. In use it proved to be not only more economical, but also more efficient in several respects than any available apparatus.

It is a modification of an ordinary autoclave such as is used in sterilizing under pressure. A glass tube gage which is added shows the level of the contained fluid and has a charging funnel and a draw-off spigot. The autoclave is converted into a refluxing or extraction apparatus by unscrewing the blow-off valve and inserting the upright condenser. The condenser is of such a type that, by changing its position, it may be converted into a condenser for a still.

The apparatus consists of six parts: (1) The main body with lid, (2) extraction trays, (3) autoclave attachment, (4) a special fitting or stuffing box, (5) a connecting tube, and (6) a condenser with stand.

The main body (Fig. 1) of the apparatus consists of a riveted copper cylinder to which is soldered a seamless copper bottom. A glass tube gage connects to the body above and below through two 3-way stopcocks, A and B, and also above with a charging funnel, C, and below with a draw-off spigot, D. Thus fluid can be drawn off and fresh fluid added while the apparatus is in operation. The inner surface of the main body is heavily tinned. Connecting with

the bottom entrance of the gage is a tinned tube, E, bent to reach nearly to the bottom so that the contained liquid may be syphoned off. Near the top are riveted three right-angled strips of metal, F, 0.5 in. wide and projecting 0.5
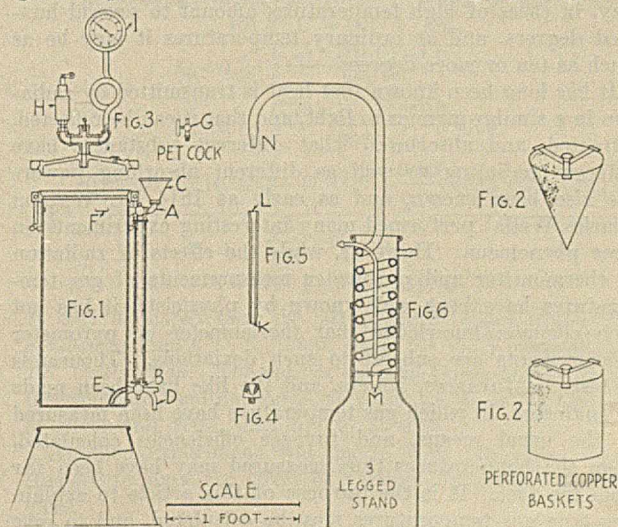
in. from the side. These are in the same horizontal plane and equidistant and are the supports for the extraction trays.

The extraction trays (Fig. 2) contain the material to be extracted. They may be either cylindrical or cone shaped.

and are made of wire mesh or of tinned metal perforated with numerous small holes. The size of the holes depends on the nature of the material to be extracted. Three strips of metal converge from the upper edge to the center, and at the union there is a knob which serves both as a handle to pick up the tray and as a spreader to distribute the extracting fluid as it drops from the condenser.

The lid of the apparatus is of cast brass. This lid is seated on the cast brass ring which forms the top of the main body by means of a ground joint. It is held in place by six toggle bolts with wing nuts. There are two threaded holes through the lid. The central hole carries the autoclave attachment. The other is provided for a thermometer.

The autoclave attachment (Fig. 3) consists of a blow-off valve, G, which screws into hole O, and also, attached by right-angle side arms to the central tube carrying the blow-off valve, a safety valve, H, and a pressure gage, I. A special fitting or stuffing box (Fig. 4), with ground joint, of the same size and thread as the blow-off valve, can be screwed in place of the blow-off valve when the apparatus is used as an extractor, still, or reflux condenser. The ground joint, J, of Fig. 4 is tapered and is female. Into this nut fits a connecting tube. This connecting tube (Fig. 5) is of brass, lined with block tin. It has a ground male taper joint, K, at one end and a ground female taper joint, L, at the other, so that below it connects with the main body of the apparatus and above with the condenser.

The condenser (Fig. 6) is a block-tin, coiled pipe surrounded by a copper cylinder water jacket. One end of the pipe, M, extends a short distance below the condenser, while the other end, N, extends above the condenser in a rough semicircle. Both ends are tapered male ends. The water jacket fits into a stand made of two bands of strap iron held together by and resting on three legs. The heating is accomplished by gas or by an electric hot plate.

When the stand supporting the condenser is placed upon the lid of the main body, the legs of the stand interlock their feet with three of the wing nut clamps and thus hold the condenser in position. By inserting tube (Fig. 5), that is, fitting K into J and L into M, the apparatus is in position to be used as an extractor or as a reflux condenser.

When the condenser stand rests beside the apparatus with the upper end of the condensing tube N fitted into the tapering joint J, the apparatus is in position to be used as a still.

When the blow-off valve G is screwed into hole O, the apparatus is ready for use as an autoclave.

The apparatus is most satisfactory for the extraction of material either in the dry, powdered state or in the fresh, moist state, with the different fat solvents or with water. Without removing or disturbing the material, the solvent can be drawn off and fresh solvent added for reëxtraction. Then without cooling the extract can be concentrated and the solvent recovered by distillation. Absolute alcohol can be made from ordinary alcohol by refluxing the alcohol over lime, and the absolute alcohol can then be distilled without exposure to the air. Extraction or distillation can be conducted under either positive or negative pressure.

The advantages of this apparatus are that it is easily set up and readily transported; it is easy to clean, and, above all, simple to operate. Its greatest value is that it allows a combination of procedures such as refluxing and distilling, or extracting and distilling, in a single piece of apparatus.

Radiation Effects in Thermometry

By Clark S. Robinson

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A thermometer, pyrometer, or other temperature measuring device, when inserted in a gas for the purpose of measuring its temperature, does not, except under unusual conditions, record the true gas temperature, and the deviation may, in cases of high temperature, amount to several hundred degrees, and at ordinary temperatures it may be as much as ten or more degrees.

It has long been known that heat is transmitted by radiation in a similar manner to light, and that it can be reflected, refracted, and absorbed. That different substances have different radiating as well as different absorbing powers has also been known, and as early as 1814 Dr. William Charles Wells[2] performed many interesting experiments on these phenomena. However, while the effects of radiation on thermometer and pyrometer measurements of gas temperatures have been well known by physicists, it has not been common knowledge that thermometer or pyrometer measurements are subject to such deviations. Thousands of tests on furnaces, boilers, and the like have been made by engineers, in which gas temperature have been measured by the usual means, and furnace efficiencies calculated, when the temperatures thus measured may have been far from the fact. It is the purpose of this article to explain how true gas temperatures may be calculated, and to give the results of some experiments made by Mr. Goodman Mottelson in connection with his thesis on this subject at the Massachusetts Institute of Technology during the past year.

[1] Received June 24, 1921.
[2] An Essay on Dew, London, 1914.

THE CALCULATION OF TRUE GAS TEMPERATURES

A thermometer or other temperature measuring instrument, when introduced into a gas, tends to approach the temperature of the gas. In order to do this it must receive heat, if the gas is at a higher temperature, or it must lose heat, if the gas is at a lower temperature. This flow of heat to or from the thermometer occurs in two ways, by conduction and convection between the gas and the thermometer, and by radiation between the thermometer and the surroundings, usually the walls of the chamber or flue. Imagine, for instance, a tube in a fire-tube boiler, through which hot furnace gases are passing, giving up part of their heat to the cooler walls of the tube. A pyrometer inserted in the tube, if at the gas temperature, would radiate heat to the cooler tube, which would lower the thermometer temperature. Heat would then flow into it from the gas, and when equilibrium was reached the pyrometer would be at a temperature sufficiently below gas temperature, yet sufficiently above tube temperature, so that its loss of heat by radiation to the tube would just compensate for the heat gained by conduction from the gas.

On the other hand, a thermometer inserted in the air between the tubes of a steam coil heater for air, where the heating tubes are hotter than the air, would indicate a temperature between that of the air and that of the hot surfaces, the thermometer reading too high where in the former case it would read too low.

The rate of flow of heat by conduction from the gas to the thermometer can be expressed by the equation

$$\frac{Q}{\theta} = h_c A \, (T - t_t) \tag{1}$$

where $\frac{Q}{\theta}$ = heat flow per unit time

h_c = coefficient of heat transfer by conduction, expressed in suitable units, such as B.t.u. per °F. temperature difference between gas and thermometer per hr.

T = air temperature, in °F. abs.

t_t = thermometer temperature, in °F. abs.

A = area of surface thermometer through which heat is flowing.

The rate of flow of heat by radiation from the thermometer to the surrounding walls can be expressed by the equation (in English units)

$$\frac{Q}{\theta} = R_t \times 0.162 \times A \left[\left(\frac{t_t}{100}\right)^4 - \left(\frac{t_w}{100}\right)^4 \right] \tag{2}$$

where R_t = black body coefficient of material from which thermometer is made.

t_w = temperature of surrounding walls, in F. abs.

At equilibrium Equations 1 and 2 are equal. Therefore,

$$h_c \, (T - t_t) = R_t \times 0.162 \times \left[\left(\frac{t_t}{100}\right)^4 - \left(\frac{t_w}{100}\right)^4 \right] \tag{3}$$

From this equation it is possible to calculate the true gas temperature, T, from the thermometer reading t_t, if the values of h_c, R_t, and t_w are known.

The heat transfer coefficient, h_c, can be calculated from the Beckett equation[1] when the gas is moving under forced draft:

$$h_c = \frac{0.44 \, V^{0.8} T^{0.5} Cp \, (m - 0.081)}{M^{0.1}(m - 0.027)} \tag{4}$$

where h_c = B.t.u./hr./sq. ft. of heating surface/°F. difference

V = lbs. of gas/sq. ft. of cross section of gas pass./sec.

T = temperature of gas in °F. abs.

Cp = specific heat of gas at constant pressure

m = mean hydraulic radius of the gas passage in ft.

M = molecular weight of the gas

When the gas is moving under convection currents only, Equation 6 is to be used.

The black body coefficient (R_t) for a number of substances are given approximately in the following table:

SUBSTANCE.	R.
Absolute black body	1.0
Highly oxidized iron	0.90
Polished copper	0.07 to 0.10
Oxidized copper	0.70
Monel metal	0.06
Gold, polished	0.05
Silver, polished	0.03
Nickel, polished	0.35
Platinum	0.24
Glass	0.90

For the wall temperature, t_w, when the walls are incandescent, the optical pyrometer may be used, or, for lower temperatures, thermocouples may be immersed in the wall surface. Where the wall temperature cannot be measured, another method, to be described below, may be used.

EXAMPLES

The following data were taken with a small electric furnace, 2-in. inside diameter, with the walls heated to approximately 725°C., as measured by an optical pyrometer. Thermometers were suspended just at the level of the open top of the furnace. Three thermometers were used, all of the usual mercury-in-glass laboratory type, and calibrated against each other. One of these was used as such, while the second had the bulb covered with a tightly fitting, polished silver shield, and the third was shielded with polished copper.

The following readings were made:

[1] M. I. T. Thesis 1920.

UNSHIELDED °C.	SILVER SHIELD °C.	COPPER SHIELD °C.
255	158	179
255	162	185
261	162	185
255	158	182
263	160	181
261	161	184
265	162	178
267	165	182
265	163	177
269	162	180
Aver. 261.6	161.3	181.3

Any motion of the air about the thermometers was due in this case to convection currents alone.

Calling t_t the temperature of the unshielded thermometer, and t_s that of the one with the silver shield, Equation 3 may be written for each as follows:

$$(T - t_t) h_c = R_t \times 0.162 \left[\left(\frac{t_w}{100}\right)^4 - \left(\frac{t_t}{100}\right)^4 \right]$$

$$(T - t_s) h_c = R_s \times 0.162 \left[\left(\frac{t_w}{100}\right)^4 - \left(\frac{t_s}{100}\right)^4 \right]$$

Eliminating t_w and solving for T

$$T = \frac{R_s \times 0.162 \left[\left(\frac{t_t}{100}\right)^4 - \left(\frac{t_s}{100}\right)^4 \right] + \frac{R_s}{R_t} t_t h_c - t_s h_c}{\frac{R_s}{R_t} h_c - h_c} \tag{5}$$

The value for h_c may be calculated from the formula (English Units)

$$h_c = 0.7 - \frac{\Delta t}{375} \tag{6}$$

which is for use when the flow of gas by a surface is due to convection currents only, Equation 4 being used for forced draft. In this case Δt is the difference in temperature between the hot walls and the thermometers, and must be calculated for each one separately. Under the conditions, Equation 5 must be rewritten, using h_{ct} for the value of h_c for the unshielded thermometer and h_{cs} for the silver shielded one.

$$T = \frac{R_s \times 0.162 \left[\left(\frac{t_t}{100}\right)^4 - \left(\frac{t_s}{100}\right)^4 \right] \times \frac{R_s}{R_t} t_t h_{ct} - t_s h_{cs}}{\frac{R_s}{R_t} h_{ct} - h_{cs}}$$

$R_s = 0.03$, $R_t = 0.90$. $t_t = 261.6°$ C. $= 963°$ F. abs., $t_s = 161.3°$ C. $= 783°$ F. abs.

$$h_{ct} = 0.7 + \frac{(725 - 261.6) \times 1.8}{375} = 2.9$$

$$h_{cs} = 0.7 + \frac{(725 - 161.3) \times 1.8}{375} = 3.4$$

$$T = \frac{0.03 \times 0.162 \, [(9.63)^4 - (7.83)^4] + \frac{0.03}{0.90} \times 963 \times 2.9 - 783 \times 3.4}{\frac{0.03}{0.90} \times 2.9 - 3.4}$$

$$T = 772° \text{ F. abs.} = 155° \text{ C.}$$

It will be noted that the silver thermometer under these conditions read 6°C. too high, while the plain glass one read 107°C. too high. The copper covered thermometer gave an intermediate reading, since its value of R_t is between that of silver and glass, that is, 0.07 to 0.10.

Another experiment was made with the same electric furnace to show the effect of various shields for thermometers.

Unshielded Thermometer °C.	Silver Shield °C.	Black Iron Shield °C.	Glass Shield °C.
272	169	313	292
281	174	316	297
275	171	316	299
279	164	312	299
284	166	316	297
Aver. 278	169	315	296

The shields were then removed, giving the following readings, the thermometers remaining in practically the same positions as before.

287	290	282	272
277	291	280	260
281	290	293	266
281	293	284	263
281	292	293	263
Aver. 281	291	286	265

The following data were obtained in a heated galvanized pipe 12 in. in diameter, through which a warm mixture of air and burner gases was passing at the rate of 2.3 lbs. per sq. ft. of cross-section of the pipe per second.

Silver thermometer = 123°, 126°, 124° C. Aver. = 124° C.
Plain thermometer = 152°, 150°, 149° C. Aver. = 150° C.

Using Equation 4, h_c was found to be 3.0 in English units.

$$h_c = \frac{0.44 \times (2.3)^{0.8} \times (715)^{0.5} \times 0.24 \times (0.25 - 0.081)}{(30)^{0.1} \times (0.25 - 0.027)} = 3.0$$

using for T the value 715 obtained from the reading of the silver thermometer as being near the true temperature, a small error in this temperature being negligible. Using Equation 5,

$$T = \frac{0.03 \times 0.162 \left[\left(\frac{150 \times 1.8 + 492}{100} \right)^4 - \left(\frac{125 \times 1.8 + 492}{100} \right)^4 \right] + \frac{0.03}{0.90} \times (762 - 715) \times 3.0}{\frac{0.03}{0.90} \times 3.0 - 3.0}$$

$$T = 712° \text{ F. abs.} = 122 \text{ C.}$$

In this case, the silver thermometer read 2° C. too high, and the glass one 28° too high.

Two thermometers, one silver and the other plain, were inserted in the intake manifold of a gasoline engine whose intake gases had been previously heated, and which were moving at a high velocity, 7.5 lbs. per sq. ft. per sec. Under these conditions, the value of h_c was great enough nearly to overcome the effect of radiation, and the two thermometers read the same at 60° C.

Tests were made in a galvanized iron pipe 7 in. in diameter, in which burner gases containing some sulfur dioxide were flowing at the rate of 0.125 lbs. per sq. ft. per sec.

The silver became tarnished during the test, and its reading fell off somewhat, as is shown in the following table:

Silver	292	292	290	292	293	256	253	251	248°C.
Plain	276	277	278	278	278	247	245	243	241°C.
Difference	16	15	12	14	15	9	8	8	7°C.

The tarnished silver was then compared in a heated pipe with a thermometer shielded with polished monel metal.

Tarnished silver	188	188	183	185	187	189	189	192
Average = 188°C.								
Monel metal	186	185	180	170	179	182	185	189
Average = 183°C.								
Plain glass	276	274	280	278	278	286	287	288
Average = 281°C.								

The silver shield was then polished and compared again with monel metal, the gas velocity having changed.

Polished silver	174	175	177	178	177	178	170	169
Average = 173°C.								
Monel metal	195	199	204	204	204	205	201	204
Average = 202°C.								
Plain glass	283	285	283	277	290	282	287	287
Average = 284°C.								

CONCLUSIONS

1—Thermometers for measuring gas temperatures must have their readings corrected for the effect of radiation to the surroundings.

2—For measurements permitting small errors, a silver shield will give fairly close approximations if uncorrected. It is necessary, however, to correct the silver thermometer reading in order to get accurate temperatures.

3—For corrosive gases monel metal can be used in place of silver, but the reading should be corrected except for very approximate work.

4—Where gas is moving at very high velocity, any thermometer will read practically the true temperature, the large deviations occurring where the gas velocities are very low.

5—Thermometers will read true gas temperature exactly only when the surrounding walls are at the same temperature as the gas.

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ADDRESSES AND CONTRIBUTED ARTICLES

The Chemistry of Acenaphthene and Its Derivatives [1,2]

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The purpose of this paper is to present an outline of the chemistry of acenaphthene, accompanied by a fairly complete bibliography of the substance. Such an outline has not as yet been attempted, and it seems desirable because of the fact that it may serve to call attention to the many gaps which exist in the chemistry of this very interesting substance and thus may lead to a thorough and systematic investigation of its derivatives. In this connection it may be pointed out that within recent years methods for separating acenaphthene from coal tar have been perfected so that it is no longer the rare and expensive preparation which it was when the first systematic investigation of its derivatives was undertaken by C. Graebe[3] and his co-

workers in Germany and by T. Ewan and J. B. Cohen[1] at about the same time in England. The research initiated by these men was neglected for a period of seven years, when F. Sachs and G. Mosebach[2] entered the field with the avowed purpose of systematically filling in the gaps in the chemistry of acenaphthene. These investigators point out in the introduction to their second paper that the extreme meagerness of the information which exists in regard to the chemistry of acenaphthene is very surprising in view of the fact that the chemistry of napthalene, to which it is so closely related, has been brought to a state of dazzling completeness. The very fact that so many derivatives of naphthalene have been prepared and their constitution exactly determined is, however, of the greatest importance for the future development of acenaphthene chemistry. This fact will be referred to again later in this paper, but at the present time it need only be pointed out that by the appli-

¹ J. Chem. Soc., 55 (1889), 578.
² Ber., 43 (1910), 2473; 44 (1911), 2852.

cation of a method developed by Graebe[1] in 1903, derivatives of acenaphthene may be readily transformed into the corresponding derivatives of naphthalene, thus affording a direct and easy method for the definite identification of new compounds.

The practical aspects of the chemistry of acenaphthene have also been emphasized by Sachs and Mosebach, who call attention to the fact that the recent discovery of such valuable dyes as Ciba Scarlet G,[2] Thioindigo Scarlet 2G,[3] and Ciba Red R[4] make a thorough investigation of the substitution products of acenaphthene increasingly desirable. Unfortunately the task which Sachs and Mosebach set for themselves has only been begun, and the investigation even of those substances which have been described has not been completed.

In summary it may be said that this field offers considerable attraction for research since the orientation of new derivatives may be readily elucidated and since acenaphthene itself is now available in the United States.[5] The present article aims to present the chemistry of the hydrocarbon in such a way as to emphasize the many gaps which exist in the literature relating to acenaphthene and its derivatives in the hope that a realization of the vast amount of work still to be done may stimulate American chemists to further research in this field.

OUTLINE OF TREATMENT OF SUBJECT

The various topics to be considered will be arranged in the following order: The discovery of acenaphthene and its relation to acenaphthylene will first be described. The hydrogenation, pyrogenic syntheses, the thermo- and photochemical transformations of the substance, and its various addition products will then be reviewed briefly. This will be followed by a few general remarks in regard to the constitution of acenaphthene, acenaphthylene, and some of the more important oxidation products which have been obtained from these substances. The possibilities of isomerism among the substitution products of acenaphthene will be considered, together with methods for identifying the different compounds according to the general method developed by Graebe. A systematic study of the halogen, nitro, amino, hydroxy, and sulfonic acid derivatives of acenaphthene will follow. Finally a careful analysis of methods of oxidation and a systematic review of the various products of oxidation will be attempted. The chemical properties and commercial applications of these substances will be considered in some detail, and in all cases where patents have been issued the fact will be noted. In this connection acknowledgment must be made to The Barrett Company for their courtesy in allowing the use of abstracts covering all patents mentioned in this paper.

Methods have been developed for the synthesis of substituted acenaphthenes,[6] but the products which have been obtained in this way will not be considered in the present survey of the chemistry of acenaphthene.

DISCOVERY OF ACENAPHTHENE AND ITS RELATION TO ACENAPHTHYLENE

Acenaphthene, $C_{12}H_{10}$, was discovered by Berthelot, who

1 *Ann.*, 327 (1903), 77.

2 Ciba Scarlet G, Basler chemischen Fabrik, D.R.P., 205,377.

3 Thioindigo scarlet 2G, Kalle and Co.

4 Ciba Red R, M.L.B.

5 Acenaphthene may be obtained in small lots for research purposes by application to the Research Department of The Barrett Company.

6 Compare C. Graebe, "The Synthesis of Substituted Acenaphtylenes," *Ann.*, 327 (1903). 77; E. Beschke, *Ann.*, 369 (1909), 157, 184; M. Freund and K. Fleischer, "Synthesis of the Higher Indandiones," *Ann.*, 373 (1910), 291; 399 (1913), 182; 402 (1913), 51; C. Graebe, *Ann.*, 327 (1913), 77.

succeeded in isolating it from coal tar,[1] and who also prepared it by the action of acetylene upon naphthalene at the red heat.[2] The formula determined by Berthelot was later verified by C. Graebe[3] as a result of vapor density determinations. Further investigation of the chemistry of the substance by Berthelot and Bardy led to its synthesis by heating ethylnaphthalene at red heat.[4] The pioneer work of these earlier investigators was confirmed by that of A. Behr and W. A. van Dorp,[5] who also succeeded in establishing a definite relationship between this hydrocarbon and a very closely related, but less saturated compound, $C_{12}H_8$, which they called acenaphthylene. The discovery of the latter substance led to a number of experiments which involved the hydrogenation and halogenation of both hydrocarbons, and which were made the subject of investigation by M. Blumenthal,[6] by E. Bamberger and W. Lodter,[7] and by C. Liebermann and L. Spiegel.[8] This work was, however, of very little importance, except in so far as it tended to establish somewhat more definitely the relationship between acenaphthene and acenaphthylene, since the compounds which were prepared in this way were not always pure chemical individuals and, even in cases where they were, their exact constitution was not established.

The first really systematic and exact work on acenaphthene was that of Graebe and his co-workers. These investigations will be reviewed in some detail, but before proceeding to their consideration the fact should be noted that interest in the hydrogenation[9] and in the pyrogenic syntheses[10] of acenaphthene have continued up to the present time. Indeed photo- and thermochemical changes have come definitely to be recognized as playing an extremely important role in the chemistry of acenaphthene. The extended investigations of Dziewonski and his coworkers can only be mentioned in this connection.[11]

The separation of chemically pure acenaphthene from coal tar presented many experimental difficulties, in view of the fact that the hydrocarbon possesses the power of forming addition products with an unusually large number of other compounds. This property seems to extend to at least some of its derivatives, with the result that unstable compounds or eutectic mixtures arise. Since these substances frequently possess more or less constant melting points and boiling points their formation is often confusing and harassing to the investigator. In certain instances, however, as in the case of the picrates, such addition products may be utilized for the separation or identification of the hydrocarbon in question. The extent to which investigations along these lines have been carried can only be indicated.[12]

1 *Jahresber*, 1867, 594.

2 *Bull. soc. chim.*, 9 (1868), 265.

3 *Ber.*, 5 (1872), 15.

4 *Bull. soc. chim.* [2] 18 (1872), 231.

5 *Ber.*, 6 (1873), 753.

6 *Ber.*, 7 (1874), 1092.

7 *Ber.*, 20 (1887), 3073; 21 (1888), 836.

8 *Ber.*, 22 (1889), 779.

9 P. Sabatier, *Bull. so c. chim*, [3] 25 (1901), 610, 671, 678; *Compt. rend.* 132 (1901), 1254; M. Padoa and W. Fabris, *Atti. accad. Lincei*, [5] 17 (1908), I, 111; W. N. Ipatiff, *Ber.*, 42 (1909), 2092.

10 R. Meyer and A. Tazen, *Ber.*, 46 (1913), 3183; J. E. Zanetti and G. Egloff, THIS JOURNAL, 9 (1917), 474; R. Meyer and W. Meyer, *Ber.*, 51 (1918), 1571.

11 Dziewonski, *Ber.*, 36 (1903), 962; P. Rehlander, *Ber.*, 36 (1903), 1583; Dziewonski, *Ber.*, 45 (1912), 2491; 46 (1913), 1986; 47 (1914), 1679, 2680; 48, 1915), 1919, 457.

12 Berthelot, *Compt. rend.*, 102 (1886), 1211; W. R. Hodgekinson, *Proc. Chem. Soc.*, 12 (1896), 110; C. L. Speyers, *J. Am. Chem. Soc.*, 18 (1896), 146; W. H. Perkins *J. Chem. Soc.*, 69 (1896), 1025; G. Pellini, *Gazz. chim. ital.*, 31 (1901), 1, 1; E. Billows, *Z. Kryst Mineralog.*, 37 (1903), 396; 38 (1904), 505; G. Schultz,

The Constitution of Acenaphthene and Certain of Its Derivatives

Fairly large quantities of acenaphthene became available in 1873, when it was observed to separate in the form of flat prisms from tar distillates collected between the temperatures of 250° and 300°. The substance obtained in this way on recrystallization from alcohol gave a relatively pure product which melted between 94° and 96° and which boiled between 267° and 269° (uncorr.).[1] This discovery marks the beginning of a more exact investigation of the chemical properties of the substance. Acenaphthene readily loses two atoms of hydrogen to form acenaphthylene and on further oxidation gives naphthalic acid. The latter fact was used to establish the exact constitution of acenaphthene. It was found, for example, that the crystalline product melting at 266° which is formed by the action of potassium bichromate and sulfuric acid upon acenaphthene was identical with an acid having the same formula, $C_{12}H_8O_4$, and the same properties, which had been synthesized by E. Bamberger and M. Philipp[2] from Estrand's nitronaphthalic acid. Since the latter had been identified as an a-*à* or peri-derivative of naphthalene, the corresponding dicarboxylic acid was assumed to have the configuration
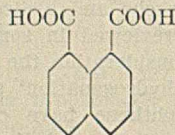
and from this it followed that the relationship between acenaphthene and acenaphthylene must be expressed in the following manner:
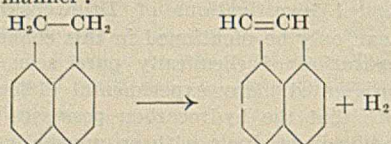
This conclusion was confirmed many years later by Baly and Tuck[3] as a result of their investigations upon the absorption spectra of naphthalene and acenaphthene.

The solution of the problem as to the constitution of acenaphthene served at once to elucidate the relationship of acenaphthene to other of its oxidation products which were formed simultaneously with naphthalic acid. When oxidation was carried out, for example, in acetic acid by means of chromic oxide a crystalline compound melting at 232° was obtained. On analysis this was found to correspond to the formula, $C_{12}H_6O_2$. Its constitution was assumed to be
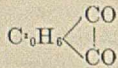
since on oxidation with potassium permanganate it was readily converted into naphthalic acid,[4]
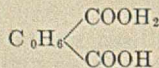
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1 A. Behr and W. A. van Dorp, *Ber.*, 6 (1873), 60.

2 E. Bamberger and M. Philipp, *Ber.*, 20 (1887), 237.

3 *Proc. Roy. Soc.*, 24 (1908), 223; *J. Chem. Soc.*, 93 (1908), 102.

4 C. Graebe, *Ber.*, 20 (1887), 657.

The discovery of these relationships paved the way, moreover, for the development of a general method by means of which it is now possible to determine the position taken by different substituents in the various derivatives of acenaphthene. According to the nomenclature adopted by F. Sachs and G. Mosebach,[1] all derivatives of acenaphthene may be regarded as representing substitutions in the following formula:
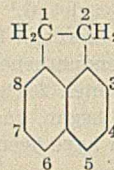
From this it is apparent that four different monosubstitution products of acenaphthene are possible, of which three represent substitution in the naphthalene ring. On the basis of theory, seventeen disubstitution products are possible if the entering groups are alike, and of these nine represent compounds in which both substituents are present in the aromatic part of the molecule. It will be shown later in this paper that these theoretical possibilities have not as yet been realized in the case of any single type of acenaphthene derivative. As early as 1874, however, Blumenthal[2] found it convenient to employ oxidation reactions in order to distinguish between compounds in which the hydrogen of the methylene groups had been replaced and those in which the substituent occupied a position in the naphthalene ring. If, for example, a substance having the formula $C_{12}H_9Br$ gave naphthalic acid upon oxidation it was assumed to possess the formula
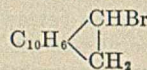
This very crude method was later perfected by C. Graebe[3] who, as the result of some very brilliant work, was able to assign exact formulas to monosubstituted nitro, bromo, acetyl, and benzoyl derivatives of acenaphthene. All of the substances under investigation by Graebe at this time were found to give a-substitution products of naphthalene, and from this it followed that these respective groups occupied the 5-position in acenapthene. For example, Graebe was able to establish the constitution of Quincke's nitroacenaphthene by converting it into a-naphthylamine as a result of the following transformations:
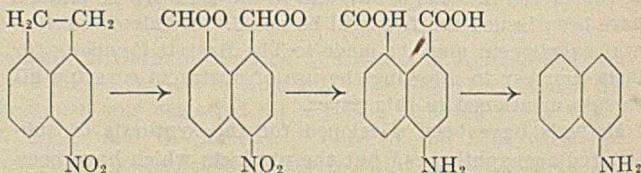
The constitutions of only a very few monosubstitution products of acenaphthene have been established with certainty. They include those which have just been mentioned, *viz.*, 5-nitro-, 5-bromo-, 5-acetyl-, and 5-benzoyl-acenaphthene, and one or two others which can be dismissed almost as briefly. For example, 5-nitroacenaphthene gives the corresponding amino compound upon reduction, and this in turn yields halogen derivatives when treated according to the Sandmeyer reaction. A 5-carboxyl derivative has also been obtained and identified. All

1 *Ber.*, 44 (1911), 2852.

2 *Ber.*, 7 (1874), 1092.

3 *Ann.*, 327 (1903), 77.

4 Compare N. Brione's Dissertation, Genf. 1893; also M. Guinsbourg's Dissertation Genf. 1894, and P. Haas's Dissertation, Freiburg, 1901.

other monosubstitution products, as well as a large number of the higher substitution products, of acenaphthene which have been described in the literature possess structures which are more or less uncertain, since their exact constitutions have not as yet been accurately determined according to the method developed by Graebe.

HALOGEN DERIVATIVES

Halogen derivatives of acenaphthene were first investigated by Blumenthal,[1] who studied the action of halogen upon acenaphthene and acenaphthylene under a variety of different conditions. Several different compounds containing a halogen are mentioned, but most of these are of such doubtful purity as to leave their chemical constitution very much in question. Among them, however, is to be found a white crystalline compound which is described as melting at 52° to 53° and to which the probable formula

$$C_{10}H_5Br\langle^{CH_2}_{CH_2}$$
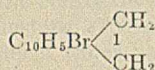
is given. These investigations were followed by others equally indefinite by J. T. Kebler,[2] E. Bamberger,[3] and T. Ewan.[4]. In all of these cases it seems probable that the separation of pure products was handicapped by the presence of eutectic mixtures, so that it was not until 1903 that perfectly pure 5-bromo-acenaphthene was isolated.[5] This substance corresponds to the compound described by Blumenthal and was obtained in excellent yields by a modification of his method. The corresponding chlorine derivative was prepared by H. Crompton[6] by an application of the same method. Crompton's later investigations were directed toward the study of other halogen derivatives of acenaphthene and of their oxidation products,[7] and included important data in regard to the freezing points of eutectic mixtures. In this connection it should be noted that the spectrochemical behavior of the halogen derivatives of acenaphthene has been studied by J. E. Purvis[8] and by K. von Auwers.[9] In 1910 the constitutions of 5-chloro-, 5-bromo-, and 5-iodo-acenaphthene were confirmed by F. Sachs and G. Mosebach, who succeeded in preparing these substances from 5-amino-acenaphthene.[10]

NITRO DERIVATIVES

The nitration of acenaphthene was first investigated by F. Quincke,[11] when a mixture, consisting of two substances which were later identified as 5-nitro-acenaphthene and 5,6-dinitro-acenaphthene, was obtained. It is to be noted that under what seem to be very much the same conditions, E. Jandrier[12] obtained a mono-nitro derivative melting at 155°. The results described by Quincke have been confirmed by N. Briones[13] and by C. Graebe.[14] The latter succeeded in so modifying the procedure as greatly to improve the yield and was the first investigator to prepare a perfectly pure product, melting at 106° (Compare Quincke,

1 *Ber.*, **7** (1874), 1092.
2 *Am. Chem. J.*, **10** (1888), 217.
3 *Ber.*, **21** (1888), 836.
4 *J. Chem. Soc.*, **55** (1889), 591.
5 *Ann.*, **327** (1903), 85.
6 *Proc. Chem. Soc.*, **24** (1908), 241.
7 *Proc. Chem. Soc.*, **26** (1910), 226; **28** (1912), 194; *J. Chem. Soc.*, **101** (1912) 1315; **103** (1913), 1302.
8 *J. Chem. Soc.*, **11** (1912), 1315.
9 *Ber.*, **46** (1913, 2988.
10 *Ber.*, **43** (1910, 2473.
11 *Ber.*, **20** (1887), 609; **21** (1888), 1454.
12 *Compt. rend.*, **104** (1887), 1858.
13 *Bull. soc. chim.*, (3) **14** (1895), 116.
14 *Ann.*, **327** (1903), 80.

101° to 102°). The method of Graebe was later slightly modified by F. Sachs and G. Mosebach, who detail experiments by means of which yields averaging 84 per cent of theory were obtained. These investigators[1] also succeeded in improving the yield of 5,6-dinitro-acenaphthene (40 per cent) and in definitely establishing its constitution:

$$CH_1—CH_1$$

1NO 1NO
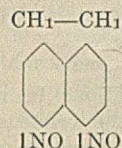
They have also prepared 4-nitro-5-amino- and 4-nitro-5-oxy-acenaphthene as a result of nitrating the acetyl derivatives of 5-amino-acenaphthene.

AMINO DERIVATIVES

The reduction of nitro derivatives of acenaphthene has been effected by the application of a variety of different methods.[2] The best yields have been obtained by Sachs and Mosebach, who claim 77 per cent of theory in the case of 5-amino-acenaphthene, against 50 per cent yields by Graebe and still smaller yields by all earlier methods. According to Sachs and Mosebach the acetyl derivative of 5-amino-acenaphthene shows a melting point of 192°, as against 185° (Graebe) and 174° (Quincke). 5-Amino-acenaphthene has been made the starting point in the preparation of a number of interesting derivatives, among which are 4-nitro-5-amino-acenaphthene, 4-nitro-5-oxy-acenaphthene, and 4,5-diaminoacenaphthene. 5,6-Diamino-acenaphthene has been obtained by reducing the corresponding dinitro derivative.

In conclusion it may be noted that the chemistry of the amino derivatives of acenaphthene is at the present time very incompletely developed. This is the more striking because of the number of possibilities for research which these compounds afford. For example, mono-amino derivatives may be diazotized and the resulting diazo compounds may then be coupled in a great variety of ways. Acenaphthene-azo-β-naphthol

$$\begin{matrix}CH_2\\CH_2\end{matrix}\rangle C_{10}H_5{}^5NH^1C_{10}H_6{}^2OH$$
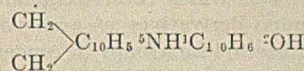
has, for example, actually been obtained from 5-amino-acenaphthene in this manner.[3] The diamino derivatives, of which seventeen are theoretically possible while only two have actually been prepared, afford an opportunity for still other lines of work. For example, 4,5-diamino-acenaphthene has been observed to condense with diacetyl in alcohol solution to give

$$\begin{matrix}CH_2—CH_2\\—N=C—CH_3\\—N=C—CH_3\end{matrix}$$
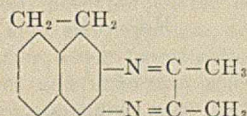
while 5,6-diamino-acenaphthene has been found to yield a number of different products under the action of carbonyl oxygen. The same substance reacts readily with phthalic anhydride to give

$$\begin{matrix}CH_2—\quad—N=C\\CH_2—\quad—N\diagdown C_6H_4\\\qquad\qquad CO\end{matrix}$$

and with formic acid to give a somewhat similar compound, *viz.*,

1 *Ber.*, **44** (1911), 2860.
2 Compare Quicke, *Ber.*, **21** (1888), 1456; Graebe, *Ann.*, **327** (1903), 81; H. Crompton, *Proc. Chem. Soc.*, **27** (1911), 165; F. Sachs and G. Mosebach, *Ber.*, **43** (1910), 2473; **44** (9111), 2852.
3 Sachs and Mosebach, *Loc. cit.*

$$CH_2 \diagdown \hspace{1cm} N \diagdown CH$$
$$CH_2 \diagdown \hspace{1cm} N \diagup$$

Moreover, when 5,6-diamino-acenaphthene[1] is gently warmed with carbon bisulfide it reacts to give

$$CH_2 - \hspace{1cm} - NH \diagdown$$
$$CH_2 - \hspace{1cm} - NH \diagup CS$$

A number of observations in regard to the products which are formed by the condensation of acenaphthenequinone with aromatic diamines suggests the possibility that this type of reaction might yield interesting results if applied to the diamino derivatives of acenaphthene itself. For example, Liebermann and Zsuffa[2] have observed that acenaphthenequinone combines readily with 5-ethoxy-2-amino-diphenylamine to form a product

$$C_{10}H_6 \diagdown \frac{C = N}{C = N} \diagup C_6H_3OC_2H_5$$
$$Cl \quad C_6H_5$$
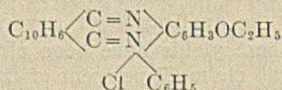
which reacts with woolen fabrics to produce a yellow dye. The possibilities represented by this type of reaction become apparent from a consideration of the fact that acenaphthenequinone has been found to react readily with amino hydrogen in a number of other different compounds. For example, its action when condensed with amines, with hydrazines, and with hydroxylamines has been made the subject of investigation by G. Ampola and V. Recchi,[3] L. Behrend,[4] J. Hermes,[5] K. Auwers,[6] F. Ullmann and E. Cassirer,[7] A. Cruto,[8] G. Charrier,[9] L. Fransconi and F. Pirazzoli,[10] and certain of the observations along these lines have been deemed of sufficient commercial importance to cover by patents.[11] Ortho-oxy-aryl hydrazines, for example, condense with ortho-diketones, acenaphthenequinone, etc., to give products which dye wool different colors varying from orange to red to green. It should be borne in mind, moreover, in this connection that the original methylene groups present in acenaphthene remain unchanged in all compounds which result from reactions which involve the amino hydrogen of mono- and diamino derivatives of acenaphthene, and that the existence of methylene groups in condensation products of this type suggests the possibility of a variety of further reactions.

Hydroxy Derivatives

Very little work has as yet been done upon these hydroxy derivatives of acenaphthene which represent substitution of ring hydrogen, and at present only three have been mentioned in the literature. 5-Oxy-4-nitroacenaphthene,

$$H_2C - CH_2$$
$$-NO_2$$
$$OH$$
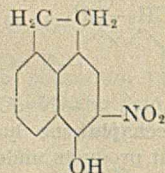
1 Compare Sachs and Mosebach, *Ber.* 44,[(1911), 2852.

2 *Ber.*, 44 (1911), 852.

3 *Atti. accad. Lincei*, 8 (1899), 209.

4 *J. prakt. Chem.* [2] 60 (1899), 1.

5 Dissertation, Kiel, 1898.

6 *Ann.*, 378 (1910), 210; also compare A. Cruto, *C. A.*, 10 (1916), 1857, and G. Charrier, *C. A.*, 10 (1916), 1172.

7 *Ber.*, 43 (1910), 439.

8 *Gazz. chim. ill*, 45 (1925), II, 324.

9 *Ibid.*, 45 (1915), I, 516.

10 *Gazz. chim. ital.*, 33 (1903), I. 36.

11 Compare Holiday and Hodgekinson Brit. Patent 3730 (1883); M.L.B., D.R.P. 258,099; Leonhardt and Co., D.R.P. 258,017; Basler chemischen Fabrik, D.R.P. 218,992 (1910).

and the corresponding 5-oxy-4-amino derivative have been described by Sachs and Mosebach,[1] while the preparation of 5-acenaphthol is covered by patent.[2] Patents also exist[3] which describe the preparation of indigoid dyes by condensing 5-oxyacenaphthene or its derivatives with the usual reagents. The chemistry of those hydroxy derivatives of acenaphthene which result from the substitution of methylene hydrogen will be discussed fully in connection with the oxidation products of acenaphthene.

A number of investigations have been undertaken with the aim of substituing a carboxyl group for a ring hydrogen atom in acenaphthene. Berthelot[4] tried treating acenaphthene with phosgene and was unsuccessful. E. P. Harris[5] used chlorocarbamic acid and obtained an acid amide as the immediate product of the reaction. This when hydrolyzed gave acenaphthoic acid, m. p. 217°.

$$H_2C - CH_2$$
$$COOH$$
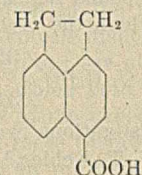
The same substance was prepared by C. Liebermann[6] by the direct action of oxalyl chloride upon acenaphthene (yield 30 per cent) and by Grignard,[7] both by the action (a) of CO_2 upon the magnesium derivative of acenaphthene and (b) by the hydrolysis of the nitrile. The latter was obtained by treating 5-bromo-acenaphthene with magnesium and cyanogen chloride. The acid which is prepared in these different ways is the only compound of its class which has been investigated up to the present time.

Sulfonic Acid Derivatives

Very little is known in regard to the action of sulfuric acid upon acenaphthene and only two sulfonic acid derivatives are described in the literature. One of these substances was obtained by E. Oliveri-Mandala[8] as a result of heating acenaphthene with an equal weight of concentrated sulfuric acid on the water bath for 2 hrs. and then at 115° to 120° for half an hour. The following formula was assigned to the product:

$$H_2C - CH_2$$
$$SO_3H$$
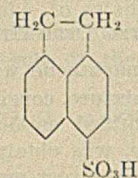
The preparation of the other acid is covered by a German patent[9] and involves the formation of a monosulfonic acid derivative of acenaphthene in which a hydrogen atom of the methylene group has been substituted. This acid was obtained by the action of chlorosulfuric acid at a temperature ranging between 15° and 20° and is described as being very reactive in the presence of halogen and of oxidizing agents.

1 *Loc. cit.*

2 Elberfelder Farbenfabriken, See *Ber.*, 44 (1911), 2860.

3 F. Bayer and Co., D.R.P. 237,199, 237,266, 241,825, 241,823 and 241,827. Also compare Brit. Patent 3730 (1818), which corresponds to D.R.P. 237,266.

4 *Bull. soc. chim.* [2, 13 (1870), 391.

5 Gattermann, *Ann.*, 244 (1888), 29; E. P. Harris, Dissertation Gottingen, 1888.

6 *Ber.*, 44 (1911), 202.

7 *Ann. chim. phys.*, [9] 4 (1915), 28.

8 *Atti. accad. Lincei*, 21 (1912), I, 779.

9 Kalle and Co., D.R.P. 248,994 (1910).

OXIDATION PRODUCTS

The most detailed work which has as yet been done in the field of acenaphthene chemistry has been concerned with a study of the products which are formed as a result of its oxidation. This has been due to the fact that the great majority of important commercial applications of acenaphthene deal with substances which are obtained by the action of various reagents upon acenaphthenequinone, acenaphthenone, or naphthalic acid, or upon some mixture of these and other derivatives which contain oxygen. The results of even the earliest studies in the oxidation of acenaphthene and its derivatives[1] showed conclusively that the products obtained as the result of any given reaction varied very considerably and that the yield of any single component of the reaction product depended very definitely upon the conditions.

It remained for C. Graebe in a series of brilliant investigations[2] to clear up the confusion which inevitably arose in regard to the relationships existing between acenaphthene and the various products which are formed as a result of its oxidation, and to establish the exact conditions under which the best yields of the more important of these products could be obtained. It is not within the scope of this paper to describe these processes in detail, but attention may properly be called to some of the conclusions which were arrived at as a result of this work.

Reasoning from purely theoretical considerations the oxidation of acenaphthene may be assumed to proceed in the following stages:

acenaphthene   acenaphthylene   acenaphthyleneglycol

acenaphthenequinone naphthaldehydic acid naphthalic acid

Intermediate between acenaphthene and acenaphthenequinone, though deviating slightly from the straight course of oxidation indicated above, is still another substance which may also be regarded as a product of direct oxidation, namely, acenaphthenone.

All of these substances have been found actually to exist, although all have not been obtained by the direct action of oxidizing agents upon acenaphthene itself. In addition to these, still other compounds are known which may be assumed to represent secondary products of oxidation, and one of which at least has been shown to be present in all oxidizing mixtures. They are biacenaphthylidene ketone and biacenaphthylidene diketone, and may be assumed

$$C_{10}H_6 \begin{matrix} C = C \\ | \quad | \\ CH_2\ CO \end{matrix} C_1H_6 \ \text{and}\ C_{10}H_6, \begin{matrix} C = C \\ | \quad | \\ CO\ CO \end{matrix} C_1\ H_6,$$
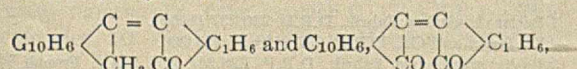
to result from the condensation of one molecule of ace-

1 Compare Behr and Van Dorp, *Ber.*, 6 (1873), 60; *Ann.*, 172 (1874), 263; M. Blumenthal, *Ber.*, 7 (18/4), 1092; Quincke, *Ber.*, 20 (188/), 609; 21 (1888), 1454; Crompton, *Proc. Chem. Soc.*, 28 (1912), 194.

2 *Ber.*, 20 (188/), 23/, 65/, 25 (1892), 652; *Ann.*, 276 (1893), 12; 290(1896)· 290 (1896), 195, 205; 327 (1903), /7.

naphthenequinone with one molecule of acenaphthene or with one molecule of acenaphthenone, respectively.

The mixture which is actually formed by the action of oxidizing agents upon acenaphthene always contains a number if not all of these substances. The three which are practically always present and which are produced in relatively large quantities are acenaphthenequinone, naphthalic acid, and biacenaphthylidene diketone. Two others, acenaphthene and naphthaldehydic acid, have also been isolated in small quantities,[1] while the presence of acenaphthenone is at least indicated. The practical importance of acenaphthenequinone and naphthalic acid was immediately recognized, and the researches of Graebe had as their principle objective the determination of the exact conditions under which these substances were respectively formed. As a result of these experiments, methods were finally developed by means of which 40 per cent acenaphthenequinone and practically theoretical yields of naphthalic acid could be obtained by the direct action of reagents upon acenaphthene. These classical researches of Graebe represent such an exact and careful study that no reports as to modifications and improvements in method occur in any of the succeeding literature on the subject. It has in fact been found difficult always to realize fully the yields which are described in these experiments, and F. Ullman,[2] for example, states that although he has followed Graebe's procedure as closely as possible he has been unable to obtain yields above 40 per cent of naphthalic acid, although theoretical yields are claimed for the process. Graebe himself emphasizes the need of the most minute care in maintaining the very exact conditions which he describes during the entire course of the oxidation. He also emphasizes the need of great precision in handling the resulting mixture, since the exact concentrations of sodium hydroxide and sodium carbonate which are used at different stages in the separation seem to be of the utmost importance. If these reagents are used carelessly, or in other concentrations than those which are described, they may act to produce chemical changes in the substances whose separation is desired. For example, the separation of acenaphthenequinone depends upon its solution in aqueous sodium hydroxide. If the alkali is dilute (5 per cent) practically all of the quinone is precipitated unchanged upon the addition of mineral acid, while if the alkali is concentrated (30 to 35 per cent) the solution gives an almost quantitative yield of naphthaldehydic acid.

The history of the development of the chemistry of the oxidation products of acenaphthene followed the natural course. Separate methods for the preparation of acenaphthylene glycol, acenaphthenone, acenaphthenequinone, naphthaldehydic acid, and naphthalic acid were first studied and perfected, after which investigations in regard to the chemical reactions and important commercial applications of these respective compounds were undertaken. The latter portion of this paper will be devoted to a summary of the results which have been arrived at in each case to date, but before proceeding to the separate discussion of these different substances the fact may be noted that at least in one of their applications, namely in the field of dye chemistry, it is not always necessary to separate them individually from the mixtures in which they occur. Recent German patents cover the condensation of the crude products obtained by the direct oxidation of acenaphthene, with such substances as indoxyl, isatin, oxythionaphthene, and others which may be used in the preparation of red vat dyes. According to D. R. P. 236,536 of the Basler chem-

1 *Ber.*, 43 (1910), 440.
2 *Ber.*, 43 (1910), 440.

ischen Fabrik, for example, the crude oxidation product from acenaphthene and sodium bichromate in acetic acid is treated in the presence of an amine with bisulfite in aqueous solution, when a substance which is assumed to be an arylido-bisulfite derivative of acenaphthenequinone separates from the solution in crystalline form.[1] This is then treated with 3-oxy-1-thionaphthene or the corresponding acid according to the method described in D.R.P. 196,016. In cases where the oxidation of acenaphthene is effected by the action of esters of nitrous acid such as ethyl and amyl nitrite,[2] the crude product, which contains along with other substances a compound having the composition of acenaphthenequinone monoxime, may be condensed in the presence of formic or oxalic acid with indoxyl, 3-oxy-1-thionaphthene, or their respective derivatives.[3] A supplement to this patent covers condensations in the presence of reducing agents other than formic and oxalic acid.[4] The significance of these facts will become more apparent after a more detailed study of the chemistry of the oxidation products of acenaphthene.

Acenaphthylene glycol,

$$C_1H_6\diagdown\begin{matrix}CHOH\\ |\\ CHOH\end{matrix}$$
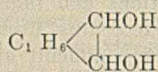
represents a product which has not as yet been obtained by the direct oxidation of acenaphthene. It has been prepared from acenaphthylene bromide (1) by first transforming the latter into its acetate and then saponifying the product,[1] and (2) by boiling the bromide with water.[2] In both instances the yields are relatively small, and for this reason the substance is at present of little more than theoretical interest.

Acenaphthenone,

$$C_1H_6\diagdown\begin{matrix}CH_2\\ |\\ CO\end{matrix}$$
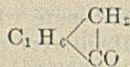
has been prepared from acenaphthylene glycol (1) by treating the substance with sodium alcoholate and methyl iodide,[3] and (2) by boiling for a few minutes with concentrated hydrochloric acid and then distilling with steam, when acenaphthenone appears in the distillate.[4] It has also been prepared by starting with acenaphthenequinone. In this case two methods of procedure are possible. The quinone may either be subjected to direct reduction in acetic acid solution by means of zinc dust, or it may be converted into its dichloride by treatment with phosphorus pentachloride and the product then reduced. Both methods give approximately the same yield (35 to 37 per cent of the acenaphthenequinone taking part in the reaction), but the second is the more convenient since less care is required in carrying out the experiment. The dichloro derivative of acenaphthenequinone

$$C_1H_6\diagdown\begin{matrix}CCl_2\\ |\\ CO\end{matrix}$$
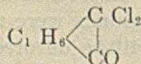
which is formed as the intermediate product in this reaction is an interesting substance and its possibilities as a reagent in condensation reactions seem never to have been fully exploited.[1]

Still another method for the preparation of acenaphthenone involves the action of aluminium chloride upon α-naphthylacetyl chloride dissolved in nitrobenzene. The product is poured upon ice, and the acenaphthene is separated first by steam distillation and then by distillation under reduced pressure.[2] The reaction in this case may be expressed in terms of the following equation:
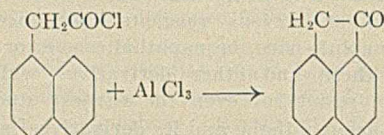
Acenaphthenone has been applied in a number of condensation reactions. It itself polymerizes in the presence of alcoholic alkali or acetyl chloride to give biacenaphthylidene ketone,

$$C_1H_6\diagdown\begin{matrix}C=C\\ |\quad\;|\\ CO\;CH_2\end{matrix}\diagup C_1H_6$$
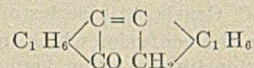
Acenaphthenone, or derivatives of acenaphthenone in which the hydrogen of the methylene group has not been replaced, gives indigoid dyes[3] when condensed with derivatives of isatin, or naphthisatin which contain an α-ketone oxygen atom. A supplement to D.R.P. 212,858 provides for the substitution of 2,3-diketo-dihydrothionaphthene in place of acenaphthenequinone in condensation reactions with acenaphthenone.[4] It should be noted that in addition to a reactive carbonyl group acenaphthen one possesses methylene hydrogen hich is very reactive. In view of this fact it seems rather remarkable that the literature dealing with the chemistry of this substance should be relatively so meager.

ACENAPHTHENEQUINONE—Acenaphthenequinone is always formed in the oxidation of acenaphthene. Neither the character of the oxidation medium nor the quantities in which it is used seem to influence the yield of acenaphthenequinone very materially, but, on the other hand, the speed with which the reaction is carried on appears to be of great importance. Even under the most favorable conditions, however, the yield of acenaphthenequinone does not exceed 40 per cent of theory. This is due at least in part to the fact that the substance itself is very reactive. In the presence of oxidizing agents, for example, it tends to undergo further oxidation, passing into naphthalic acid, and in the presence of alkali (employed to effect the separation of acenaphthenequinone in most of the earlier investigations) it may undergo a variety of transformations. To mention but two of many reactions which may result from the action of alkali, the substance may add one molecule of base to form a salt of naphthaldehydic acid or it may condense to give biacenaphthylidene-diketone. The device of precipitating the quinone in the form of its bisulfite addition product[2] or in the form of its monoxime[3] does not appear to have eliminated completely the difficulties presented in the preparation of this valuable and important compound. Methods of catalytic oxidation, involving as they do the immediate removal of the oxidation product from further action of the oxidizing medium, would seem to offer promising results but, so far as is indicated by any

1 Compare Basler chemischen Fabrik, D.R.P. 205,377, and 211,696.
2 Kalle and Company, D.R.P. 224,979 and 228,698 (1911); also Brit. Patent 19,340 and 19,341; also French Patent 419,370.
3 Basler chemischen Fabrik, D.R.P. 232,714 (1911).
4 Basler chemischen Fabrik, D.R.P. 233,473 (1911).
5 T. Evan and J. B. Cohen, *J. Chem. Soc.*, 55 (1889), 580.
6 C. Graebe and J. Jequier, *Ann.*, 290 (1896), 205.
7 T. Evan and J. B. Cohen, *Loc. cit.*
8 C. Graebe and J. Jequier, *Loc. cit.*
9 Basler chemischen Fabrik, D.R.P. 210,813 (1909).

1 Basler chemischen Fabrik, D.R.P. 230,237 (1909).
2 Fr. Bayer and Co., D.R.P. 237,819 and 237,266.
3 Basler chemischen Fabrik, D.R.P. 226,244 (C.I.B.A.); French Patent 10,542; Compare D.R.P. 212,858 (C.I.B.A.); also D.R.P. 218,992 (B.A.S.F.); French Patent 10,541.
4 *Ann.*, 276 (1893), 7.
5 A. Reissert, *Ber.*, 44 (1911), 1749. Compare Kalle and Co., D.R.P 2 24,979 and 228,698; Brit. Patent 19,340 and 19,341; French Patent 419,379; also Francesconi, *Gazz. chim. ital.*, 33 (1903), 42; and J. C. Cain, "The Manufacture of Intermediate Products and Dyes," p. 242, 1919, Macmilian Co.

references in the literature, they have not as yet been applied to the solution of this particular problem.

The literature dealing with the chemistry of acenaphthenequinone is very voluminous. It consists in large part of descriptions of condensation reactions which commonly involve one molecule of the quinone and one or more molecules of the different compounds which have been found to be capable of coupling with it. Some of these reactions, as for example, those which are brought about by the action of amino hydrogen and which result in the elimination of water, have already been considered in connection with a discussion of the properties of the amino derivatives of acenaphthene. Another general type of reaction takes place when acenaphthenequinone is condnsed with aromatic hydrocarbons or their derivatives in the presence of aluminium chloride.[1] In this case the oxygen of the carbonyl group reacts with ring hydrogen atoms, and the elimination of water is accompanied by the formation of substances which belong to the group of fluorescoin dyes:

$$C_{10}H_6 \begin{matrix} CO \\ | \\ CO \end{matrix} + 2C_6H_6 \longrightarrow C_{10}H_6 \begin{matrix} CO \\ | \\ C(C_6H_5)_2 \end{matrix}$$
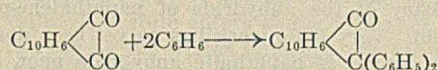
This reaction seems to be capable of as many different forms of application as are possible in the case of phthalic anhydride and other substances of this class. A third general type of condensation takes place as a result of the action of acenaphthenequinone upon organic combinations which contain halogen. Here the elimination of halogen acid is accompanied by the substitution of organic residues for one or both of the hydrogen atoms which occupy peri-positions to the carbonyl of the quinone. References to this type of reaction have already been considered in connection with the preparation of certain of the derivatives of acenaphthene and also in connection with the synthesis of the higher indandiones.

The fourth and most important general type of condensation reaction involves the preparation of vat dyes belonging to the class of indigoids. This particular phase of the chemistry of acenaphthenequinone is of great commercial importance. The literature is voluminous and includes a large number of German patents. This field of work was opened up as a result of the discovery, made more or less simultaneously in 1908 by A. Bezdrik coöerating with P. Friedlander[2] and by A. Grob,[3] that the oxygen of the carbonyl groups in acenaphthenequinone is capable of entering into condensation reactions with indoxyl and with oxythionaphthene to form products which are analogous to indigo and which possess the following unsymmetrical formulas:

$$C_{10}H_6 \begin{matrix} CO \\ | \\ C = C \end{matrix} \begin{matrix} CO \\ NH \end{matrix} C_6H_4$$

and acenaphthene-indol-indigo

$$C_{10}H_6 \begin{matrix} CO \\ | \\ C = C \end{matrix} \begin{matrix} CO \\ S \end{matrix} C_6H_4$$
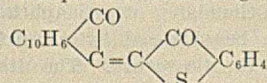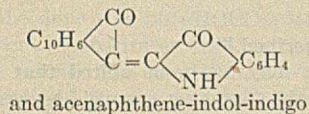
acenaphthene-thionaphthene-indigo

The second of these two substances represents a valuable sulfur vat dye and is known commercially under a number of different names, viz., Ciba Scarlet G (B.A.S.F.). Thioindigo Scarlet 2G (Kalle and Co.), Helidone Scarlet C (M.L.B.).

The original patents[4] which covered the preparation of

the parent substances were quickly supplemented by others which describe their bromination,[1] the dye obtained from Ciba Scarlet G, for example, being known under the trade name of Ciba Red R. Later patents describe the formation of halogenated red vat dyes which are formed under a variety of different conditions.[2] These are so phrased as to cover all halogenated products which may be regarded as derived from acenaphthenequinone, its homologs, and substances analogous to it.

Succeeding patents describe the behavior of acenaphthenequinone in the presence of various *derivatives* of indoxyl and oxythionaphthene respectively.[3] Ciba Orange G represents, for example, a substance which is obtained by brominating the condensation product from acenaphthenequinone and 6-amino-3-oxythionaphthene,

$$H_2N \begin{matrix} CO \\ | \\ S \end{matrix} CH_2$$
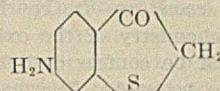
A gray-black vat dye[4] is prepared by condensing 5-amino-3-oxythionaphthene with acenaphthenequinone, and coupling this compound with that obtained by condensing 6-amino-3-oxythionaphthene with acenaphthenequinone. Bromination of the product is included in certain instances. The scope of this work has gradually broadened and has come to include reactions between acenaphthenequinone and a large number of different organic compounds such as, for example, B-naphthindoxyl,[5] phenyl-thioglycol-o-carboxylic acid,[6] etc. Indeed the patent literature on this subject is frequently very difficult to follow, since the specifications which cover the condensations of acenaphthenequinone and its derivatives with derivatives of indoxyl, oxythionaphthene, and similar substances are phrased in such general terms that they may be said to include all the reactions which are possible between carbonyl oxygen, present in every variety of α-diketone grouping, and reactive methylene or methine hydrogen present in any form of combination.[7]

Other indigoids are theoretically possible and acenaphthene-selenonaphthneindigo, for example,

$$C_{10}H_6 \begin{matrix} CO \\ | \\ C = C \end{matrix} \begin{matrix} CO \\ Se \end{matrix} C_6H_4$$
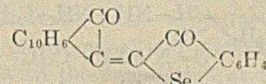
has been prepared and described by I. R. Lester and R. Weiss.[8] This appears, however, to be a substance of no commercial importance.

Kalle and Company suggest the treatment of acenaphthene quinone with caustic alkali prior to condensation, since a water-soluble body,

$$C_{10}H_6 \begin{matrix} C = O \\ | \\ C \end{matrix} \begin{matrix} OH \\ ONa \end{matrix}$$
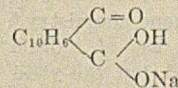
has been observed to form as a result of this action. This yields vat dyes when condensed with 3-oxythionaphthene, etc.[9] The same firm also describes the treatment of acenaphthenequinone with mild reducing agents when the following transformations occur:

1 Compare M. Zsuffa, *Ber.*, **43** (1910, 2915).

2 *Monatsch.,*, **29** (1908), 359.

3 *Ber.*, **41** (1908), 3331.

4 D.R.P. 206,647 and 205,377 (B.A.S.F.).

1 Compare D.R.P. 198,510 and 196,349 (B.A.S.F.) respectively.

2 D.R.P. 213,504, 212,870, 237,199, 237,266, 241,825, 241,826, 241,827; also Brit. Patent 3730.

3 D.R.P. 234,178 (Fr. Bayer and Co.).

4 D.R.P. 258,099 (M.L.B.).

5 D.R.P. 235,811 (M.L.B.).

6 D.R.P. 205,377 (B.A.S.F.).

7 D.R.P. 209,910, Kalle and Co., 1909.

8 *Ber.*, **45** (1912), 1835.

9 Compare D.R.P. 209,910, 243,536, 246,338 (Kalle and Co.).

$$2C_{10}H_6{<}^{CO}_{CO} \rightarrow C_{10}H_6{<}^{C-O-C-OH}_{C-OH\ CO}{>}C_{10}H_6 \rightarrow 2C_{10}H_6{<}^{C-OH}_{C-OH}$$
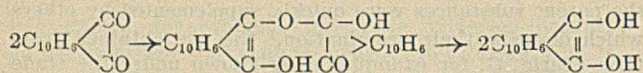
The last compound is capable of condensing with indoxyl or with 3-oxynaphthene to form violet or violet-red vat dyes.[1] Both modes of treatment of acenaphthenequinone are covered by French patents[2] which include the preparation of all derivatives of the above dyes which can be obtained by brominating, diazotizing, etc.

In conclusion it should be noted that many of the reactions described in these patents have not been applied since the use of simple derivatives of acenaphthenequinone in the various types of condensations has been prevented by the fact that very few of these compounds are as yet actually known.

OTHER OXIDATION PRODUCTS—In continuing the systematic survey of the chemistry of the oxidation products of acenaphthene it must be confessed that very little of importance remains to be said. Biacenaphthylidene ketone and biacenaphthylidene diketone,

$$C_{10}H_6{<}^{C=C}_{CO\ CH_2}{>}C_{10}H_6 \text{ and } C_{10}H_6{<}^{C=C}_{CO\ CO}{>}C_{10}H_6$$
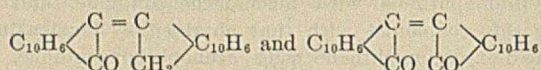
represent secondary products formed by the action of various reagents upon acenaphthenone and acenaphthenequinone. Both compounds were investigated by Graebe and have already been referred to.

Naphthaldehydic acid is an interesting substance, the salts of which seem to exist in two tautomeric modifications, viz.,

$$C_{10}H_6{<}^{C{<}^{OH}_{OK}}_{CO} \text{ and } C_{10}H_6{<}^{CHO}_{COOK}$$
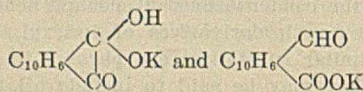
It is formed when acenaphthenequinone is dissolved in aqueous potassium hydroxide (30 to 33 per cent). The free organic acid is precipitated by mineral acids and purified by crystallization from dilute alcohol. The yield is almost quantitative.[3] Naphthaldehydic acid condenses with phenylhydrazine to give

$$C_{10}H_6{<}^{CH-NH-NH-C_6H_5}_{\ \ \ \ >O}_{C=N=NH-C_6H_5}$$
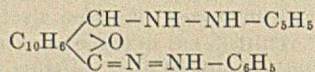
Its condensation products with acetone and acetophenone have been investigated by J. Zink,[5] and those with methyl-*m*-tolyl ketone and pinacoline by S. Wiechowski.[6] Patents based upon the formation of naphthaldehydic acid from acenaphthenequinone have already been referred to.[7]

The oxidation of acenaphthene to naphthalic acid or its anhydride was studied by all of the earlier investigators in the field of acenaphthene chemistry.[8] The process in every instance involved the use of sodium or potassium bichromate and sulfuric acid, but the yield seems to have varied very considerably. Behr and van Dorp obtained yields of 16 to 20 per cent, while Graebe was able to secure results which he described as almost quantitative. F. Ullmann[9] was, however, unable to increase his yields above 40 per cent even by using sodium bichromate and following

Graebe's procedure very exactly. The difficulty seems to be that of carrying the reaction far enough to avoid the presence of the lower oxidation products of acenaphthene and yet stopping it before any appreciable quantities of naphthalic acid have been decomposed. It may be noted in this connection that the ease with which peri-derivatives of naphthalene undergo oxidation is very great.[1]

As its name shows, the similarity in the behavior of naphthalic and phthalic acids was recognized at an early date.[2] The fact that the resemblance between the two substances is very close and very striking might be assumed to indicate the possibility of a large number of important applications for naphthalic acid. For example, the very valuable but somewhat incomplete collection of names and references to derivatives of phthalic anhydride which has been compiled by Dr. Max Phillips of the Color Laboratory, Bureau of Chemistry, Washington, D. C.,[3] suggests many interesting lines of investigation which might be undertaken in connection with a more extended study of the chemistry of the anhydride of naphthalene-peri-dicarboxylic acid. Very little work has as yet been done in this field. The action of naphthalic anhydride upon dimethyl-*m*-aminophenol has been the subject of investigation by E. Ferrario and L. F. Weber,[4] but aside from this no references to direct condensations have been noted in the literature.

A number of derivatives of naphthalic anhydride have been described. F. Ullmann and E. Cassirer[5] have succeeded in preparing naphthostyril by means of the following transformations:
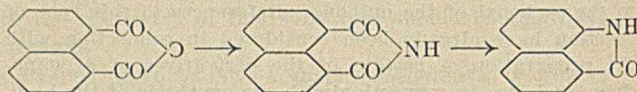
Among the other derivatives which have been investigated are chloronaphthalic acid,[9] bromonaphthalic acid and the corresponding iodide,[7] 4-nitronaphthalic acid and the cor-

$$C_{10}H_5Br{<}^{CO}_{CO}{>}NH$$

responding imide,[8] 4-aminaphthalic acid, 4-hydroxynaphthalic acid, 3-nitronaphthalic anhydride, and 3-aminonaphthalic anhydride.[9] The oxidation of 4-bromonaphthalic acid to bromophenylglyoxyldicarbonic acid
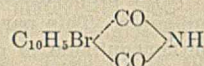
has also been described.[10]
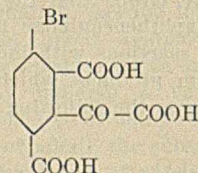
In conclusion it may again be stated that the footnotes which accompany the foregoing synopsis represent all of the references to the chemistry of acenaphthene and its derivatives which can be obtained by a fairly close and systematic study of the literature. The discussion has been as detailed as it has seemed practical to make it in the hope that the material presented might prove of actual service as a basis for further research in this field.

1 D.R.P. 224,158, 224,979; also U. S. Patent 985,170 and Brit. Paten 21,519.

2 French Patent 401,224, 401,225, 401,226, 401,227, 407,228.

3 *Ann.*, 290 (1896), 202; *Ber.*, 25 (1892, 657; *Ann.*, 276 (1893), 18

4 *Ann.*, 276 (1893), 14.

5 *Monatsh.*, 22 (1901), 813.

6 *Monatsh.*, 26 (1905), 749.

7 D.R.P. 243,536 (Kalle and Co.).

8 Behr and W. A. van Dorp, *Ber.*, 6 (1873, 60; *Ann.*, 172 (1874), 263; E. Bamberger and M. Philipp, *Ber*, 20 (1887), 237; C. Graebe, *Ber.*, 20 (1887), 657; 25 (1892), 652; T. Ewan and J. B. Cohen, *J. Chem, Soc.*, 55 (1889), 578.

9 Ber., 43 (1910), 440.

1 Compare G. Errera and G. Ajon, *Gazz. chim. ital.*, 44 (1914), II, 92.

2 A. Behr and W. A. van Dorp, *Loc. cit.*

3 THIS JOURNAL, 13 (1921), 247.

4 *Arch. sci. phys. nat.*, 25 (1908), 517.

5 *Ber.*, 43 (1910). 439; Cpomare C. Graebe, *Ber.*, 35 (1902), 44.

6 H. Crompton and W. R. Smythe, *Proc. Chem. Soc.*, 25 (1912), 194.

7 Blumenthal, *Ber.*, 7 (1874), 1092; Graebe, *Ann.*, 327 (1903), 86.

8 Quincke, *Ber.*, 21 (1888), 1455; Graebe, *Ann.*, 327 (1903), 82.

9 See Graebe, *Loc. cit.*

10 *Ann.*, 327 (1903), 90.

European Practice in Cellulose Acetate and Dopes During the War [1,2]

By Philip Drinker

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Although many substances have been suggested and many formulas developed for the coating and preservation of airplane fabrics, with the exception of the relatively non-inflammable cellulose esters typified by the cellulose acetates, none have received governmental recognition for any extended period of time. In this connection, the cellulose nitrates have received but minor consideration, primarily on account of their greater inflammability, combined with the fact that they do not exhibit properties other than those shown by the corresponding acetic esters.

An historical account of the development of airplane dopes necessarily involves an account, first, of the trial and rejection of cellulose ester substitutes, and secondly, of the improvement of the many combinations and modifications in which cellulose acetate enters as the primarily solid constituent. So far as the writer is aware, the most complete and comprehensive data on the general subject of airplane dopes and cellulose acetate thermoplastic combinations are contained in a 1050-sheet typewritten *Report* 10,086 of E. C. Worden, made in 1918, and the 5040-sheet typewritten *Report* 13,228, with index, of E. C. Worden, Philip Drinker, J. S. Buford, Leo Rutstein, and R. G. Dort,* made in 1919, to the Bureau of Aircraft Production in Washington—reports embodying the results of extended investigations made by the writers abroad and in the United States. Many of the facts and figures incorporated in this article have been abstracted from these reports.

In Europe, at least, the term *dope* was in use in 1914[2] as indicating the nitrocellulose and cellulose acetate solutions which are applied to airplane fabrics to impart increased tensile strength, tautness, and resilience, and to increase impermeability. Present practice requires the several coatings to give a total weight increase to the fabric of approximately 2 ounces per square yard (60 to 70 grams per square meter), and to retain their protective beneficial qualities on exposure to atmospheric weathering conditions, usually for periods of 60 to 90 days. These specifications are the outgrowth of experience during the war, at the commencement of which requirements were less rigorous.

An account of the various French dopes has been given by M. Deschiens,[3] who records the use of nitrocellulose coating, in 1896, on a balloon destined for polar exploration. In this case the dope was purely for protection and not for tautening effects. Substitutes such as casein, glue, gelatin, starch pastes, rubber, etc., have been tried at various times, in both England and France, but their use has never passed beyond the experimental stage, and, at the outbreak of the war, the use of nitrocellulose and cellulose acetate dopes was firmly established in Europe and existed to a certain extent in the United States. As a result of its greater inflammability, the nitrocellulose product was soon rejected by the French, while, as the war progressed, the British program called for a like procedure when adequate supplies of cellulose acetate were available. Marked preference was also shown by the Italians for cellulose acetate dopes. The example of the other Allies was later followed by the United States, the American program calling for all planes destined for the front to be coated with acetate dopes, nitro dopes being limited to training planes. This procedure was identical with that of the British.

Commercial Development of Cellulose Acetate

Prior to the summer of 1914, cellulose acetate was manufactured in commercially interesting quantities by only three European firms, *viz.;* the Bayer Company at Leverkusen, the Société Chimique des Usines du Rhône at Lyons, and the Cellonite Company (Dreyfus Bros.) at Basle. Bayer acetate was used by certain British firms and is reliably reported as being satisfactory, while that furnished by the French company was also received with favor. In France the Usines du Rhône product was in general use, so that the outbreak of hostilities found the British depending for their supply on their French Allies and on the product of a neutral country, no adequate supply of German acetate having been accumulated.

As the war progressed and their aircraft program augmented, the French required more and more of their own product, with the result that shipments to Great Britain were reduced to a minimum. The British program called for an amount of acetate soon evident to be far in excess of the assured supply, coming as it did from outside sources. This state of affairs resulted in negotiations with the Dreyfus Bros.[4] whereby the erection of a large plant for the manufacture of cellulose acetate was undertaken at Sponden, England. This plant also included a synthetic acetic acid and acetic anhydride unit. To assure further their own supply, a similar but smaller Dreyfus plant was built by the French at Rouen, while plans for a Dreyfus plant at Milan were laid down by the Italians. This example was later followed by the United States at Cumberland, Md. Throughout the war, the French used the Usines du Rhône product in greater part—a product characterized by its uniformity in the chemical and physical qualities essential for dopes. With the completion of the Dreyfus English plant, British dopes were made almost solely from this latter source of acetate, a state of affairs prevailing at the close of the war when a standard dope formula, obligatory for all manufacturers, had been developed. That the Dreyfuss acetate successfully met the specifications for this standard dope over an extended period is sufficient proof of its uniformity.

The cellulose acetate resources of Germany have been said to be greater than those of the Allies. The acetate of the Bayer Company has already been mentioned as one of the three types produced in Europe at the outbreak of the war. Personal visits by E. C. Worden[5] and the writer,[6] on behalf of the Bureau of Aircraft Production, to a small plant at Mainz showed an additional source which is known to have been utilized by the Germans during the war. Samples of gelatin-coated gas-mask eye pieces, made of cellulose acetate, from the Aktiengesellschaft für Anilin Fabrikation were also observed from time to time. Fabrics from German and Austrian planes invariably showed cellulose acetate dope, and, knowing their plant resources, it is but reasonable to presume they had no special difficulties in meeting requirements, although no reliable data are available to us on their cellulose acetate output. All the plants known to have been engaged in its production were located far from the front, and evidences of destruction of

their chemical factories by Allied aircraft were not apparent. In fact, the general atmosphere of the enemy chemical plants, as disclosed from visits to their factories in the occupied region, was decidedly one of prosperity and preparedness for the future.

Chemical Characteristics of Cellulose Acetate

Of the many variations in processes used for the production of cellulose acetate all employ the same basic principles, *viz.;* acetylation of cellulose by glacial acetic acid and acetic anhydride in the presence of a catalyst such as sulfuric acid. The Dreyfus processes[7] involve the use of paper as the preferred source of cellulose, while it is understood that the Société Chimique des Usines du Rhône[8] employs a long-staple cotton, previously treated. For airplane dope, in both cases the objective is an acetone-soluble acetate, between the diacetate and triacetate in acetic content, which is attained by acetylation temperature control and the subsequent ripening process. In an exhaustive study of the subject, E. C. Worden[9] has traced the development of cellulose acetate from the carbohydrate acetylations of Schützenberger through to the modern period, and has pointed out the importance of the Dreyfus discoveries in the development of this art. In this article, he shows that the acetates preferred for photograph films and artificial filaments differ fundamentally from the product used for dopes, the former demanding clarity as an essential characteristic, while the latter must possess relatively greater tensile strength, clarity of the dope film being of less importance. Primary acetates, possessing acetone solubility as a permanent characteristic, and having passed through the chloroform-soluble stage, are among the qualities necessary for dopes in which chlorinated solvents do not enter. H. Ost,[10] C. Cross and E. Bevan,[11] and G. J. Esselen, Jr.[12] have contributed to the literature on this subject, the last author discussing the colloidal nature of the cellulose acetate molecule and distinguishing the chloroform and acetone-soluble acetates by the solvents which may be employed.

Of the Usines du Rhône and Dreyfus products, the former generally possessed the more rapid acetone solubility, due perhaps to finer state of mechanical division of the particles. Dreyfus aimed to produce an acetate of relatively higher viscosity[13] which could be applied in a three-coat doping scheme, and which would give a film of tensile strength equal to that formerly attained by applying as many as six coats. This resulted in a substantial solvent economy so imperative in the successful prosecution of the British aircraft program.

Solvents, Diluents, Plasticizers, and Pigments

The selection of solvents and solvent combinations was determined by each country primarily from the resources available, a condition which prevailed throughout the war, and which underwent a gradual development resulting in the ultimate adoption of standard formulas. Since over fifty different solvent combinations—a number of them secret—emanating from the Allied governments and from firms supplying dope, were suggested and used at one time or another, a detailed historical account would be inexpedient. The subject can well be covered in a review of the essential points of difference of the various combinations, as their use developed during the course of the war. The use of tetrachloroethane as a solvent was prohibited by France, and later by Great Britain, because of its toxicity and tendency towards decomposition, as result of which the fabric was materially weakened. Actual fatalities[14] were traced to the toxicity of this solvent. The work of W.

Willcox, B. Spillsbury, and T. Legge[15] showed that a characteristic type of toxic jaundice, affecting the liver, developed from inhaling tetrachloroethane fumes. Both countries, and Italy as well, prohibited the use of chlorine substitution products, an example followed later by the United States. Consequent to these discoveries, the British enforced rigid ventilation of their doping shops and required at least thirty changes of air per hour.

Somewhat before our entry into the war, the French were using a four-coat dope designed for purposes of camouflage, which at that time was considered by them to be indispensable. A typical French dope, patented under the trade name of *Acellos* by Nauton Frères et de Marsac, the patentee being their chemist, T. Tesse,[16] was in special favor, while L. Clement and C. Rivière[17] produced a somewhat similar product. In *Acellos* dope the scratch coat contained 3 to 5 per cent acetate and was low in high boiling solvents, by which means greater tautening effects were said to be produced. The second and third coats required 8 to 9 per cent acetate and about 2 per cent of mineral or metallic pigments, the vehicle for which was usually eugenol, while other high boilers and pdasticizers, such as benzyl alcohol, triacetin, isoeugenol, carvacrol, safrol, isosafrol, methyleugenol, and glyceryl benzoate, could be employed. The fourth and final coat required about 8 per cent acetate, while the high boilers were again cut down. The under surfaces of the planes received second and third coats of aluminium color and upper surfaces were given a variegated camouflage scheme intended to resemble the earth's surface. Planes used in night flying were colored dark, the dopes being applied exactly as were those for the day planes. None of the French planes destined for the front received a varnish coating of either oil or nitrocellulose base. This treatment was claimed to impart special characteristics of tautness and to increase invisibility of the plane from both above and below, an idea which gradually lost favor until, at the end of the war, the French followed the British example and adopted colorless dopes with a finishing coat of khaki color on upper surfaces.

British practice went through a similar but seemingly more logically coördinated and technically controlled development. While the French relied mainly on methyl acetate of local manufacture for their low boiling solvent, the British had recourse principally to acetone, furnished in large part by the United States and Canada. In a general report, J. Ramsbottom[2] discusses cellulose acetate solvents and points out the latent solvent effects of a mixture of benzene and alcohol, each of which in itself is a non-solvent at ordinary temperatures, a point mentioned later by G. J. Esselen, Jr.[18] Efforts to obtain a satisfactory three-coat standard formula requiring the maximum amounts of the non-pyroligneous products, ethyl alcohol and benzene, resulted in 1918 in a British formula[19] in which acetone, methyl acetate, ethyl formate, or methylethylketone could be used as the low boiling solvents, alcohol and benzene as the diluents, benzyl alcohol as high boiler, and triacetin and triphenyl phosphate as softeners.[20]

To these lists the French added a locally manufactured low boiling product, known as *C.G.H.*, which consisted in a mixture of approximately 70 per cent methyl acetate, 16 per cent acetone, 12 per cent methyl alcohol, and 2 per cent water. In addition to the high boiling solvents already mentioned, the French suggested acetoacetic ester and furfurol, and towards the end of the war, amyl and isobutyl alcohol,[21] of which a French firm offered a considerable supply. Dechitns[3] mentions their having investigated in addition the following substances: methyl, ethyl, amyl,

and butyl lactates and oxalates, glycol diacetin, benzylidene diacetate, diphenyltolyurea, and cresol,[22] none of which passed beyond experimental stages. Cyclohexanol, and cyclohexanone[23] were also suggested from both British and French sources, but were never used in any quantity, although said to be efficient. Acetic and formic acids were used experimentally as solvents and did not appear to weaken the fabric materially.[24]

Unlike the British, the French dopes contained no solid softeners such as triphenyl phosphate, although the French had attempted using both this and tricresyl phosphate, principally as fire retardants.[25]

Having adequate supplies of phenol, the Italians generally used a small percentage of this substance—2 to 3 per cent, depending on the type of fabric for which the dope was destined. Their formulas, like several of the French ones, were varied somewhat in winter and summer to compensate for rapidity of solvent evaporation. The Italians permitted a certain latitude in the choice of low boiling solvent combinations and also used no tricresyl or triphenyl phosphates.

The United States developed a standard four-coat scheme in which the scratch coat contained a small percentage of phenol and napthalene, and, as antacid, a small percentage of urea or dicyanodiamide. For the three subsequent coats, there was included in the formula about 7 per cent of diacetone alcohol, principally to prevent blushing, with small amounts of benzyl acetate and benzoate. The United States' formula embraces the greatest number of ingredients, but it must be remembered that this formula was based on supply and economy in local resources.

German and Austrian Practice

Critical periodic examinations of enemy fabric obtained from captured or destroyed aircraft, both lighter- and heavier-than-air, disclosed a few important points differentiating their fabric and dope from those of the Allies. The enemy planes were frequently camouflaged in multicolored dyes, printed on the fabric in polygonal designs. The airplane fabric was usually linen, showing evidences of heavy calendering, with a thread count averaging about 55 to 65 per inch for the warp and 45 to 55 in the weft. The tensile strength gave average minimum figures of 70 to 80 pounds per linear inch in the warp and 65 to 75 pounds in the weft, but it must be remembered that these figures are taken from used fabrics which had undoubtedly deteriorated to an appreciable extent, so that the tensile strength figures are probably low.

In most instances the doped fabrics were covered with an alcohol-soluble varnish, colorless or pigmented, showing a dry weight increase due to the varnish of anything from 0.5 to 2 ounces per square yard. The dope films were of notably less weight than those used by the Allies and were in the neighborhood of 1 to 1.5 ounces per square yard. Comparative analyses of scrap Allied fabric showed at least 2 ounces of dope film per square yard and frequently more. A few German fabrics showed evidences of chlorinated compounds as cellulose acetate softeners, but extraneous matter was, in general, not found to be present.

Methods of Applying Dopes

Since the major percentage of ingredients of both cellulose acetate and nitrocellulose dopes is made up of low boiling hygroscopic liquids, their evaporation is rapid, an effect in some measure retarded by the addition of softeners and high boiling solvents. In both types of dope the cellulose ester can readily be precipitated by the addition of water, which explains the formation of the *white spots* or *blushing* so familiar on fabrics doped in damp and exceptionally drafty doping shops. Directions by the manufacturers and by all the governments required the dopes to be applied to dry fabric, while the United States alone enforced any attempt at humidity control, the European Allies merely suggesting its advisability.

Great Britain and the United States both required special brushes, approximately 4 inches wide with 2-inch bristles firmly fixed in the stock, a special brush wash being supplied in which the brushes were kept when not in use. Special cans were provided by Great Britain and the United States, these being designed to hold a conveniently portable quantity of dope of which a minimum of surface was exposed. Towards the end of the war a British firm developed a type of brush, through the handle of which dope was fed by air pressure, the dope being contained in a standard 10-gallon (Imperial) can. This brush, however, received no general usage. Both British and French made it a practice to save the skins or films which formed on the edges of the dope cans, these films being furnished to the manufacturers, who again used them, with judicious blending, in making up fresh dope.

Cellulose acetate doped fabrics, unprotected by a varnish coating, temporarily lose their tautness on becoming soaked, the tautness again becoming normal on the fabric's drying. This effect was most noticeable on French planes doped according to their four-coat scheme which required no varnish and no solid softeners. H. Gault[26] and the writer have taken advantage of this in a patent application for a process in which fabric, both linen and cotton, is mechanically coated with a cellulose acetate dope by spreading machine, for example, on both surfaces. When a wing or other member is to be covered the doped fabric is soaked in water and applied, moist, to the frame. When dried and varnished the fabric attains the required degree of tautness, while at the same time other properties conferred by dopes applied in the conventional manner are claimed to be equaled. The signing of the armistice prevented further investigations as to the value of this process, although laboratory and large-scale tests gave every indication that it had decided practical commercial possibilities for aircraft and possibly for other industries.

Great Britain and the United States very generally applied varnish covers and the colors for the insignia or identification marks by air brush. This method of application can be used for oil or nitrocellulose varnishes with equal facility, but no cellulose acetate dope which could be sprayed was developed, although a certain amount of experimental work was done.[27]

Effect of Sunlight on Doped Fabrics

It has been shown how important a factor was the question of supply in determining the various dopes used by the Allies; no less important was this same factor in standardizing the types of fabric. In place of line the United States gave precedence to a mercerized cotton of the type developed through the investigations of the Bureau of Standards, notably by E. Walen.[28] This cotton fabric fulfilled the specifications of the Allied countries, although its general acceptance and recognition was slow. In England linen made from Irish flax was preferred although cotton had fairly general acceptance, while France used linen, cotton, and silk. From her own resources Italy obtained silk, and both France and Italy, purely from economic reasons, used considerable quantities of this fabric in spite of its high cost.

It has been stated that both France and Great Britain abandoned the use of tetrachloroethane as a cellulose acetate

solvent in dopes because of its toxicity and tendency to decompose. The cause of this decomposition was frequently ascribed to sunlight, although investigations at the beginning of the war do not appear to have been carried out to prove this point. The fact that both nitro and acetate doped fabrics gradually deteriorated, with a consequent loss in impermeability and tensile strength, was well recognized, but no means of retardation by agents, other than varnish, appears to have been attempted.

During 1918, F. Aston, at the Royal Aircraft Establishment, England, showed that the destructive action of sunlight on fabric, not the dope film, was principally due to ultraviolet light of wave lengths lying between 2950 and 4000 μ, and that the effect of these rays could be diminished by interposing an impervious layer or pigmented film. After testing various media, Aston showed that their coating, P.C. 10,[29] effectively impeded the destructive action of sunlight. This particular varnish has a base of nitrocellulose and khaki colored pigments of yellow ocher and lamp black, rendered plastic in a vehicle of castor oil. One coat of this varnish was applied by hand or air brush on upper suraces of British planes. Following Aston's work, it was shown by others, notably the French, that the action of sunlight was more serious on silk than on cotton or linen, a point of interest to the Italians and French.[30]

A three-coat pigmented dope[31] was suggested by the British for Handley-Page night bombers, the resultant color scheme being much like that already in use by them at the time, except that under surfaces were also colored. The formula used for these pigmented dopes was very close to their standard and differed from the French colored dopes principally in the use of triphenyl phosphate, of which the British made much point. Although the British pigmented dopes showed considerable promise, they had received but limited application at the signing of the armistice.

Solvent Recovery[32]

Solvents lost in the doping of aircraft fabrics were relatively small, compared with the solvents used in the manufacture of nitrocellulose powder, and it was quite natural that their recovery was of secondary importance in the question of solvent economy. By the centralization of plants engaged in covering and doping airplane parts, solvent recovery was in a fair way towards practical realization at the close of the war, so that a brief account will be given of two processes used in Europe.

L. Clement and C. Rivière attempted recovery by scrubbing the solvent vapors in cold water, a small plant for this purpose being built near Paris. The airplane wings were placed in horizontal troughs, of convenient height for the workers to dope, and the solvent vapors were drawn by fan down through a pipe running along the floor and thence to a scrubbing tower where the vapors met a descending shower of cold water, contact surface being furnished by coke. A number of doping troughs were connected in parallel to the vapor pipe, each trough having a damper for connecting into the system. Rolling curtains were placed across the end of each, and as doping progressed one curtain was rolled up and the other unrolled, thus affording a slight degree of control on the solvent content of the air entering the scrubber. The aqueous solutions at the bottom of the scrubber contained approximately 2 to 3 per cent of recoverable solvents with a total yield of about 30 per cent. The solvents captured were necessarily limited to the water-soluble, although the solubility of such substances as benzene, ordinarily water-insoluble, is enhanced by the presence of benzene solvents which in themselves are water-soluble. It is understood that the inventors

claimed better yields could be effected, but no evidence available to the writer shows that this was accomplished on a scale of commercial interest.

For the recovery of ether-alcohol in the gelatinization and drying of nitrocellulose powder, the process of J. Bregeat,[33] which utilizes cresol, received extensive application during the war. It had been shown that certain phenolic bodies formed addition products with solvents such as acetone[34] which could be liberated on heating, the complex dissociating into its original components. Bregeat used this basic principle in attempting a substitute for sulfuric acid as an agent for ether-alcohol recovery, and first suggested the sulfonic acid of benzene but later found that cresol alone served as well and, in addition, was cheap and available in large quantities. The inventor claims the possible recovery of a number of volatile solvents, among which are the methyl, ethyl, and amyl alcohols and acetates, acetone, benzene, toluene, xylene, and chloroform, from which it will be seen that the process is of interest in the cellulose acetate industries. Yields of 75 per cent of the solvents entering the system are guaranteed, while 92 per cent yields are said actually to have been obtained, figures which are supported by M. Deschiens.[32]

The success of his French plants, notably at Ripault, Sevran-Livry, and Toulouse, was such that Bregeat's process was recognized in Italy and England, where plants were built for ether-alcohol recovery. At H. M. Factory, Gretna, England,[35] sulfuric acid[36] had been abandoned and an experimental cresol plant installed, independent of Bregeat's engineering supervision. This plant proved so successful that a larger unit was undertaken, but was not finished until the close of the war.

The plants built by Bregeat usually include three scrubbing towers in which a large contact surface is obtained by a system of horizontal lattices of wood, scrubbing taking place on the countercurrent principle. At Gretna, rotary scrubbers made by the Whessoe Foundry Company were used, these being built up in twelve compartments giving a twelve-stage absorption. Contact surface was obtained by V-shaped wooden sectors, about one-quarter of an inch in thickness and sufficiently close together to pick up a film of cresol through which the solvent vapor passed as the scrubber slowly rotated.

For the liberation of ether-alcohol from cresol, Bregeat usually employs heat alone, while at Gretna live steam was considered essential. In either case the distilled solvents are subsequently rectified, while the cresol is returned to the scrubbers.

It has been shown in aircraft manufacturing that the weight decrease of freshly doped fabric proceeds at a fairly uniform rate for the first 15 to 20 minutes, after which solvent evaporation rapidly falls off. Tests, with cresol as the absorbent and using the standard British dope (D.100 specification), showed a yield of 50 to 60 per cent, with reliable indications that this would be exceeded in large-scale operations. Whether the fabric be doped in a vertical position from both sides at once or horizontally, is of no moment as regards the effect of the dope, but the former method is more rapid and will therefore give greater concentration of the solvent vapors in the air passing to the scrubbers. Vertical doping was adopted by the Voisin Company in whose aircraft works, near Paris, a Bregeat recovery plant was completed at the signing of the armistice. With locally devised improvements in the doping cabinets, all such modifications having as an objective the increased solvent concentration entering the scrubbers, this plant possessed the equipment then believed the best obtainable and endorsed by the Allied services.

RECOVERY OF CELLULOSE ACETATE FROM SCRAP AIRPLANE FABRIC

To alleviate its shortage, investigations were undertaken both by independent firms and by the Allied governments towards the recovery of cellulose acetate from discarded airplane fabric, with the object of its resolution as such or mixed in part with fresh acetate. Mention has been made of the fact that the French used only cellulose acetate dopes on all planes, while the British used nitrocellulose dopes on training planes and finished off the combat planes with a nitrocellulose varnish for protection against ultraviolet light. Of the two systems, the French afforded the better opportunity for cellulose acetate recovery, inasmuch as the British required the separation of the two esters.

Of the several recovery processes suggested, all operated on the extraction principle and differed only in the choice of solvents and in certain details of mechanical manipulation. The Société Generale du Coton Industriel[21] suggested the use of cresol or furfurol as solvents, but it is understood that the former alone was used. This process requires extraction at temperatures in the neighborhood of 40° C., filtration of suspended mineral pigments, and precipitation of the cellulose acetate by benzene, followed by its purification with steam under reduced pressure, by which means it is claimed the acetate is not injured. The acetate thus recovered is undoubtedly degraded to a certain extent, but it is claimed to be satisfactory for dopes when mixed with fresh acetate.

J. Lumsden and R. Mackensie[38] proposed the use of solvents such as acetone for extracting the cellulose acetate. In one sense this would be an improvement over cresol, as the acetate need not be precipitated from solution but fresh dope could be made up with this as a basis.

Other solvents suggested were nitrobenzene, mixtures of methyl and ethyl alcohols and acetates, and tetrachloroethane. None of these methods were investigated on a scale of commercial interest over any extended period, mainly because the salvaging of scrap fabric was, at best, an uncertainty, although the French accumulated a considerable quantity.

SUMMARY

Many processes utilized in the war for the manufacture and use of cellulose acetate and nitrocellulose dopes for the coating of aircraft fabrics have been made public since the signing of the armistice. Through the issuance of official governmental publications and articles in the technical journals, our European allies have taken a leading part in this commendable procedure.

In this brief review an account is given of the commercial development, in Europe, of cellulose acetate, certain of the physical and chemical characteristics required for its use in dopes, cellulose acetate solvents, diluents, thermoplastic combinations, pigmentation, camouflage, application of dopes, and recovery of solvents and cellulose acetate from discarded fabric.

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Motor Fuel from Vegetation[1]

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For operating the motors of the country an enormous and ever increasing amount of liquid fuel is required. This amount of fuel is so large that not only has great activity in the production of crude oil been necessary to meet the demand but the reserves of crude oil are also being rapidly depleted. The yearly production of petroleum has become so large that exhaustion of its reserves in the United States threatens to occur within a few years. The object of this paper is to present the danger with which motor transportation is threatened, with the hope of directing further attention to a possible means of solving this problem, which is of such vital importance to the country.

THE PRESENT MOTOR FUEL SITUATION

The number of automobiles and trucks in use in the
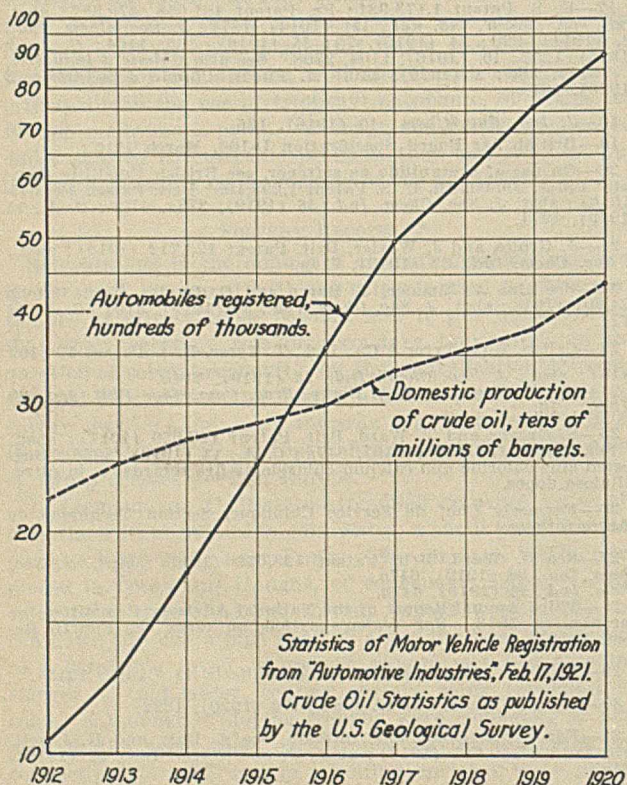
Fig. 1—Relation between automobiles registered and production of crude oil

United States has increased from about 1,000,000 in 1912 to about 9,000,000 in 1920, an average increase of over 1,000,000 a year. Crude oil, the principal source of fuel for motor vehicles, has shown an increase in domestic production during the same period from about 220,000,000 barrels to 440,000,000 barrels a year; so that, while the number of motor vehicles in use has increased about

ninefold, domestic crude oil production has only doubled. The relation between motor vehicles in use, as shown by registration figures, and the production of crude oil is given graphically in Fig. 1.

In Fig. 2 the relative growths of the three factors, motor vehicle registration, crude oil production, and gasoline production, are compared with 1909 values. The production of crude oil has increased since 1909 about 140 per cent, and that of gasoline about 800 per cent, but the number of automobiles registered has increased 2570 per cent.

The normal gasoline content of the crude oil produced
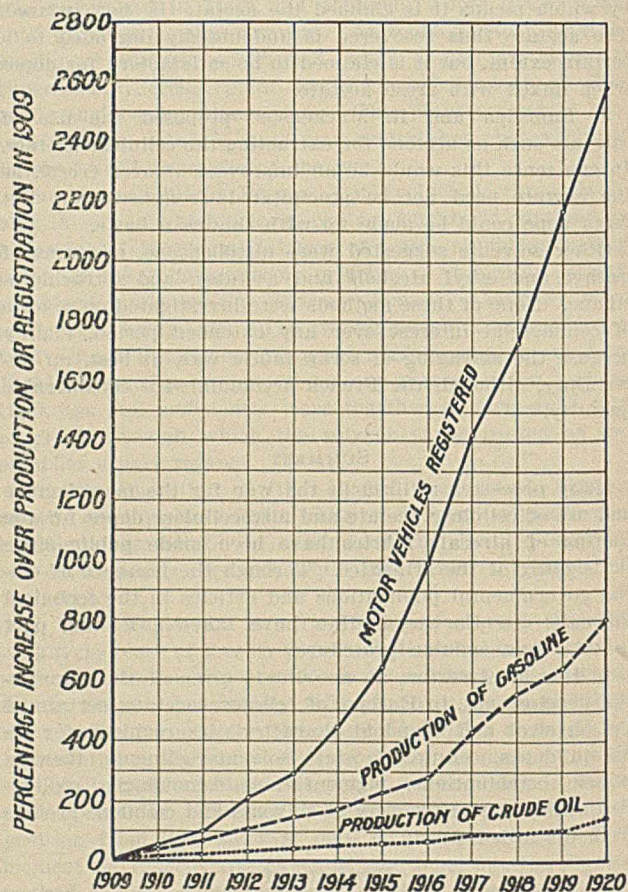
FIG. 2—PERCENTAGE INCREASES IN MOTOR VEHICLES REGISTERED, PRODUCTION OF CRUDE OIL, AND PRODUCTION OF GASOLINE, COMPARED WITH 1909[1]

[1] U. S. Bureau of Mines, *Bulletin* 191, 19: *Automobile Industries* (Feb. 17, 1921), 306; recent statistics, U. S. Bureau of Mines and Geological Survey.

in the United States is around 20 per cent.[1] The actual production of gasoline has exceeded this percentage of the crude since 1917. Refiners have met the rapidly in-

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[1] Read before the Cellulose Section at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[1] David White, *J. Soc. Automotive Eng.* 43, (1919), 61.
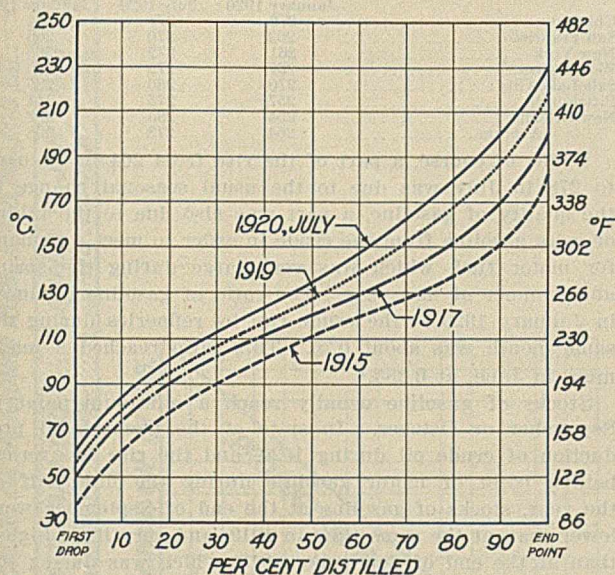
Fig. 3—Change in Volatility of Motor Gasoline, 1915 to 1921[1]

[1] U. S. Bureau of Mines data taken from "The Trend of the Oil Industry in 1920," by Joseph E. Pogue, AUTOMOTIVE INDUSTRIES, (February 17, 1921) 404.

creasing demands for gasoline from a production of crude oil which did not keep pace with the demand for motor fuel:

1—By increasing the average boiling point of gasoline.
2—By extracting liquid hydrocarbons from natural gas.
3—By cracking heavy petroleum oils.

There is a limit above which the average boiling point of gasoline cannot be raised; although, at present, no one is able to predict accurately just what this limit is. The amount of casinghead gasoline which can be manufactured is small at best, but it is very valuable both because of the low initial it gives to commercial gasoline on being blended with it, and because by proper blending it makes available for motor fuel a certain amount of high boiling oil which could not otherwise be used for this purpose. The cracking of heavy petroleum oils as it is now conducted is wasteful from a fuel conservation standpoint, and the successful operation of a cracking plant depends upon the margin between the price of fuel oil and that of gasoline. The rapid increase in the use of fuel oil for certain land and marine purposes is gradually making it an essential for a class of transportation that will use a large amount of it and that represents a high type of demand which can command a supply on a price basis.

Of the means which have been used to increase the yield of gasoline above the normal 20 per cent from the crude oil, and which have been enumerated above, the most effective one is the simple expedient of cutting deeper into the crude. The general trend of the average boiling point of gasoline has been upward ever since the early days of automobiles, when the fuel used was 76° gasoline. No authentic distillation data are available for the motor fuel in use prior to 1915. In Fig. 3 are shown average distillation curves of commercial motor gasoline in the United States since 1915. The increase in distillation temperatures from 1915 to 1920, as shown in Fig. 3, represents a change in composition of gasoline which corresponds to a marked increase in the production of straight run gasoline from a given amount of crude oil.

This increase in the end-point or the average boiling point of motor gasoline has introduced some serious problems which the automotive industry has been called upon

to face. As gasoline has become heavier, distribution and vaporization have become increasingly difficult; it has become harder to start motors; carbonization of cylinders has greatly increased; and contamination or dilution of the oil in the crankcase has become much worse. But of most importance is the increased tendency of the fuel to knock as its distillation temperature rises. Distribution and vaporization are being accomplished to a great extent by the application of heat in various ways; but still further improvements along this line are essential, and they are being made as the results of experimental work point the way. A number of expedients for starting cold motors when using commercial gasoline are now in use, and further improvements are constantly being made. Dilution of the lubricating oil, which is aggravated by high boiling fuel, is a problem which in the light of experience appears capable of being satisfactorily solved. These difficulties are present on account of physical reasons, and they can be corrected by mechanical or physical means.

The fuel knock, however, under given conditions of pressure and temperature is a function of the chemical composition of the fuel. The paraffin hydrocarbons which make up the greater percentage of commercial gasolines are comparatively bad from a knocking standpoint, and their tendency to knock increases with boiling point. Since the fuel knock increases both with compression and temperature, this characteristic of commercial motor fuel limits the initial compression at which it may be used. In limiting the compression it limits the efficiency at which the motor operates, in accordance with the curve in Fig. 4.
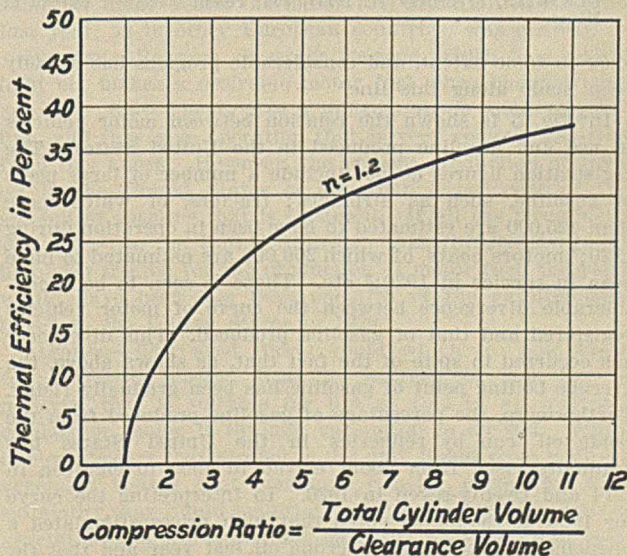
Fig. 4—Relations between Thermal Efficiency and Concussion Ratio in an Internal Combustion Engine.

[1] Dickinson, *J. Soc. Automotive Eng.*, 12 (1919), 228.

The standard compression ratio for automobile engines is now about 4:1. At the maximum compression reached with this compression ratio the knock is an inconvenience, but the seriousness of the knock lies in the fact that it interposes a barrier to any increase in compression above the present standard, and thereby limits the thermal efficiency at which motors can be made to operate. The rising average boiling point of motor gasoline introduces additional difficulties on account of the fuel knock in proportion to the increase in boiling point. This apparent barrier to more efficient utilization of gasoline as a fuel for internal combustion motors is capable of solution, at
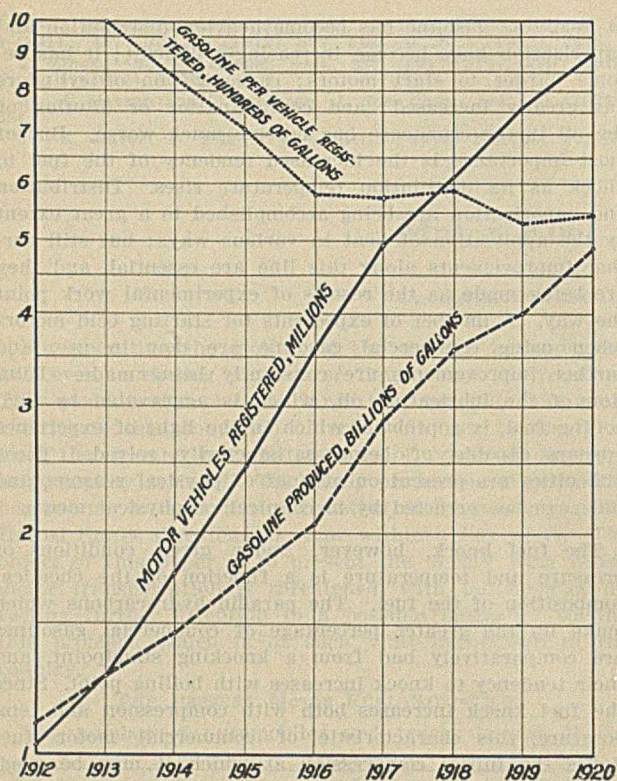
Fig. 5—Relation between motor vehicles in use and gasoline production[1]

[1] U. S. Bureau of Mines, BULLETIN 191; AUTOMOTIVE INDUSTRIES, (February 17, 1921), 306; recent statistics, Bureau of Mines.

least to some extent, and considerable progress has already been made along this line.[1]

In Fig. 5 is shown the relation between motor vehicles in use and gasoline produced in the United States. The registration figures do not include a number of large users of gasoline, such as airplanes; tractors, of which more than 425,000 are estimated to have been in operation during 1920;[2] motors boats, of which 200,000 are estimated to have been in service in 1920;[3] etc. There is seen to be a considerable divergence between the curve of motor vehicles registered and that of gasoline produced. This divergence has occurred in spite of the fact that, as shown above, the average boiling point of gasoline has been gradually rising. Furthermore, the percentage of gasoline produced from the crude oil run by refineries in the United States has gradually risen from about eleven in 1909 to eighteen in 1914 and twenty-seven in 1920. In interpreting the curve for 1920, it should be noted that high prices stimulated a phenomenal production of crude oil last year and that the sale of automobiles suffered from a serious depression during the last four months of the year.

As an illustration of the effect of demand on the end-point or the average boiling point of gasoline, the following figures are of interest. These figures have been taken from the second and third semi-annual gasoline surveys made by the United States Bureau of Mines, and they give average boiling points in ° F.[4]

[1] Thomas Midgley, Jr., "The Combustion of Fuel in the Internal-Combustion Engine," *J. Soc. Automotive Eng.*, 7 (1920), 489.

[2] An analysis of the farm market for motor trucks, published by the Goodyear Tire & Rubber Co.

[3] American Petroleum Institute, *Bulletin* 145, February 26, 1921.

[4] *Oil Paint and Drug Reporter*, Petroleum Section, August 16, 1920, and February 14, 1921.

	January 1920	July 1920	January 1921
Chicago	270	275	264
San Francisco	262	270	265
New York	261	272	265
Washington	267	279	270
Salt Lake City	270	286	285
Pittsburgh	257	275	244
New Orleans	254	285	272
Average	264	278	266

While, of course, a part of the rise from 264 in January to 278 in July was due to the usual seasonal change in the quality of gasoline, a part was also due to the taking of more gasoline from the crude in order to meet a demand for motor fuel, which was very large during the spring and summer of last year. The ratio of gasoline produced in January 1920 to the crude run by refineries during the same month was about 0.26. This ratio reached a maximum in June, at 0.283.[1]

Stocks of gasoline usually reach a minimum point in September or October. In spite of the phenomenal production of crude oil during 1920, and the rise in average boiling point of motor gasoline during the first half of the year, stocks of gasoline at the end of September were lower than at the same time in 1919, and very little higher than at the end of September 1918, which was during the war and about the time of the gasolineless Sundays. The depressed condition throughout the country during the latter part of 1920 reacted on the oil industry and influenced the quality of gasoline. The general reductions in the price of gasoline which have occurred throughout the country during the past four months are an indication of the conditions which have influenced its quality to the extent of bringing its average boiling point back almost to the January 1920 figure. But it is to be expected that a return to normal conditions will bring with it further increases in the average boiling point of motor gasoline, especially since very little prospecting or drilling of new wells has been done so far this year.

The general trends which have been given above indicate that the raising of the average boiling point of gasoline has been a necessity rather than a matter of choice with refiners. It was necessary that fuel be supplied to the motor vehicles in use, the number of which has been growing at a much faster rate than has the production of crude oil (Figs. 1 and 2). It is impossible to predict accurately what the future will be, but the automobile, the truck, and the tractor have become necessities, and it is certain that they will be exploited still further.

In order to keep up production, the oil industry must continually find new sources of crude oil. It is estimated that one-fourth of the oil produced comes from wells less than a year old.[2] Some large producers of crude oil have expressed the belief that they will be able to find plenty of new sources of oil.[3] The United States Geological Survey has made a careful estimate of the unmined supply of crude oil in the United States,[4] and their estimate, which is based on an exhaustive survey, together with the amount of crude oil that had been taken from the ground up to January 1, 1921, is given in Fig. 6. The unmined supply at that time, which was roughly 6,000,000,000 barrels, will be exhausted in about 13 years if the rate of production is maintained at the 1920 figure (about 443,000,000 barrels).

[1] U. S. Bureau of Mines, Refinery Statistics for 1920.

[2] R. D. Benson, "Production—the Present," American Petroleum Institute, *Bulletin* 132 (December 10, 1920), 31.

[3] Thos. A. O'Donnel, President of the American Petroleum Institute, "Production—the Future," American Petroleum Institute, *Bulletin* 132 (December 10, 1920), 32; Henry L. Doherty, "The Future of the Oil Business," *ibid.*, 45.

[4] David White, "The Unmined Supply of Petroleum in the United States," *J. Soc. Automotive Eng.*, 12 (1919), 361.
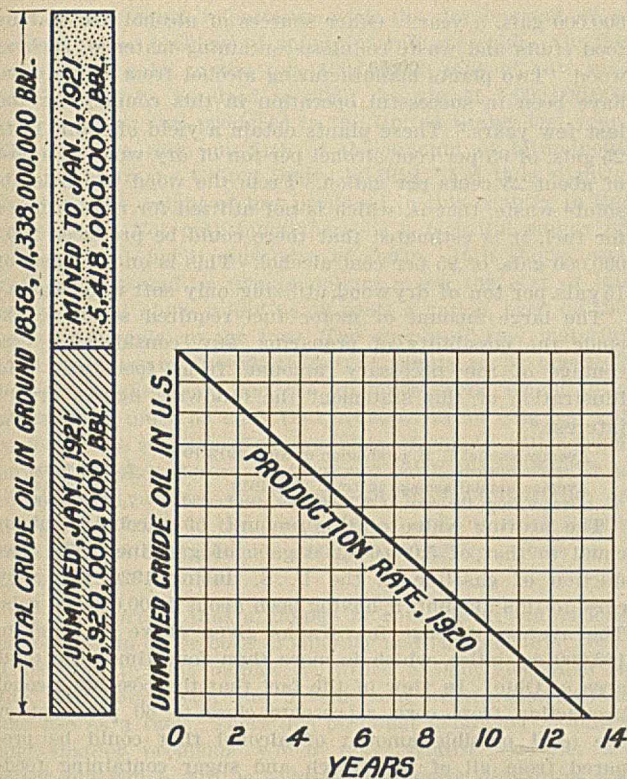
Fig. 6—Unmined Supply of Petroleum in the United States as Estimated by the U. S. Geological Survey[1]
[1] Data from David White, *J. Soc. Automotive Eng.*, 12 (1910), 361, and U. S. Geological Survey production statistics.

Assuming that the estimate of the Geological Survey is correct, it can be but a very few years until the total amount of crude oil that has been mined will approach the amount of this estimate. But, before the total amount of crude oil mined can reach the amount of crude oil originally in the earth, the slope of the production curve must fall off, on account of the reduction in the number of new producing wells being brought in and the gradual decline of old wells. This will bring the country face to face with a real shortage of motor fuel, and at the best it will make us dependent upon foreign supplies of oil. Even if the estimate of the Geological Survey should be 75 per cent in error, which Dr. David White of the United States Geological Survey thinks is extremely improbable,[1] the unmined supply of petroleum in the United States would last only twenty-three years at the rate at which it was mined in 1920.

Dr. George Otis Smith, director of the United States Geological Survey,[2] has estimated that if the burden of supplying the 50,000,000 horsepower, which he gives as the average requirement of the United States, should fall upon the coal mines, on the basis of the best steam practice of today, the present power requirements of this country could be met for 57,000 years. If this burden were to fall upon our supply of oil, however, on the same basis of the best present-day steam practice, he estimates that the oil reserves of the United States would last only nine years and three months.[3]

1 "Petroleum Resources of the World," *Sibley Journal Eng.*, November 1920, 156.
2 "A World View of the Oil Supply," American Petroleum Institute, *Bulletin* 132 (December 10, 1920), 8.
3 The United States Bureau of Mines has estimated that only about 20 per cent of the oil is recovered from the earth by present methods of extraction (G. A. Burrell, *Oil Gas J.*, October 22, 1920, page 84). It is unlikely that all of this oil can be recovered by any means, but it seems likely that a process will be devised for making a higher percentage of this oil available.

Motor Fuels Other Than Petroleum Oils

In view of the petroleum oil situation outlined above, conservation of materials suitable for motor fuel would appear to be a matter of vital importance. As a means toward such conservation any liquids other than petroleum oils that are suitable for motor fuels should be utilized to the fullest possible extent, and an increase in the production of such materials should be encouraged. Two liquids which are now used as motor fuel to some extent, *viz.*, benzene and alcohol, appear to be very promising allies to petroleum oils as fuels for internal-combustion engines.

SHALE—It is probably only a matter of time until some motor fuel will be manufactured in this country from shale. But oil does not occur in shale as such, and it must be produced from the shale by a cracking process. Furthermore, the oil so obtained usually contains but a small percentage of low boiling material that is suitable for motor fuel, and the production of an increased percentage of light oil necessitates further cracking. The resulting material is high in content of olefines and must be blended with a large percentage of a saturated oil before it can give satisfaction as a fuel for automotive engines. It would seem that the greatest value of shale is as a source of fuel oil rather than of motor fuel. Conditions in England and other countries where motor fuel is produced from shale are quite different from those in the United States. The price of motor fuel in England during the latter part of 1920 was more than four shillings per imperial gallon. In spite of this price, and of the facts that a large percentage of their motor trucks are steam driven and that they have had a domestic production of gasoline from shale for many years, the motor fuel situation in England last year, as in other European countries, was critical.

BENZENE—Benzene, or motor benzene, which is a refined light oil, makes a desirable motor fuel when blended with gasoline. Such blends give a mileage about equal to gasoline, and they give operation that is very smooth and free from fuel knock. However, the present production of light oil in the United States is less than 3 per cent of the amount of gasoline that is produced. If all the bituminous coal mined in the United States in 1918 (579,386,000 tons) had been treated for the production of motor fuel, the yield would have been less than one-fifth of the gasoline produced in the United States in 1920.[1]

ALCOHOL—The most direct route which we now know for converting energy from its source, the sun, into a material that is suitable for use as fuel in an internal-combustion motor is through vegetation to alcohol. While it now appears that alcohol is the only liquid from a direct vegetable source that combines relative cheapness with suitability, any liquid material which can be prepared from vegetation and which is right from the standpoints of cost, boiling point, heating value, and operation in an internal-combustion motor will serve the purpose. The use of gasoline or benzene is drawing on the reserves which nature has stored up, but which have required long periods of time for formation. Because a long period of time is necessary for the formation of these materials the supply cannot be renewed. Alcohol is obtained from a source the supply of which can be renewed from year to year and which does not depend upon a definite amount of raw material that has been stored up in the past.

Alcohol as a Motor Fuel

Alcohol has been used as a motor fuel to a considerable

1 The average yield of light oil from a ton of coal is given as 1.54 gal. "Mineral Resources of the United States," 1916, II, 515.

extent and it has been found to be suitable for this purpose, and indeed it has certain advantages. Its combustion is marked by cleanliness and freedom from any deposition of carbon in the combustion chamber. Because it boils at a definite and comparatively low temperature it can be well distributed in multi-cylinder motors. On account of its low boiling point it should give no trouble from dilution of crankcase oil. Alcohol will stand very high initial compressions without knocking, and at high compressions its combustion is smooth and highly satisfactory. Because of the high compression at which alcohol may be used the available horsepower of a definite size of motor is much greater with alcohol than with motor gasoline, if each be run at its most economical compression.

The curve in Fig. 4 shows how an increase in initial compression affects thermal efficiency. Since alcohol does not knock even at compression ratios in excess of 8.2:1, which at wide open throttle and average motor speeds gives a compression considerably above 200 pounds per square inch, it may be run at such a compression that it will give as good fuel economy as gasoline, although its heating value is considerably lower than that of gasoline. Comparative tests of alcohol and gasoline run at 180 and 70 pounds initial compression, respectively, have shown that, in general, equal volumes of these fuels are required per brake horsepower-hour.[1]

DISADVANTAGES OF ALCOHOL.—As a motor fuel alcohol has certain disadvantages which should be enumerated here:

1—*Low heating value—around 80,000 B.t.u. per gallon, as compared to about 120,000 B.t.u. per gallon of gasoline.* Because of the freedom of alcohol from tendency to knock, this difficulty may be overcome by initial compressions which are high enough so to increase the thermal efficiency that the output per gallon of alcohol is equal to that of a gallon of gasoline. Such a motor, however, would be a special device which could not run on gasoline, and which, therefore, would not be feasible under present conditions.

2—*High latent heat and low vapor pressure make it hard to start.* This difficulty has been overcome by blending with light petroleum oils, for which purpose casinghead gasoline is very suitable.

3—*Is absorbed by cork carburetor floats, thus rendering them useless. Loosens gummy or other materials deposited in fuel system and thereby clogs screens in the fuel lines.* If alcohol alone or blended is used as a fuel it necessitates metal carburetor floats and clean fuel lines.

4—*Will not blend with petroleum oils unless it is either practically free from water, or unless a binder is used.* A number of materials have been used to blend 95 per cent alcohol with petroleum oils, of which benzene is probably the best. The unsaturated materials in cracked petroleum oils are effective and cheap, but the final percentage of unsaturation must be kept low so as not to cause motor trouble resulting from the polymerization of such materials to gums or tars.

While some of the above difficulties are real, from the standpoint of a large percentage of the nine million motors now in use, they are such that old and new motors can readily be adapted to utilize alcohol as a fuel at a much faster rate than the production and distribution of alcohol can be increased. So far alcohol as a motor fuel has been of very minor importance. The production of denatured alcohol in the United States has never exceeded 100,000,000 gals. a year. While this is apparently a large figure, it is only about 2 per cent of the volume of motor fuel consumed in the United States last year.

SOURCES OF INDUSTRIAL ALCOHOL

At present the principal source of industrial alcohol is the blackstrap molasses obtained in the refining of cane sugar. The yearly consumption of Cuban and Porto Rican blackstrap in the principal American plants is about 130,-

000,000 gals. a year.[1] Other sources of alcohol are starchy food stuffs and waste cellulose-containing material, such as wood. Two plants manufacturing alcohol from waste wood have been in successful operation in this country for the last few years.[2] These plants obtain a yield of from 15 to 25 gals. of 95 per cent alcohol per ton of dry wood at a cost of about 25 cents per gallon. From the wood which is absolute waste, that is, which is not utilized for reworking or for fuel, it is estimated that there could be produced 240,000,000 gals. of 95 per cent alcohol. This is on the basis of 15 gals. per ton of dry wood, utilizing only soft wood waste.[3]

The large amount of motor fuel required seems to exclude the possibility of preparing any considerable percentage of the necessary amount from foodstuffs. In illustration of this statement the following figures are of interest.[4]

Average annual U. S. production of corn, 1913-1919, bushels	2,740,000,000
Average annual acreage in corn, 1913-1919	106,000,000
Alcohol from the corn at 2.75 gallons per bushel	7,500,000,000

The heating value of this amount of alcohol is about equal to that of 5,000,000,000 gals. of gasoline. The production of gasoline in the U. S. during 1920 was very close to this amount, it having been about 4,900,000,000 gals. The average acreage in corn as given above is equal to 166,000 sq. miles, which is more than four times the total area of Ohio. In view of the fact that the possible alcohol production from corn represents close to 60 per cent of the total possible amount of alcohol that could be prepared from all of the starch and sugar containing foodstuffs produced in the United States, and that such a large acreage is required for its production, the possibility of a sufficiently large increase in production of such materials to be diverted to the manufacture of motor fuel seems very unlikely. At any rate if large quantities of motor fuel are to be prepared from vegetation another material, if not instead of foodstuffs, at least in addition to foodstuffs, must be relied upon as a source.

CELLULOSE AS A SOURCE OF MOTOR FUEL

This material is cellulose. It is suitable from a chemical standpoint, it is readily available, it is easily produced, and its supply is renewable. By the return to the soil of the refuse material from the production of alcohol the soil would lose none of its constituents that are necessary in order to keep up its fertility. But a number of large problems will have to be solved before cellulose can be relied upon as a source of motor fuel.

The largest of these problems is the development of a commercial process that will give a good yield of alcohol from cellulose. This is a problem which must be solved by men trained in chemistry. A yield of 20 gals. from a ton of material which is about 50 per cent cellulose is considerably less than one-half of what it should be. A yield of 50 gals. of alcohol from a ton of wood or other cellulose containing material would give the manufacture of motor fuel from such material an entirely different aspect. If a yield of 60 to 65 gals. of motor fuel could be obtained from a ton of cellulose-containing material by a process that would compare favorably in cost with that now used to make alcohol from wood its success would be assured, and the danger of a serious shortage of motor fuel would disappear.

1 Geo. M. Appell, "Alcohol Production from Molasses," *Chem. Age (N.Y.)*, 29 (1921), 53.

2 E. C. Sherrard, "Manufacture of Ethyl Alcohol from Wood Waste," *Chem. Age*, 29 (1921), 53.

3 E. C. Sherrard, private communication "Brief Report on Wood Waste Available for Production of Ethyl Alcohol," Forest Products Laboratory.

4 Based on statistics of U. S. Dept. of Agriculture.

1 United States Bureau of Mines, *Bulletin* 43, 10.

Of almost equal importance with the development of a process is the problem of supply of raw material. On the basis of 50 gals. to the ton, 100,000,000 tons of raw material would be required to yield the almost 5,000,000,000 gals. of motor fuel produced in the United States last year. This is more than one-fifth of the amount of bituminous coal mined in the United States in 1919. Yet it is slightly less than the weight of hay produced in this country in the same year. Not only must there be a plentiful supply of raw material, but it must also be cheap. If it should cost one cent a pound or twenty dollars a ton the cost of the raw material alone would be 40 cents a gallon, even on the basis of 50 gals. to the ton. The supply of raw material must be constant enough to permit plants to be operated throughout the year, and the distance over which it is transported must be such that transportation charges will be low. The solution of the problem of supply will depend largely on the success that is met with in developing a satisfactory process, and it may lie in the utilization of waste materials and the production of rapid growing plants in a climate that permits growth during the whole or a large part of the year.

It is important that a change in government regulations be secured, in order both to simplify and cheapen this work. The adaptation of motors to utilize alcohol efficiently as fuel will come with the development of its distribution and use as a fuel. There are no doubt a number of other and smaller problems which may require considerable effort, but which will be solved if the major difficulties are overcome.

The large amount of research work which has been done in the past by a number of different investigators in an effort to make alcohol from cellulose has resulted in certain definite and important discoveries. It has been demonstrated that cellulose can be changed almost quan- titatively to dextrose, which in turn can be converted to alcohol.[1] While it has been found that different materials serve as reagents for making this hydrolysis, only strong acids have so far been found to effect an approximately quantitative conversion of cellulose to dextrose. The cost of these materials and the difficulty of their recovery makes a process for the manufacture of motor fuel which is based upon their use far from commercial. But cellulose- containing materials give a considerable yield of ferment- able sugar upon being subjected to the action of very dilute acids at elevated temperatures and under pressure. This is the basis of the process that is now used in making alcohol from waste wood, and which gives a yield of from 15 to 25 gals. of alcohol per ton of dry wood.[2] The fact that a quantitative conversion of cellulose to dextrose can be accomplished shows the possibility of this material as a source of alcohol, if a process can be found which will approach on the one hand, the cheapness of the dilute acid process and, on the other, the almost quantitative yields of the strong acid process.

The progress which has so far been made in the manu- facture of alcohol from cellulose, and the great necessity for and possibilities of such a process, justify a large amount of further research being put into an effort to make the preparation of a liquid motor fuel from cellulose a commercial success. And from all indications it will re- quire a great amount of further research work to accom- plish this result. The success of the efforts which are being made to establish or determine the chemical structure of the cellulose molecule should make a large contribution to the advancement of cellulose chemistry. If the produc- tion of a liquid motor fuel from cellulose can be accom- plished on a large scale, it will add greatly to the im- portance and burden of this widely distributed and already very valuable product of nature, as well as solve the prob- lem of the future supply of motor fuel.

The Role of the Chemist in Relation to the Future Supply of Liquid Fuel[1]

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According to a recent report of the United States Geo- logical Survey, if the rate of production of crude oil in 1920, namely, about 443,000,000 barrels, continues to be maintained our supply of crude oil will have become en- tirely exhausted in about 13 years. Does the average citizen understand what this means? In from 10 to 20 years this country will be dependent entirely upon outside sources for a supply of liquid fuel for farm tractors, motor transportation, automobiles, the generation of heat and light for the thousands of country farms, the manufacture of gas, lubricants, paraffin and the hundreds of other uses in which this indispensable raw material finds an application in our daily life.

It must be frankly admitted that at the present mo- ment there is no solution in sight, and it looks as if in the rather near future this country will be under the necessity of paying out vast sums yearly in order to ob- tain supplies of crude oil from Mexico, Russia and Persia. It is believed, however, that the chemist is capable of solving this difficult problem on the understanding that he be given opportunities and facilities for the necessarily laborious and painstaking research work involved.

We already know, for example, that it is possible to obtain alcohol from corn and a variety of grains on the one hand, and from wood, on the other. Such a synthesis of liquid fuel is, in the last resort, nothing more than the utilization of the energy supplied by the rays of the sun. Through this agent the young plant is developed, crops are grown and harvested and from both a liquid fuel, namely alcohol, can be manufactured.

There appears to be no doubt that if the latter could be obtained at a reasonable cost and in quantities sufficient for the purpose the problem would be solved, since the evidence is fairly conclusive that alcohol is capable of re- placing gasoline with but little alteration necessary in the present type of engine design.

The problem thus becomes one of finding a sufficient supply of suitable raw material. As indicated by Boyd,[3] the available quantity of blackstrap molasses is sufficient to supply only a very small fraction of the alcohol re- quired, while the utilization of cereals cannot be under- taken without seriously endangering the nation's food supply. On the other hand, as indicated in the interesting communications of both Boyd and Whitford,[4] it would seem that cellulose in one form or another should be cap- able of filling the role.

It is known that when wood (which consists of about 50 per cent cellulose) is treated with acids it is converted

1 Willstätter and Zechmeister, *Ber.*, 46 (1913), 2401; H. Ost, *ibid.*, 2995.
2 E. C. Sherrard, *Chem. Age*, 29 (1921), 76.
3 JOURNAL, 13 (1921), 836.
4 To be published later.

into dextrose, which latter, on fermentation, yields ethyl alcohol, one ton of sawdust giving about 20 gallons of alcohol or roughly about 35 per cent of the theoretical quantity. On this basis the supply of wood necessary to produce 4,430,000,000 gallons (the present annual requirement assuming equal value per unit of motive power) would amount to around 221,500,000 tons, equivalent to about 14,760,000,000 cubic feet (assuming a cubic foot of wood to weigh 30 pounds). The total amount of wood available for liquid fuel which could be secured from the forests of the United States without encroachment upon the supply of other forest products is estimated by Professor Hawley of the Yale Forestry School as amounting to about 11,030,000,000 cubic feet, or roughly 75 per cent of present requirements. This is made up as follows:

Waste in the woods and at the mills.................. 4,800,000,000
Losses from fire, insects and fungi (thinnings)........ 1,730,000,000
Excess of possible growth over annual cut (thinnings)... 1,750,000,000
Increased growth due to more intensive crop management (thinnings) 2,750,000,000

TOTAL.... 11,030,000,000

It is evident from these figures that a considerable percentage of the necessary raw material can be obtained from domestic sources, but is it available as the basis of a commercial proposition? No definite figures are obtainable as to the cost of transporting this enormous quantity of waste lumber to suitable locations for conversion into alcohol, but the evidence indicates that it would be prohibitive under present conditions.

As stated above, the present yield of alcohol is only about 20 gallons per ton of wood, whereas, theoretically, it should be around 60. Furthermore, the present cost of conversion, not assuming any value for the wood, cannot amount to less than approximately 20 cents per gallon. If the chemist could improve the yield considerably there is the possibility of decreasing this to around 10 cents, whereby the utilization of a wide variety of waste cellulosic material would then appear much more inviting.

In view of the cost of "assembling" waste wood it would seem that products such as flax straw, hemp hurds, sorghum, bagasse, corn straw and cobs, sugar cane and sawdust would seem to merit prior consideration, since the cost of "assembling" or "partially assembling" such materials has already been borne in connection with the manufacture of the primary raw product.

The problem as to the best and cheapest source of raw cellulosic material is one which does not admit of easy solution, and the interesting and valuable data in Professor Whitford's paper indicate the great importance of location, namely, tropical growths as compared with those of more temperate zones. His figures relative to bamboo and nipa palms are of interest, since they indicate that an area of the Philippines equal to some 63,300 square miles, if planted to bamboo, could probably be made to yield, by proper selection and cultivation, sufficient cellulose to supply our present demands for liquid fuel in the form of alcohol.

The whole subject requires serious consideration on the part of plant physiologist, cellulose chemist and forester, and the activity at present being shown by the Government in furtherance of reforestation might, with advantage, also be extended to a study of the widest variety of "annuals" as a source of raw material for liquid fuel.

The amount of alcohol obtained on fermentation depends on the yield of sugar from the original cellulosic material, and the higher the content of this the greater the yield. In other words, if the plant physiologist could develop a rapid-growing species of tree or shrub, consisting of an outer cover of cellulose with an inner packing of starch granules, this would presumably go a long way towards providing a solution of the problem of obtaining the necessary raw material.

The task is one of such magnitude that none of the usual chemical manufacturing processes, involving only cheap chemicals and simple apparatus, need be taken into consideration, since the cost of operating by the usual methods would presumably be prohibitive.

A process requiring, for example, only five pounds of any given chemical for the manufacture of 100 gallons of alcohol, would mean for an output of 4,430,000,000 gallons (the present requirements) some 100,000 tons. Similarly, each one per cent of by-products would represent about 20,000 tons. Figures such as these would seem to indicate that the solution of the problem will have to be found in some process, not strictly chemical, and in which there are no by-products which cannot be utilized.

Is there any possibility of finding such? Fortunately there is.

SACCHARIFYING ORGANISMS

Of all chemical processes those carried out by living organisms or enzymes are, comparatively speaking, the cheapest to operate, since the expense for labor, etc., is small, due to the efficient manner in which the tiny organisms operate.

The recent work carried out by Boulard in France on the production of alcohol from starch by the action of certain alcohol-producing fungi indicates a new method of approach from which apparently much may be expected. By the action of these new agents it is claimed that starch may be converted directly into alcohol, although in practice it has been found better to use the fungi only for converting the starch into sugar and then to ferment the latter with yeast. Much higher yields are claimed than where the saccharification is effected by acids or by malt. Large-scale experiments are stated to show a yield of 39 to 44 liters of pure alcohol from 100 kilograms of grain compared with 27 to 33 by the acid and 34 by the malt process.

This utilization of fungi for effecting saccharification (conversion of starch, etc. into sugar) would seem to have an important bearing on the subject under discussion.

The evidence which is accumulating with such extraordinary rapidity from day to day relative to the constitution of starch and cellulose[1] indicates that they are relatively simple products, the properties of which it is now possible to predict with some degree of certainty. There is also no doubt but that in a short time the nature of the intimate connection between these two materials will have been definitely established. This being the case, the recent work of Pringsheim[2] in Germany on the action of certain fungi on cellulose assumes considerable importance.

This scientist (not inventor, technical or consulting chemist, be it noted, guided by the epoch-making work of Buechner on fermentation and the action of ferments, has been able to show that there is a strict analogy between the fermentation of certain carbohydrates such as maltose, cane sugar, starch dextrins, etc., and that of cellulose. In the former cases fermentation takes place in two stages in which two different groups of ferments play an active role. These are the "hydrolytic" and "fermenting" types, respectively. The former bring about the

1 Karrer and Naegeli, HELVETICA CHIM. ACTA, 4 (1921), 169, 185, 263; Hess, Z. ELEKTROCHEM., 26 (1920), 232; Karrer and Widmer, HELVETICA CHIM. ACTA, 4 (1921), 174; Freudenberg, BER., 45 (1921); Hibbert, THIS JOURNAL, 13 (1921), 256, 334.
2 Hans Pringsheim, Z. PHYSIOL. CHEM., 78 (1912), 266.

hydrolytic conversion of the maltose, starch dextrins, etc. into glucose, while the latter induce fermentation of this with formation of alcohol.

Similarly under the action of certain ferments, associated with specific microörganisms found in horse-manure, river mud, etc., cellulose is converted into glucose. The first change is brought about by the action of the hydrolytic ferment "cellulase" which converts the cellulose into cellobiose. Under the action of a second ferment "cellobiase" the cellobiose is converted into glucose.

Cellobiose has recently been shown[1] to possess the structure

CH₂OH-CHOH-CH-CHOH-CHOH-CH-O-CH-CHOH-CHOH-CHOH CH₂OH
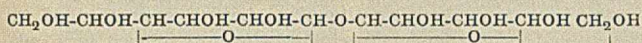
and its close relationship to dextrose on the one hand and to cellulose on the other has been recently emphasized by various chemists, including the author.[2]

The data obtained by Pringsheim would appear to have an important bearing on the subject under discussion, since if it were possible to translate the same into commercial practice, in which any type of waste cellulosic material (vegetation, fibers, etc.) could be utilized, the problem of a future supply of liquid fuel would seem to be much nearer a solution.

It thus becomes possible, and permissible, to draw on the imagination and to visualize our future supply of liquid fuel as resulting from a direct conversion of the sun's rays through the medium of vegetation, the cellulose in which, under the influence of specific microörganisms is transformed first into cellobiose, secondly into glucose, and then into alcohol. This would mean the utilization of most of our waste fiber such as corn stalks, flax, waste wood, etc., by the cheapest and most economical of all processes, namely a combined saccharification-fermentation process brought about by the ceaseless activity of myriads of tiny microorganisms.

The apparatus would probably consist of a simple type of vat for conducting the fermentation of the ground cellulosic material, together with stills for the rectification of the alcohol.

This visualization of the important role to be played by alcohol in the future economic life of the nation points to the imperative necessity for the fostering of anything calculated to develop and maintain the manufacture of industrial alcohol at the highest point of efficiency. At the moment there is some danger that the recent brilliant accomplishments in this field, may, under the influence of pernicious and unenlightened legislation, be stultified to such an extent as not merely to cripple existing chemical industries, but to endanger our national standing and security, associated as it is so intimately with that of an adequate future supply of liquid fuel for transportation purposes.

Sources Other Than Alcohol

While throughout this paper especial importance has been placed on the production of alcohol, the possibility of a cheap fuel from other sources of available raw material such, for example, as that of furfuraldehyde from corncobs should not be overlooked, and the interesting results of La Forge in this field are entitled to serious consideration, especially in view of the data submitted. According to this authority the corn waste (stalks and cobs) amounts to about 130,000,000 tons, capable of yield-

ing 13,000,000 gallons of furfuraldehyde or a total of 2,900,000,000 gallons. In addition to this there is also obtained an immense quantity of cellulose which could be converted into alcohol. While the few experiments already carried out on the use of furfuraldehyde as a motor fuel apparently indicate its unsuitability on the ground of "pre-ignition" in the motor, it is not improbable, should the necessity arise, that this could be overcome.

There is also the question of the extensive deposits of shale awaiting suitable development for conversion into liquid fuel, and it may reasonably be expected that exploitation of these will take place in the not-too-distant future.

The important task for our domestic companies concerned with the production and marketing of gasoline, and faced with an impending shortage of their raw material in the near future, would seem to lie in intensive scientific research work in the fields of cellulose and plant chemistry on the one hand, and of bacteriology on the other.

It would be no small laurel in the crown of one of the two or three leading oil companies, to whose ingenuity, skill, and daring the present generation owes no small part of its everyday comfort, if within the next ten years they were able to announce the completion of the first commercial unit, in which pulped cellulosic material from any source could, under the action of sturdy microörganisms be converted with theoretical yield, first into sugar and then into alcohol. Failing the necessary interest on the part of the oil companies, perhaps that peculiarly American genius, Mr. Ford, might be induced to add to his industrial conquest of the "cheapest car," not only "cheap fertilizer" but also "cheap synthetic fuel," and in so doing increase still further the debt of gratitude on the part of the American public.

For the moment the solution outlined above is simply a "scientific dream" but wilder phantasies than this have proved capable of realization!

"Patient, intensive, scientific research" is the keynote the writer desires to leave as his closing phrase to those most interested in the solution of this fascinting problem.

The Bureau of Chemistry, United States Department of Agriculture has just completed a compilation of reports from the individual producers and consumers of naval stores for the 1920 producing season, which shows that 488,548 casks of gum spirits of turpentine, and 1,577,398 round barrels of gum rosin were made. There were on hand at the stills on March 31, 1921, the close of the 1920 season, 30,429 casks of spirits of turpentine and 327,055 round barrels of rosin. The following table shows the above data in comparison with that for the 1919

	Season 1920		Season 1919	
	Turps.	Rosin	Turps.	Rosin
Production from pine gum	488,548	1,577,398	366,000	1,237,000
Production from wood and still wastes	34,932	180,138	30,889	159,271
		March 31, 1921	Feb. 2, 1920	
Stocks on hand at stills, end of season	30,429	327,055	*3,394	138,525
		Season 1920	Season 1919	
Stocks at wood distilling and rosin reclaiming plants end of calendar year	7,616	50,822	1,764	22,593
		March 31, 1921	Feb. 2, 1920	
Stocks in hands of consumers	30,528	217,302	26,340	290,045
Stocks at ports and yards, primary southern ports	60,916	432,238	34,519	211,238
Eastern ports and distributing points	2,558	11,063	2,363	23,417
Central distributing points	10,364	35,567	14,558	28,594
Western distributing points	848	275	2,634	777
Total	74,686	479,142	54,174	263,946
Total production	523,480	1,757,536	396,889	1,396,271
Exports, calendar year	189,168	652,023	213,442	677,662
Left for domestic uses	334,312	1,105,513	183,446	718,609

[1] Haworth and Hirst, J. CHEM. SOC., 119 (1921), 193.
[2] Pringsheim, LOC. CIT., 280; Hess, LOC. CIT., Karrer and Widmer, LOC. CIT., Heuser, "Lehrbuch der Cellulosechemie," 1921; Hibbert, LOC. CIT.

SOCIAL INDUSTRIAL RELATIONS

The Science of Human Engineering

By H. W. Jordan

SYRACUSE, N. Y.

Under the title, "Manhood of Humanity," the Polish engineer Alfred Korzybski has just issued a book on The Science of Human Engineering. E. P. Dutton & Co. are the publishers.

Korzybski's work, in conjunction with Professor Edwin G. Conklin's, "The Direction of Human Evolution," provides a solid foundation of eternal natural law upon which chemists and engineers can build a new, unique, social industrial structure which shall characterize industry of the twentieth century by scientific humanitarianism as industry of the nineteenth century was characterized by scientific materialism.

Robert B. Wolf, vice president of the American Society of Mechanical Engineers and a member of the Federated Engineers' Committee on Elimination of National Economic Waste says, "I consider Count Korzybski's discovery of man's place in the great life movement even more epoch-making than Newton's discovery of the law of gravitation. It will have a far greater effect upon the development of the human race."

And A. F. Sheldon, president of the International Rotary Club, writes, "In my judgment Korzybski's 'Manhood of Humanity' is potent with possibilities of being a mighty contributing factor in restoration of financial equilibrium and economic balance throughout the world and the bringing about of a status of justice to all parties concerned in industrial and commercial relationships, employee as well as employer."

Without further comment "The Manhood of Humanity" is commended to the earnest study of American chemists.

We are living in an age of swift social action. In England, the status of labor has advanced further toward effective political power in the past seven years than in the previous two centuries. In our own country, as well as in England, direct political power of women has grown more in the last decade than in all previous ages. And the Russian Revolution, of some five years' duration, marks the transition of the peoples of the eath from competitive, individualistic industrialism to cooperative, democratic industrialism; just as the French Revolution marked the passing of feudalism and the beginning of individualism.

The rapid transition will bring no greater disturbance than that which attends hurried installation of any improved process of manufacture, with erection of much new apparatus while keeping the plant in full operation ,if we be guided by the basic laws of evolution disclosed by Conklin and Korzybski. On the other hand, if we disregard these eternal laws and let ourselves be led by emotion and selfish, momentary expediency we will bury the social industrial world plant in a muddle of chaotic disorder.

If we remain content to let temporizing political leaders enact manmade laws, in utter disregard and defiance of laws of biological evolution, we will have "burned the barn to roast a pig."

Discussing the social industrial trend of 1921 and the rather ruthless regard of chemists and engineers by non-resident financial managers of great industries which the chemists and engineers have created by scientific research and applied science, a leading American engineer recently wrote, "The worst of the situation is that those responsible for it are not onscious of the fact that they are violating natural law. But natural law always works, regardless of whether we violate it consciously or unconsciously. To say, 'we didn't know it was hot, does not make the blister any less painful.'"

Chemists and engineers, collectively constitute the keystone of the social industrial structure. They stand between capital, executive management, and government regulation on the one hand, and labor, intellectual workers, and the public on the other. By their practical knowledge of science they rise head and sholders above either curve of the arch. They attained that preeminence through material science applied to industry.

To-day the keystone is in danger of disintegrating under the influence of corrosive seepage from active domination on the side of capital, and from crass indifference on the side of the public. The arch will collapse in ruin unless the keystone be protected by the acid resisting power of research applied to the Science of Human Engineering.

SCIENTIFIC SOCIETIES

The New York Meeting

This issue of the JOURNAL is scheduled to reach our readers a day or two before the great rally of Anglo-Saxon chemists takes place in New York under the auspices of the American Chemical Society and the American Section of the Society of Chemical Industry. Doubtless, it will be the largest meeting approaching international proportions which has ever been held in this country. Our guests of the Society of Chemical Industry of Great Britain and its various Canadian sections will be receiving a welcoming hand in New York probably before they read these lines, yet, in order to be all-inclusive, a formal welcome to both, members of the American Chemical Society and their guests, from our own

President Edgar Fahs Smith is published herewith:

A Message of Welcome and a Call to Duty from President E. F. Smith

Honored Guests and Fellow Members of the American Chemical Society:

You are aware that Chemistry is to-day much in the eye and on the tongue of every true, wide-awake American; hence it behooves us to make every effort to attend the meeting in New York, that we may hear subjects of vital importance discussed by thoughtful, far-sighted men. Through the fearful ordeal, visited upon it by the world war, our Country has learned the powers of the American chemist. To maintain the position won by him it is absolutely essential that chemists should foregather with their colleagues and participate in the meetings and advise on the various topics which will come before the

DR. MILTON L. HERSEY
Past Chairman, Canadian Section, S.C.I.

H. W. MATHESON, M.Sc., F.C.I.C.
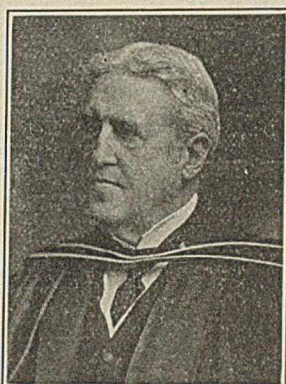Chairman, Montreal Section

DR. FREDERICK W. ATACK
Editor, "Chemists' Year Book"

CAPT. C. J. GOODWIN
Honorary Treasurer, Chemical Industry Club

MR. C. R. HAZEN
Chairman, Arrangements Committee, Canadian Meeting
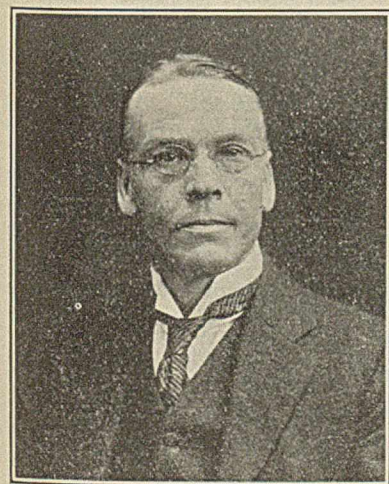
DR. R. F. RUTTAN
Past President, Canadian Section, S.C.I.

E. V. EVANS, O.B.E., F.I.C.
Honorary Treasurer, Society of Chemical Industry

DR. J. P. LONGSTAFF
General Secretary, Society of Chemical Industry

Society in its several sections. Further, chemists should fraternize more than they have in the past. As far as possible we chemists must become a unit—learn to know one another more intimately.

In the several Bulletins, issued by sections during the year and which have been thoughtfully sent to my desk, I note the enthusiasm with which local interest is being developed but our main objective must continue to be a strong unified national viewpoint. This can be secured only by the opportunity of personal contact which our general meetings afford. Come, hear what your colleagues have to say.

Is there to be an American Chemistry?

This question surely will be answered affirmatively by all of us. That there may be no doubt make it a point to be in New York in September.

We are to have the privilege and pleasure of greating fellow chemists from the Dominion to the North and from beyond the seas. They are bringing worth-while messages. Let them our love and enthusiasm for a common Science.

These lines are hastily written—and only written—that you may know of my great desire to have you come out and let yourselves be seen. I shall be delighted, as always, to greet my brethren, who have so splendidly made chemistry come home to every man's business and bosom. If we hope to achieve success as a profession it devolves upon us to act unitedly.

The opportunity to make chemistry secure in America is now.

There is no exaggeration in declaring that the present is a very critical moment for chemistry and chemists in this Country.

Let us make this the best meeting the Society has ever enjoyed.

Faithfully yours,

(Signed) EDGAR F. SMITH.

SIR WILLIAM J. POPE, D.Sc., F.R.S., K.B.E.
President, Society of Chemical Industry

PROGRAM OF THE MEETINGS

A general outline of the program and activities of the New York meeting was printed in the August issue of THIS JOURNAL, but some of the main features and particularly the final details as nearly as they could be ascertained at the time of going to press are given below.

The program of the Society of Chemical Industry will have been completed at Montreal by September 1st. The committee in charge have outlined the following entertainment program for visiting members upon the completion of their trips to Ottawa, Toronto and Niagara following the meeting at Montreal:

MONDAY, SEPTEMBER 5

Foreign guests will be met by a Committee from the American Section and conducted through industries on the American Side of the Falls. Luncheon at the Falls. Dinner at Buffalo. Special train of Sleeping Cars to Syracuse, N. Y.

TUESDAY, SEPTEMBER 6

The Solvay Process Company, Syracuse, N. Y., will entertain at luncheon and a tour through the great factory. Luggage will be left on the train which will not depart until mid-afternoon and will proceed to Albany, where we will take the night boat down the Hudson River to New York.

WEDNESDAY, SEPTEMBER 7

New York, 1:00 P. M.—Luncheon by the American Section to Foreign guests.

    4:00 P. M.—Reception and tea to Foreign guests, and to Scientific Societies, at Columbia University.

    8:00 P. M.—Smoker and Entertainment of American Chemical Society. (Foreign guests, invited.)

THURSDAY, SEPTEMBER 8

The usual general, divisional, and sectional meetings of the American Chemical Society, to which all foreign guests are cordially invited.

FRIDAY, SEPTEMBER 9

The usual general, divisional, and sectional meetings of the American Chemical Society, to which all foreign guests are cordially invited.

7:00 P. M.—Banquet of American Chemical Society. Foreign guests welcome.

SATURDAY, SEPTEMBER 10

Golf and tea.

SUNDAY, SEPTEMBER 11

Boat trip and tea.

MONDAY, SEPTEMBER 12 TO SATURDAY, SEPTEMBER 18

The National Exposition of Chemical Industries.

The regular business and scientific program of the American Chemical Society so far as known in detail at the time of going to press is as follows:

TUESDAY, SEPTEMBER 6

9:00 A. M.—Registration begins at The Chemists' Club, 52 East Forty-first Street.

3:00 P. M.—Council Meeting at The Chemists' Club, 52 East Forty-first Street.

6:30 P. M.—Dinner to the Council at The Chemists' Club, 52 East Forty-first Street.

6:30 P. M.—Dinner to wives of Councilors.

9:00 P. M.—Adjourned Meeting of Council, if necessary.

WEDNESDAY, SEPTEMBER 7

10:00 A. M.—General Meeting at Columbia University.

    Address by SIR WILLIAM POPE, D. Sc., F.R.S., K.B.E., President of the Society of Chemical Industry of Great Britain.

    Address by HON. HERBERT HOOVER, Secretary of Commerce of the U. S. A.

12:30 P. M.—Society of Chemical Industry Luncheon to British and Canadian visitors.

2:00 P. M.—Divisional Meetings at Columbia University.

4:00 P. M.—Reception and Lawn Party given by Columbia University.

8:00 P. M.—Smoker at Waldorf-Astoria Hotel.

THURSDAY, SEPTEMBER 8

9:30 A. M.—Divisional Meetings at Columbia University.

2:00 P. M.—Divisional Meetinsg at Columbia University.

2:30 P. M.—Organ Recital at Great Hall, College of the City of New York, by Prof. Samuel A. Baldwin, Head, Department of Music.

3:00 P. M.—International Meeting at Great Hall, College of the City of New York, on "Chemistry and Civilization." (Dr. Edgar F. Smith in Chair.)

    Science and Civilization; the Role of Chemistry. CHARLES BASKERVILLE.

    Energy; Its Sources and Future Possibilities. ARTHUR D. LITTLE.

    The Engineer; Human and Superior Direction of Power. LEO H. BAEKELAND.

    Chemistry and Life. SIR WILLIAM J. POPE.

    Theories and Their Development. WILLIS R. WHITNEY.

    Research Applied to the World's Work. C. E. K. MEES.

    Problem of Diffusion and Its Bearing on Civilization. ERNST COHEN.

    Catalysis; Directing Factors in all Changes. WILDER D. BANCROFT.

8:00 P. M.—Banque at Waldorf-Astoria Hotel.

FRIDAY, SEPTEMBER 9

9:30 A. M.—Divisional Meetings at Columbia University.

2:00 P. M.—Divisional Meetings at Columbia University.

8:00 P. M.—Public Meeting. President's Address.

    Progress of Chemistry. EDGAR FAHS SMITH, American Chemical Society.

SATURDAY, SEPTEMBER 10

Excursions.

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Calendar of Meetings

American Pharmaceutical Association—Sixth-ninth Annual Meeting, Hotel Grunewald, New Orleans, La., week of September 5, 1921.

American Chemical Society and Society of Chemical Industry—New York, N. Y., September 6 to 10, 1921.

Seventh National Exposition of Chemical Industries— Eighth Coast Artillery Armory, New York, N. Y., September 12 to 17, 1921.

American Institute of Mining and Metallurgical Engineers —Fall Meeting, Wilkes Barre, Pa., September 12 to 17, 1921.

American Electrochemical Society—Fall Meeting, Lake Placid, N. Y., September 29 to October 1, 1921.

Technical Association of the Pulp and Paper Industry— Fall Meeting, Washington, D. C., Philadelphia, Pa., Spring Grove, York, York Haven, Pa., and Wilmington, Del., October 18 to 20, 1921.

American · Institute of Chemical Engineers — Annual Winter Meeting, Baltimore, Md., December 6 to 9, 1921.

SEVENTH NATIONAL EXPOSITION —

PROGRAM

MONDAY, SEPTEMBER 12

2:00 P. M.—EXPOSITION OPENS.

7:00 P. M.—MOTION PICTURES (In Auditorium):

    1: "Iron Mining Operations." (4 reels) (Courtesy Bureau of Mines.)

      (*a*) Stripping.

      (*b*) Exploration and Stripping.

      (*c*) Underground Mining.

      (*d*) Logging Operations.

    2: "The Jewels of Industry." (8 reels) (Courtesy, The Carborundum Company.)

      (*a*) Creating Power from Water.

      (*b*) Within the Power Plant at Niagara.

      (*c*) In and About the City of Niagara Falls.

      (*d*) Power at Work in the Carborundum Plant.

      (*e*) Making the Crystal Masses in the Electric Furnace.

      (*f*) And Making Them into Stones, Grinding Wheels, Paper and Cloth.

      (*g*) Unusual and Usual Uses for Abrasives in some Fifty Industries.

8:00 P. M.—OPENING ADDRESSES (Colonel's Reviewing Stand):

Opening Address by Chas. H. Herty.

Brig. Gen. Amos A. Fries, Chief, Chemical Warfare Service, U. S. A.

TUESDAY, SEPTEMBER 13

2:30 P. M.—CRUSHING, GRINDING AND PULVERIZING SYMPOSIUM.

Harry J. Wolf, *Chairman.*

"Ball and Pebble Milling for Pulverizing and Mixing," H. F. Kleinfeldt (Abbe Engineering Company).

"Grinding and Pulverizing with Air Separation," S. B. Kanowitz (Raymond Bros. Impact Pulverizer Company).

"Crushing, Storing and Pulverizing," L. H. Sturtevant (Sturtevant Mill Company).

"Dust Collection as Applied to Grinding and Pulverizing Problems," M. I. Dorfan (Allis-Chalmers Manufacturing Company).

"The Development of Compound Grinding Mills," H. Schifflin (Allis-Chalmers Manufacturing Company).

INDUSTRIAL PROBLEMS SYMPOSIUM

"Solvent Extraction of Edible Fats and Oils," H. Austin (Ernest Scott & Company).

"Materials Handling in Industrial Plants," R. H. McLain (General Electric Company).

"Utilization of Industrial Waste: Its Economic Importance," W. H. Dickerson (Industrial Waste Products Company).

To be followed by motion pictures upon the subject of the *Handling of Materials* if time permits. See the first six titles upon this evening's program.

7:00 P. M.—MOTION PICTURES:

1: "Use of the Steam Shovel in Mining." (1 reel) (Courtesy Bureau of Mines.)
2: "Transportation and Storage of Iron Ore." (1 reel) (Courtesy Bureau of Mines.)
3: "Transporting and Handling Coal by Various Means." (1 reel) (Courtesy Bureau of Mines.)
4: "Dredging Anthracite Coal." (1 reel) (Courtesy Bureau of Mines.)
5: "Saving Wasted Millions through Material Handling Equipment." (2 reels) (Courtesy Economy Engineering Company.)
6: "The Story of Sulfur." (2 reels) (Courtesy Texas Gulf Sulphur Company.)
7: "Mining and Extraction of Radium from Carnotite Ore." (2 reels) (Courtesy Bureau of Mines.)
8: "DuPont Dyes. Showing their Manufacture." (2 reels) (Courtesy E. I. duPont de Nemours & Company.)
9: "Making Soap." (1 reel) (Courtesy Baumer Films.)
10: "Mine Explosion and Rescue." (1 reel) (Courtesy Bureau of Mines.)

WEDNESDAY, SEPTEMBER 14

2:30 P. M.—EVAPORATING AND DRYING SYMPOSIUM.

Wallace Savage, *Chairman.*

(Subject to be announced.) E. G. Rippel (Buffalo Foundry & Machine Company).
"The Relation of Atmospheric Conditions to Chemical Processes," A. E. Stacy, Jr. (Carrier Engineering Corporation).
"Drying and Drying Problems," H. S. Landell (Proctor & Schwartz).
"Special Problems for Enameled Evaporators," Max Donauer (Elyria Enameled Products Company).
"Drying with Moist Air," Arthur B. Stonex (Hunter Dry Kiln Company).
"Drying as an Air Conditioning Problem," A. W. Lissauer (W. L. Fleisher & Company, Inc.).
"Atmospheric Drying by Means of Compartment, Tunnel and Continuous Belt Conveyor Dryers with some Practical Applications," J. D. Stein (Grinnell Company, Dryer Division).
"Spray Drying," W. H. Dickerson (Industrial Waste Products Company).
"Evaporation," H. Austin (Ernest Scott & Company).
"A New Arrangement of Heating Tubes in Heat Exchange Apparatus," Robert V. Cook (Chemical Equipment Company).
"A New Arrangement of Heating Tubes in Heat Exchange Apparatus," Robert V. Cook (Chemical Equipment Company).

7:00 P. M.—MOTION PICTURES:

1: "The Manufacture of Dry Sausage." (2 reels) (Courtesy Armour & Company.)
2: "The Making of Oleomargarine." (1 reel) (Courtesy Armour & Company.)
3: "The Electric Heart—The Dry Cell." (1 reel) (Courtesy Baumer Films.)
4: "Canning Electricity—The Wet Cell." (1 reel) (Courtesy Baumer Films.)
5: "The Manufacture of Pyrex Glassware." (3 reels) (Courtesy Corning Glass Company.)
6: "The Manufacture of Portland Cement." (2 reels) (Courtesy Bureau of Mines.)
7: "The Manufacture of Dynamite." (1 reel) (Courtesy Bureau of Mines.)
8: "Exterminate the Mosquito." (1 reel) (Courtesy Bureau of Mines.)

THURSDAY, SEPTEMBER 15 (PAINT AND VARNISH DAY)

2:00 P. M.—PAINT AND VARNISH SYMPOSIUM

R. S. Perry, *Chairman.*

"Paint and Varnish Waste Control," R. S. Perry (Perry & Webster, Inc.).
"Reflection Factors on Industrial Paints," H. A. Gardner (Institute of Paint & Varnish Research).
"Laboratory Control," L. P. Nemzck (E. I. duPont de Nemours & Company).

"Rust: Its Cause and Prevention," Maximilian Toch (Toch Brothers).
"Physical Testing of Paints and Paint Materials," Frank G. Breyer (New Jersey Zinc Company).
"The Ideal Paint and Varnish Specification," F. P. Ingalls (John W. Masury & Company).
"Limitations of Standardization of Paint and Varnish Manufacture," D. A. Kohr (Lowe Brothers Company).

7:00 P. M.—SAVE THE SURFACE.

"Save the Surface and You Save All with Paint and Varnish," Ernest T. Trigg (*Chairman,* "Save the Surface" Committee, Paint Manufacturers Association of the United States).
"What is Paint?" G. P. Heckel, (*Secretary,* Paint Manufacturers Association of the United States).

MOTION PICTURES:

1: "Making White Lead." (2 reels) (Courtesy Bureau of Commercial Economics and National Lead Company.)
2: "Making of Varnish." (1 reel) (Courtesy Bureau of Commercial Economics and Murphy Varnish Company.)
3: "Making of Paint and Varnish." (2 reels) (Courtesy Bureau of Commercial Economics and Sherwin-Williams Company.)
4: "Making of Paint." (1 reel) (Courtesy Bureau of Commercial Economics and Lowe Bros.)
5: "Making of Paint." (1 reel) (Courtesy Bureau of Commercial Economics and Mathews & Company.)
6: "Making of Varnish." (1 reel) (Courtesy Bureau of Commercial Economics and Taylor, Tregent & Company.)
7: "The Manufacture of Pyrex Glassware." (3 reels) (Courtesy Corning Glass Company.)
8: "The Manufacture of Portland Cement." (2 reels) (Courtesy Bureau of Mines.)

FRIDAY, SEPTEMBER 16

2:30 P. M.—THE POWER PLANT IN THE CHEMICAL INDUSTRIES SYMPOSIUM

R. C. Beadle, Editor *Combustion,* Chairman.

"Modern Boiler House Arrangement and Equipment" (Illustrated), R. M. Gordon (The Solvay Process Company).
"Suggestions for Reducing Heat Losses in Chemical Plants," John Primrose (Power Specialty Company).
"Boiler Feed Water Treatment and Treatment Control," E. G. Bashore (Rice & Bashore).
"Compressed Air Installations in Industrial Plants," A. R. Stevenson, Jr. (General Electric Company).
"The Application of Electric Power in Chemical Industry," D. B. Rushmore, J. A. Seede, and E. Pragst (General Electric Company).
"The Limitation of Silent Chain Drive," F. G. Anderson (Morse Chain Company).
"A New Method for Coking Coal as Required for Industrial Fuel," D. S. Chamberlin (Distillation Industries, Inc.).
"The Application of Pulverized Fuel," H. D. Savage (Combustion Engineering Company).

To be followed by Motion Pictures upon *The Power Plant* if time permits. See the first four titles upon this evening's program.

7:00 P. M.—MOTION PICTURES:

1: "The Cost of Careless Firing." (2 reels) (Courtesy Bureau of Mines.)
2: "Getting the Most out of Coal." (1 reel) (Courtesy Bureau of Mines.)
3: "Conserving Coal and Saving Heat Values by Insulating Steam Pipes and Boilers." (1 reel) (Courtesy Magnesia Association of America.)
4: "Modern By-Product Coking." (2 reels) (Courtesy The Koppers Company.)
5: "The Story of Rock Drilling." (4 reels) (Courtesy Sullivan Machinery Company and Bureau of Mines.)
6: "The Story of Armco Ingot Iron." (3 reels) (Courtesy American Rolling Mill Company.)

SATURDAY, SEPTEMBER 17

2:30 P. M.—AMERICAN DYES:

Justin B. Weddell, National Aniline & Chemical Company, *Chairman.*

7:00 p. m.—MOTION PICTURES (subject to change):

1: "Zinc Mining, Milling and Smelting." (4 reels) (Courtesy Bureau of Mines.)

2: "Manufacture of Zinc Oxide." (1 reel) (Courtesy

3: "Making duPont Dyes." (2 reels) (Courtesy E. I. duPont de Nemours & Company.)

4: "Manufacture of Dynamite." (1 reel) (Courtesy Bureau of Mines.)

5: "Mining Magnetic Iron Ore." (2 reels) (Courtesy Bureau of Mines.)

NOTES AND CORRESPONDENCE

The Detection of Phenols in Water

Editor of The Journal of Industrial and Engineering Chemistry:

By reason of familiarity and former connection with certain trade waste investigations relating to water supplies in Western Pennsylvania, the writer takes the liberty of offering a correction to the above paper by Mr. R. D. Scott in the May issue of THIS JOURNAL, **13** (1921), 422.

Credit for the adaptation of the Folin-Denis reagent (phosphotungstic, phosphomolybdic acid) to water examination belongs to Mr. E. P. Fager who, prior to January 1920, was chemist in charge of the filtration plant of the South Pittsburgh Water Company, Pittsburgh, Pa. During the early part of 1919 some water supplies on the lower Monongahela River, particularly the McKeesport and South Pittsburgh plants, experienced considerable complaint on account of disagreeable taste and odor due to phenol wastes from chemical plants upstream. Following the South Pittsburgh experience Mr. Fager was assigned the problem of detecting and identifying this class of waste and succeeded in developing several methods suitable for the purpose, of which the Folin-Denis adaptation seemed the most promising. In the winter of 1919 to 1920 practical application of the method was made in studying the trade waste problems of the New Castle works, which are under the same management; namely, The American Water Works & Electric Company of New York. In the New Castle studies the direct colorimetric method was improved by the distillation method to avoid interference due to other impurities.

In tracing what is believed to be the first use of the Folin-Denis test for phenols in water supplies, the writer in nowise disparages the subsequent excellent work done by Mr. Trowbridge at the New Castle works. So far as the writer is aware, this is the only waterworks in the country where an effort has been made systematically to record quantitatively the phenols present in a public water supply, the toleration by consumers after chlorination, and the reductions feasible with a rapid sand filter plant. The writer is cognizant of the painstaking investigations at Milwaukee in correlating the phenol pollution with the occurrence of taste and odors in the water supply and wishes to acknowledge the great value to the waterworks fraternity, and chemical industries as well, of the published conclusions (*Eng. News-Record*, **82** 181; **84**, 1155), first calling attention to the aggravated effects of this class of wastes in chlorinated supplies.

Mr. Scott is somewhat inaccurate in stating that the detection of phenols in water rests upon the Folin-Denis test. It is nearer the truth to state that the method is probably the most convenient of several methods available, especially for field work. As a matter of fact, the literature shows many more interfering substances than those mentioned by the author. In any careful investigation of phenols in a water supply, proper precautions should be taken to establish the specificity for the local problem, and should preferably include differentia of the very large group of phenolic compounds liable to occur as polluting substances. With proper precautions, and using the distillation method, it may be said that the Folin-Denis test gives the water analyst a method which closely approximates the free and albuminoid ammonia determinations in sensitiveness.

WELLINGTON DONALDSON

FULLER & McCLINTOCK
170 BROADWAY, NEW YORK, N. Y.
June 11, 1921

. . . .

Editor of The Journal of Industrial and Engineering Chemistry:

Reference was made by Mr. Scott in his article to my experiments at the filtration plant in New Castle, Pa., on the detection of phenols in water, without a knowledge of the extent or the facts concerning the work that has been done by Mr. Donaldson, Mr. E. P. Fager, and myself. Mr. Donaldson is correct in stating that credit for the adaptation of the Folin-Denis reagent to water examination belongs to Mr. E. P. Fager.

When Mr. Fager was in charge of the filtration plant of South Pittsburgh Water Company, I had access to the results of his experiments and later used them, in connection with my investigation at New Castle, Pa.

I appreciate the value of the application of the phosphotungstic phosphomolybdic acid reagent for the detection of minute quantities of phenol wastes in water, and I shall be very grateful if Mr. Donaldson's correction is published.

Mr. Scott has pointed out that the reagent is not specific for phenols and has named some of the substances which may effect the determination. In our work, we were entirely familiar with the limitations of the test.

CHARLES E. TROWBRIDGE

AMERICAN WATER WORKS & ELECTRIC CO., INC.
50 BROAD ST., NEW YORK, N. Y.
June 18, 1921

. . . .

Editor of The Journal of Industrial and Engineering Chemistry:

I am grateful for the correction which Mr. Donaldson offers, for it appears from his comment that Mr. E. P. Fager, rather than Mr. Trowbridge, first applied the Folin-Denis test for phenols in water examination. Although it appears further in Mr. Fager's study that "the direct colorimetric method was improved by the distillation method to avoid interference due to other impurities," it would seem that this modification was not employed by Mr. Trowbridge at New Castle since no mention was made in a personal communication from him of any method other than the direct colorimetric. The distillation method was adopted by us solely on the basis of our own experience.

With respect to the implication of inaccuracy in the writer's statement that the detection of phenols in water rests upon the Folin-Denis test, it would perhaps be well to emphasize again the fact that the detection of traces of phenol cannot be accomplished satisfactorily by any of the other methods described in the literature, for after careful trial of these it was found that none except the Folin-Denis was reliable in detecting amounts of one part per million or less. Amounts higher than this would rarely

be found in a public water supply. In this connection it is interesting to note that in the work at Milwaukee, to which Mr. Donaldson refers, the phenol determination did not rest upon a definite quantitative chemical test but upon the chemist's sense of taste and smell after chlorinating a water suspected of containing phenols. One of the prime factors promoting the study of this problem and influencing us in publishing our results was the fact that the chemist who had charge of the Milwaukee studies encountered similar conditions at Cleveland and was at a loss for a definite method for determining phenols in water. It was deemed inadvisable to include in the original article a discussion of this and similar points, since an attempt was made to outline briefly only the essential points in connection with the test from the laboratory standpoint. For this reason also a detailed discussion of the various substances which respond to the Folin-Denis test was not presented.

In our opinion it would be a somewhat hopeless task to attempt, as suggested by Mr. Donaldson, any differentiation of the large group of phenolic compounds likely to be found in waters. It would be much more promising to make a study of the wastes from individual establishments before such materials enter a water supply. This, of course, is a subject not considered in the article under discussion.

<div align="right">R. D. SCOTT</div>

STATE DEPARTMENT OF HEALTH
COLUMBUS, OHIO
July 5, 1921

Assignment of Patents

Editor of the Journal of Industrial and Engineering Chemistry:

The findings of fact and law in the action by Air Reduction Co., Inc., against Warren R. Walker, to which reference is made in the July issue of the JOURNAL, will perhaps leave your readers in doubt as to the governing principle of the decision.

The action was brought to compel assignment by Walker to the Company of an application for Letters Patent covering an invention made jointly by Walker with Floyd J. Metzger and involves the right of the employer to inventions made by an employee. This right has been the subject of numerous controversies and, in the absence of express agreement, depends upon the character of the employment. Walker's relation to his employer in this case is stated in the decision of Mr. Justice Cropsey, from which the following is quoted:

There was no express agreement making any invention of the defendant the property of the plaintiff, nor was there any express agreement that the defendant would assign to the plaintiff any patent he might obtain. But he was employed to give his time and scientific skill for the very purpose of trying to discover and invent some practical use for this gas. In other words, he sold his inventive powers to the plaintiff during the period of his employment. Under these circumstances I think there is an implied agreement that the results of defendant's work shall belong to plaintiff and that any patent obtained by defendant should be assigned by him (Annin v. Wren, 44 Hun, 352; Connelly Mfg. Co. v. Wattles, 49 N. J. Eq., 92; Meissner v. Standard Railway Equipment Co., 190 S. W. Rep., 730; Supreme Court of Missouri; Dowse v. Federal Rubber Co., 254 Fed. Rep. 308; Famous Players-Lasky Corporation v. Ewing, 194 Pac. Rep. (5, Cal.). No case in this state holding the contrary has been brought to the Court's attention. Clark v. Fernoline Chemical Co. (5 Supp., 190) decides only a question of pleading. Its statements upon this subject are purely *obiter*. There are decisions in some other jurisdictions which seem to be at variance with those above cited (see American Circular

Loom Co. v. Wilson, 198 Mass., 182, 201; Dalzell v. Dueber Mfg. Co., 149 U. S., 315; Barber v. National Carbon Co., 129 Fed. Rep., 370; Pressed Steel Car Co. v. Hansen, 137 Fed. Rep., 403; Hildreth v. Duff, 143 Fed. Rep., 139; Hapgood v. Hewitt, 119 U. S., 226). Some of these cases may be distinguishable, but even if they be not, I believe the sounder rule is set forth in the cases first cited. Hence the plaintiff is not entitled only to a shop right to use the patent, but is entitled to own it outright, and hence should have judgment against the defendant, with costs.

It may also be of interest to note the language of Mr. Justice Pratt in Annin v. Wren, 44 Hun, 352, which is as follows:

The special service of *inventing* under special *employment to invent* gives the master the servant's inventions which result from that service. (Simonds Manual of Patent Law (Ed. 1883) pp. 202-204). This is also the principle of that part of the decision of Burr v. DeLaVergne (102 N. Y. 415), which relates to the inventions made by DeLaVergne alone. The same is true of Binney v. Annan (9 Am. Rep. 10; 107 Mass. 94). None of the patent cases are inconsistent with the principles above indicated. Even in Hapgood v. Hewitt (11 Fed. Rep. 422), lately affirmed (110 Fed. Rep. 227), Judge Gresham excepts the case of a special employment *to invent*. The special service of inventing is the entire scope of the employment. There is no room left within the employment for inventing on his own hook. The servant has no right to think or invent for himself on this particular subject matter in hand. He must get out of such a relation before he can claim the product of his work under such an employment. He cannot carry off both his salary and the only valuable product of his work under such an employment, leaving his master with his useless models, the result of his uselessly spent money on tools, machinery, time, labor of self and employees with only a license or shop right, which is not assignable or useful in any way than to himself.

The foregoing will serve to indicate quite clearly the relation of employer and employee with respect to inventions, where the employee is engaged in research or is employed for the purpose of making inventions.

<div align="right">E. H. MERCHANT</div>

AIR REDUCTION CO., INC.
342 MADISON AVE., NEW YORK CITY
August 3, 1921

A Study on the Oil Bromide Test of Linseed Oil

This drawing was inadvertently omitted from its proper position in column 1, page 802, of this issue.
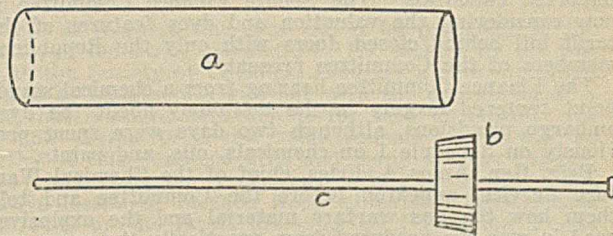
At the twelfth annual convention of the Flavoring Extract Manufacturers Association, the Resolutions Committee brought in a report declaring for a strict observance of all provisions in the prohibition amendment. This recommendation, together with an agreement binding members of the association in a war against unscrupulous extract manufacturers, was adopted unanimously. It was also agreed that the flavoring extract men should instruct the Research Committee to continue its efforts to find a substitute for alcohol. At the executive session, the association pledged itself to force certain manufacturers who are not members of the association, and who are evading the Volstead law, out of the business.

WASHINGTON LETTER

By Watson Davis, 1418 Rhode Island Ave., Washington, D. C.

THE TARIFF BILL

By Watson Davis, 1418 Rhode Island Ave., Washington, D. C.

The tariff bill has spent an eventful month in Congress. After the discussion in the House, the bill was passed on to the Senate without the dyes embargo provision. The bill itself passed the lower chamber by a substantial majority, but the provisions protecting the American dye industry for three years were thrown out by only a few votes.

The action of the House was a surprise, and it precipitated a bitter and lively fight, for and against the embargo, at the hearings that have just been held by the Senate finance committee. What the final fate of the dyes embargo will be is known only by Senator Penrose and his committee, if they have made up their minds.

Meanwhile, the three months' lease on life given to the licensing system for control of dyes imports by the emergency tariff law has been fleeting away. It would expire on August 27, and would allow a flooding of American markets with dyes that would supply our needs of months and ruin the industry. This danger was foreseen by those who have been fighting for the chemical industry in Congress, and Representative Longworth has introduced a bill providing for the extension of the licensing system for three months longer. Under the urge that was provided by a letter from President Harding, stating "we would be both unmindful and unjust if we failed in a suitable protection of this country until the new and complete tariff revision act is made effective," the House to-day passed the extending bill and prompt action on the part of the Senate is expected to complete the extension of time.

Representative Young has just introduced a bill to extend the life of the emergency tariff act itself for two months from November 27 and this is taken to indicate that it will not be until the end of this year at least that the regular tariff is placed on the statute books. If this is the case, it is probable that even further extension of the life of the dyes licensing feature than that provided in the Longworth bill will have to be secured later.

SENATE FINANCE COMMITTEE HEARINGS ON DYE EMBARGO

It is reported currently that the Senate Finance Committee has virtually decided to retain the American valuation provision of the tariff bill, probably slightly modified. This is of interest to the chemical industries, as American valuation will in effect mean higher duties on imported chemicals. The Senate Finance Committee is now considering the valuation and dyes features of the tariff bill behind closed doors with only the Republican members of the Committee present.

The Finance Committee hearing from a chemical standpoint centered largely in the testimony about the dyes embargo provisions, although two days were spent previously on Schedule 1 on chemicals, oils, and paints.

Brig. Gen. Amos A. Fries, chief of the Chemical Warfare Service, appeared before the Committee and told them how the gas warfare material and the explosives used in war are produced from practically the same materials as dyes. With no embargo protection, the American dye industry would be killed by a flood of German dyes, and this would destroy the military safeguard that those chemical plants are to this country. During the questioning of General Fries, he was asked whether he thought that disarmament among the nations would not have as one of its chief results the abolition of gas, and he brought out the fact that gas is the only kind of armament that would cost us very little in times of peace. Dye plants could be turned into poison gas plants in time of war, and, with a proper development of the coal-tar industry, this country could keep up to date in gas warfare easily and at little cost, he said. Admiral W. Strother Smith of the Navy also declared that the embargo or some other dye protection was necessary as a military measure.

Herman A. Metz, president of the Consolidated Color and Chemical Co., of Newark, N. J., was the principal witness against the embargo, who testified at length. Jos. H. Choate, representing the American Dyes Institute, presented the side of the dye manufacturers and declared that America was up against a most unscrupulous competitor in the commercial world, in referring to Germany's dye industry. Throughout the hearings, there were continual verbal encounters between these two men.

Among those who appeared in favor of the embargo were: Charles H. Stone, vice president of the Atlantic Dyestuff Co.; Gaston Du Bois, president of the Monsanto Chemical Works; W. Parker Jones, representing the Victor Chemical Works, Chicago; S. Isermann, representing the Chemical Company of America; B. T. Bush, representing the Antoine Chiris Co.; Henry B. Thompson, president of the United States Finishing Corporation, and Dr. Marston Taylor Bogert, professor of organic chemistry at Columbia University. Among those who opposed the embargo were: Granville MacFarland, representing the Amoskeag Manufacturing Co.; William H. Brehm, of Brehm and Stehle, and C. B. Reid, representing the American Farm Bureau Federation. The Senate Finance Committee is headed by Senator Penrose, who presided at the hearings.

The hearings involved the Chemical Foundation, and the charges that had been made previously by Representative Frear and Senator King that the Chemical Foundation seized alien patents and that it was engaged in a "pernicious dye lobby" were aired, principally in the examination of Mr. Choate and Mr. Metz.

The dye embargo was aided when Senator Penrose recently made public letters from Secretary Weeks and Denby declaring that the military safety of the country depends to a great degree upon the dye embargo.

THE PROHIBITION BILL

The prohibition bill that had been drawn in the House so that it endangered the industrial and chemical alcohol production has been radically amended and passed by the Senate. When it was being sent to conference in the House, however, it hit a snag in the way of another amendment, and it now seems that it will not be acted upon until October. On the floor of the Senate, objections to the pending bill were raised by Senators Broussard of Louisiana, Stanley of Kentucky, and Brandegee of Connecticut, on the ground that it allows arbitrary changes of the formula of proprietary compounds. The manufacturers have declared, however, that the amended bill suits them.

Present plans provide for a month's recess by Congress beginning about August 20, and this is expected to provide a legislative breathing spell.

The House Ways and Means Committee is now engaged in framing tax legislation.

The bill affording relief for the patent office has made little further progress in Congress, while the applicants offering new inventions and demanding action on their claims have flooded the Patent Office. All previous records have been broken by the number of applications filed in the last six months, and there are now 51,865 patents awaiting action.

The Muscle Shoals Nitrate Plant

The Government had arrived at no decision as to whether the Ford proposal for the Muscle Shoals nitrate plant and dam will be accepted. The bid has been submitted to the Chief of Engineers, and Maj. Gen. Beach has recommended that it be accepted. This recommendation and his analysis of the proposition have been attacked by experts, according to press reports current here, on the ground that the proposal fails to cover the cost of the dams and that additional water storage at high cost would have to be provided by the Government. It has also been announced that several groups of financiers, including the du Pont interests, have submitted proposals, but these cannot compete with the Ford offer, it is said. The Alabama Power Company, said to repre-

sent powerful New York banking interests, will also submit a bid that will compete with Ford's, according to current reports.

DEPARTMENT OF COMMERCE CONFERENCE

Industrial trade and technical organizations were called into conference with bureau chiefs of the Department of Commerce last week for the purpose of getting advice as to the kind and amount of governmental statistics in industry that should be gathered and compiled in the biennial census next year.

Many suggestions were made and accepted, as a result of which the department will make further report on the probable changes.

A number of changes in the specifications used by the Government for the purchase of gasoline, kerosene, fuel and lubricating oil, were recently proposed at an open meeting of the Technical Committee on Standardization

of Petroleum Specifications held under the chairmanship of N. A. C. Smith of the Bureau of Mines.

The Bureau of Mines is beginning research work on the coke that can be used in blast furnaces for fuel. This work will be undertaken in the Birmingham, Ala., district.

It is believed here that the Chemical Warfare Service of the Army should have not less than $4,000,000 next year to insure the proper development of this arm of the service.

Many Washington chemists are looking forward to a relief from their regular work next month when they go to New York to attend the meetings of the AMERICAN CHEMICAL SOCIETY and to see the Chemical Exposition.

AUGUST 11, 1921.

LONDON LETTER

By STEPHEN MIALL, 28, Belsize Grove, Hampstead, N.W.3, England

I think it was Lord Rosebery who said "There are two occasions when men make speeches, one, when they have something to say, the other, when they have to say something." I feel the truth of this observation very acutely; a letter on developments in industrial chemistry must be written. The heat and the drought do not promote a nimbleness of the mind; I have wandered up and down my parched little garden trying to think of the chemical developments which I well know are not taking place. It occurred to me to speak of the Synthetic Ammonia plant now being erected by Messrs. Brunner, Mond & Co. at Billingham, but it will be a year or a couple of years before it is turning out its several tons a day and many changes may have to be made in the interim.

This opportunity of an iteresting piece of news having been eliminated, the task still remains to be done, or perhaps begun. Then the historical method seemed possible and I commenced "On this day exactly one hundred and forty-seven years ago Priestley discovered oxygen," but the prospect of a history of oxygen and its developments to date filled me with dismay. Priestley made a greater discovery: soda-water, two words, as Webster said, connected by a syphon. This presented possibilities, but a liter of practice is worth a couple of pages of precept and I turned to the better course. Being still gravelled for want of matter—what fool was it who spoke of the indestructibility of matter?—I again stirred up the gruel I seem to have in place of cerebellum:

> "It's easy to bid one rack one's brain—
> I'm sure my poor head aches again,
> I've scratched it so, and all in vain."

Thrice, and even four times, blessed are those who will travel to America in the flesh, who can meet their colleagues face to face, sharpen their wits on each other and expound their views on the philosophy of life and the deceitfulness of riches without having the agony of seeing their feeble phrases (or is it frases in the U. S. A.?) in cold print a month afterwards. But one must be careful how one jests on a matter of spelling. When you first spelt sulfur with an "f" Professor H. E. Armstrong rashly stated that we ought to withdraw our Ambassador from Washington, whereupon eleven chemists, of whom nine were Scotsmen, solemnly explained that spelling was not the concern of the diplomatic service and that to withdraw our Ambassador seemed an extreme measure to take even for so outrageous a breach of decorum.

Industrial Chemistry and the League of Nations seem far removed, but the latter has an International Labour Office and this a Health Section which deals with questions of industrial hygiene. The International Labour Office will meet in Geneva next October and has put forward a proposal to prohibit the use of lead compounds in painting. All the chemists concerned in lead or zinc mining or smelting, in the paint and varnish industry,

and in allied occupations are busy with propaganda on one side or the other while medical men men and factory inspectors talk learnedly of arteriosclerosis and statisticians scrawl hieroglyphics alarming. Some facts seem to emerge from the fog of controversy and are, as yet, not sufficiently appreciated by chemical manufacturers; to begin with, the vapors of benzene, petroleum, turpentine and volatile thinners seem to be much more injurious than is commonly supposed. This point has been alluded to both in America and England before, but recent work by Sir Kenneth Goadby and others shows that there is a considerable danger to health from this cause. Another fact is that prevention of dust is the same thing as the prevention of disease, not only in the paint trade but in almost every occupation, farming only excepted. In some experiments on the detection of very small quantities of lead, Mr. C. A. Klein was for a while puzzled by dark stains when almost any solution was sufficiently concentrated, filtered, and treated with ammonium sulfite. Finally he proved that all filter papers are liable to contain copper in sufficient quantity to produce the necessary reaction, and it seems that the drying of the paper on bronze rollers or gauzes introduces this disturbing factor. In some cases the microscope reveals a dendritic growth of copper compound, and in exceptional cases the phenomenon is very marked.

What is research and how can it be promoted in the domain of industrial chemistry? Dr. Messel by his will left to the Society of Chemical Industry a sum exceeding £20,000 as an absolute gift but with the expression of a hope that it might be available for such an object. We are now trying to devise some scheme which will be worthy of this generous gift, and many are the suggestions which reach our Treasurer. While he considers the relative merits of medals, lectureships and scholarships and reads up the latest decisions on Charitable Trusts he steadily invests the income and I strongly suspect that he is mercenary enough to continue this practice until public opinion rises in its majesty and compels him to spend some money—well or foolishly—to justify his existence. A century or so ago a thrifty Englishman, named Thellusson, left a large sum of money to be accumulated until it would pay off our National Debt. Whenever I receive one of those persuasive forms appealing for income tax I curse the folly of the maniacs who prevented Mr. Thellusson's scheme from realization. And now I cry "Hands off Mr. Evans." He knows with Mr. Jingle that though there is a great deal to be done with fifty pounds, there is more to be done with a hundred and fifty. After all there are only two things which chemists should pursue, truth and money. Industrial chemists desire truth because it brings more money; pure chemists desire money because it enables them to attain more truth. How to blend the two, to discover the golden mean? This is the real problem, and the quadrature of the circle and the

trisection of the angle are nothing to it. Chemical equations are sometimes reversible, and I am hoping that a state of equilibrium will in time be reached between the reagents of truth and money. But Treasurers seldom attain to this state, they rise in the morning repeating "Take the cash and let the credit go," and they go to bed murmuring "A fool and his money are soon parted." I was once a Treasurer myself.

August 1, 1921.

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France.

The French government is at present making a study of the better utilization of coal and lignite.

The prospecting for petroleum, which I have already discussed, does not seem to have given the hoped-for results. Therefore, search is being made for a solution of the fuel problem along some other line. It is desired to produce what is known as the "national carburetant," a mixture of different hydrocarbons and alcohol, especially benzene and ethyl alcohol, each in the proportion of 33 per cent.

A competition has been instituted by the Agricultural Society of the Department of the Herault, which specifies that the mixture shall contain amounts of alcohol varying between 10 and 50 per cent, to be used with motors of the prevailing type or with modifications, these motors being devoted to motor culture, agricultural industries, motor vehicles, navigation, or aviation. If any American chemist or company is interested in this competition, I can send him the announcement.

Along this same line, distillation tests carried out on 100 tons of lignite have given the following yield per ton of lignite:

     25 kg. benzene
     25 kg. paraffin
     25 kg. ammonium sulfate

Although the United States is very rich in coal and petroleum, it is not neglecting lignite distillation, and is utilizing to the full the by-products of the coal. In France, at the present time, many small gas-works are not recovering their by-products, but a law, passed at the end of June, now obliges the gas-works to remove benzene, and also authorizes them to increase the proportion of water gas. A quantity of 15 or 18 per cent in illuminating gas has been pronounced inoffensive by the Conseil Superieur d'Hygiene. It is estimated that the application of this law, which, of course, substitutes coke for coal for the manufacture of the water gas, will reduce imports of coal by a million tons per year. On the other hand, considering all the gas-works, it is estimated that the benzene production will be from 25,000 to 30,000 tons per year. Further, the calorific value has been fixed at a maximum of 4700 calories and a minimum of 3500 calories.

THE HABER AND CLAUDE PROCESSES

The members of the committee appointed to estimate the comparative value of the Haber and Claude processes are not giving out the results of their investigation, and although the report has been submitted it is very difficult to find out what its conclusion was. French chemists are unanimous in deploring the fact that the private interests of the companies make such precautions necessary. There are involved here questions of a purely scientific sort, to which should be given the greatest possible publicity.

All one can say at present, from certain indications and with reservations, is that the committee has not pronounced itself clearly in favor of one or the other of the two processes. They seem to be equivalent, and the economy which would result from one or the other is of small value on account of the fact that the same difficulty exists in either case, that is, the cost of pure hydrogen. According to different engineers, it appears that this question of nitrogen needs to be studied in the industrial laboratory for some time longer.

HYDROGENATION OF FISH OILS

Following the example set in the United States, more and more research is being directed toward the utilization of sea products.

Mr. Marcelet has just been studying the hydrogenation of fish oil. It was already known that hydrogenation removes the odor which has made the oil unusable. Mr. Marcelet has been able to follow the lowering of the iodine number and the elevation of the melting pint, and to draw from this practical conclusions as to the utilization of the oil from the point of view of foods.

THE UNITED STATES TARIFF

A certain excitement has been manifested in France at the announcement of the appearance of the new United States customs tariff. The Chamber of Commerce of Paris, the president of which, Mr. Pascalis, is a manufacturer of chemical products, has issued a protest, based on the fact that the application of this tariff would necessitate annoying inquisitorial measures in French factories on the part of American tariff agents, and by a natural recoil American banks which have interests in Paris would have to expect to lose part of their clients.

The explanations from various sides which have appeared in the press reduce the apprehension to its true value. The list of substances admitted free to the United States is still relatively important, and it appears that the protective system adopted applies especially to the dyestuff industry, and is in a way legitimate on account of the considerable effort which is being made in this field in the United States, an effort which evidently needs a certain protection, at least for some years to come.

August 1, 1921.

Laboratory Fire at Tulane University

Fire which resulted in damage to equipment of approximately $20,000 and to the building of about $28,000 was discovered in the attic of the Richardson Chemistry Building, Tulane University, New Orleans, on the morning of July 6. No cause has been determined as to the origin of the fire. The top story of the building was completely destroyed, the second floor badly damaged, and the equipment on the main floor was damaged by water.

An interesting observation in connection with the fire is that "two shelves in the attic, which had been treated 10 years ago with aniline hydrochloride and copper sulfate were not even scorched although brass melted within three feet of them, and they were within 10 feet of where the fire is supposed to have originated."

Reconstruction has already commenced and it is hoped that the building will be back in shape in time for the opening of the fall term.

The latest report of the British Alkali Committee, which covers developments during 1920, outlines the present status of the industry as follows: During the year the number of registered chemical works was 1383; of these, 58 were registered as "alkali works," that is to say, works in which salt is decomposed with evolution of muriatic acid. There has been a decrease of four in the number of alkali works registered and of 16 in the number of other works, a total reduction of 20. The number of works by no means indicates the number of processes under inspection, as many works are registered for more than one process; in some instances the number of registerable processes in one works is as high as 10.

INDUSTRIAL NOTE

The Dye and Chemical Control Section of the Customs Service has prepared the following statement showing the commodities which are regarded as synthetic chemicals or drugs, and which therefore require special license for release from customs custody under the terms of the Emergency Tariff Act, also those which are not so considered. **Synthetic Organic Chemicals:** Formic, lactic, oxalic, pyrogallic, acetic, and valerianic acids, and all salts of the above, acetic anhydride, acetone, acetone oil, formaldehyde, chloral hydrate, urea, dionin (ethyl morphine), terpin hydrate, carbon tetrachloride, chloroform, cellulose esters, amyl acetate, amyl nitrite, ethyl acetate, ethyl chloride, sulfuric ether, butyl alcohol, iodoform, heroin, peronin, calcium cacodylate, mercury cacodylate. **Not Synthetic Organic Chemicals:** Citric, gallic, tannic, tartaric, prussic and glycerophosphoric acids, all metallic or inorganic radical salts of the above, thymol, glycerol, calcium cyanamide, sulfocyanides of metals or inorganic radicals, cocaine, morphine, caffeine, menthol, bismuth albuminate.

The French Academy of Sciences has just received a gift of 10,000,000 francs from Baron Edmond de Rothschild for use in research work.

The Baltimore and Ohio Railroad Company has reestablished its agricultural bureau to carry out the program begun in 1916 which was abandoned later on account of war conditions. The bureau is a part of the commercial development department, under the charge of Mr. H. O. Hartzell.

The United Indigo & Chemical Co., Ltd., a British corporation with offices in Boston, is required by a recent order of the Federal Trade Commission to refrain from certain competitive methods in the chemical industry. Testimony was given at the trial that during the three-year period, 1916, 1917, 1918, the United Indigo & Chemical Co., Ltd., expended for entertainment and gratuities to employees of its customers and competitors' customers an average of from $40,000 to $50,000 per year. These gifts were found to have been given without the knowledge or consent of the employers whose employees received the goods. This practice has been declared by the commissioners an unfair method of commerce, and its discontinuance ordered.

Fire damaged the Archer-Daniels Linseed Company's plant, at Buffalo, N. Y., recently. The fire was caused by spontaneous combustion, and resulted in a loss of $50,000.

The Maryland Vegetable Co., capital $1,250,000, has purchased the factory property of the Cocoanut Products Corporation, Baltimore, against which foreclosure proceedings have been instituted.

The American Society for Testing Materials has appointed a committee to work in conjunction with the Zinc Institute in testing zinc ores. The committee is headed by W. H. Bassett.

The American Chemical-Machinery Co., Philadelphia, has been incorporated in Delaware with a capital of $500,000.

PERSONAL NOTES

Major General W. L. Sibert, former head of the Chemical Warfare Service during the World War, is now back home on his farm in Warren County, Kentucky, where he is in the crude oil producing industry. Twenty wells are now going on General Sibert's land and one of these is credited with being the largest producer ever struck in Warren County.

Dr. Reuben S. Tour, government chemical expert, has been appointed professor of chemical engineering at the University of Cincinnati. Dr. Tour, who succeeds **Dr. O. R. Sweeney**, who resigned because of ill health, has served for several years as an expert for the government on nitrate and other chemicals, and will continue to act as consulting expert for the government. He had been offered, but refused, a position as chemical expert by a nation of Europe. Dr. Tour's new duties will begin September 1.

Dr. J. M. Bell succeeds **Dr. F. P. Venable** as head of the department of chemistry at the University of North Carolina. While Dr. Venable has resigned as head of the chemistry department, he will continue his duties as professor. In the fall, **Dr. F. C. Vilbrandt** of Ohio State University will assume his duties at the University of North Carolina as associate professor of industrial chemsitry, and will inaugurate laboratory courses in that subject, as well as carry on the lecture work.

Dr. Eugene P. Deatrick resigned as instructor of soil technology, College of Agriculture, Ithaca, N. Y., to become associate professor of soils, head of department, West Virginia University, Morgantown, W. Va.

Mr. W. H. Ransom, who has been stationed at the old Hickory Powder Plant as executive officer, for the past two years, has accepted a position with the Celluloid Co., Newark, N. J.

Dr. Arthur B. Ray, who has been directing certain investigations relative to carbon products at the Cleveland laboratories of the National Carbon Co., Inc., has been recently transferred to the Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y.

Mr. Alfred T. Shohl, formerly associate professor of chemical hygiene in the School of Hygiene and Public Health, Johns Hopkins University, has recently been appointed associate professor of pediatrics in the newly created department of pediatrics at the Yale Medical School, New Haven, Conn. A large part of the work will consist of research in food and metabolism connected with children.

Mr. Wallace L. Caldwell, for the past nine years director, department of roads and pavements, of the Pittsburgh Testing Laboratory with headquarters at Birmingham, Ala., is at present located at Louisville, Ky., as assistant to the president of the Kentucky Rock Asphalt Co.

Mr. Ralph C. Holder recently resigned as junior chemist in the food research laboratory, Bureau of Chemistry, to accept a position as chemist in charge of the chemical laboratory for the Collis Products Company at St. Paul, Minn.

Mr. Paul M. Stouffer left the laboratory of the Solvay Process Company in Syracuse, N. Y., to take charge of control work for the White Rock Mineral Springs Co., Waukesha, Wis.

Mr. R. H. Hoffman, food and drug commissioner of the State of Texas, for about ten years, now has charge of the laboratory and the Life Extension Service of the Great Southern Life Insurance Co., Houston, Tex.

Mr. J. P. Bonardi, who has been with the Bureau of Mines Experiment Station at Denver for the past five years, recently transferred to Reno, has accepted a position as manager of the assay and chemical department of the Mines and Smelter Supply Co. of Denver, Col.

GOVERNMENT PUBLICATIONS

By NELLIE A. PARKINSON, Bureau of Chemistry, Washington, D. C.

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

Barytes and Barium Products in 1919. G. W. STOSE. Separate from Mineral Resources of the United States, 1919, Part II. 13 pp. Issued July 28, 1921. The barytes industry had a prosperous year in 1919. The following tabular statement shows the quantity, value, and average price per ton of crude barytes produced and marketed in the United States, 1880-1919:

CRUDE BARYTES PRODUCED AND MARKETED IN THE UNITED STATES, 1880-1919

	Quantity Short tons	Value	Average price per ton
Annual average for 10 years 1880-1889..	21,410	....	....
Annual average for 10 years 1890-1899..	27,523	....	....
Annual average for 10 years 1900-1909..	58,310	....	....
Annual average for 5 years 1910-19 14....	43,389	....	$3.31
1915	108,547	$381,932	3.51
1916	221,952	1,011,232	4.56
1917	206,888	1,171,184	5.66
1918	155,368	1,044,905	6.73
1919	189,647	1,555,793	8.20

The total quantity of barium products manufactured and sold in 1919 was considerably greater than in 1918. The quantity of barium chemicals marketed in 1919 was somewhat less than in 1918, but the quantity of lithopone produced and sold was much greater than in 1918.

Magnesite in 1920. C. G. YALE AND R. W. STONE. Separate from Mineral Resources of the United States, 1920, Part II. 17 pp. Published July 27, 1921. Reports received from all producers show that 303,767 short tons of crude domestic magnesite, valued at $2,748,150, was produced and sold or treated in 1920, an increase of 94 per cent in quantity and 120 per cent in value over 1919.

BUREAU OF MINES

Nature of Shale Oil Obtained from Shale Oil Assay Retort Used by the Bureau of Mines. M. J. GAVIN AND L. C. KARRICK. Reports of Investigations. Serial No. 2254. 11 pp. Issued June 1921. Experimental work indicates that it is ossible to vary the quantity and quality of the oil obtainable with the assay retort from a given shale by varying the conditions of retorting.

An Unusual Hazard in Reopening Long-flooded Timbered Metal Mines. D. HARRINGTON. Reports of Investigations. Serial No. 2255. 3 pp. Issued June, 1921. There is a well-defined movement towards reopening of long abandoned mines with intent to extract ores of a grade formerly rejected but probably amenable to present-day methods of treatment. Many of these properties have long been under water and their recovery presents, among other problems, that of possible occurrence of explosive gas, methane. Precautions to be observed in such work are described.

Notes on The Oil-Shale Industry with Particular Reference to the Rocky Mountain District. M. J. GAVIN, H. H. HILL AND W. E. PERDEW. Reports of Investigations. Serial No. 2256. Issued June 1921. 36 pp. As yet no process for obtaining oil from oil shale has been used in actual commercial practice in this country. Indications are that the United States cannot continue long to depend on domestic petroleum to supply completely the demand for petroleum products, and that sooner or later our oil shales will have to be used to help supply the deficit. The shale-oil industry cannot hope to supplant the petroleum industry in a large way for many years.

Six-Year Accident Record of Mines of the Anaconda Copper Mining Company in Montana. D. HARRINGTON. Reports of Investigations. Serial No. 2259. 2 pp. Issued June, 1921.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. BURROUGHS. Reports of Investigations. Serial No. 22621. 28 pp. Issued June, 1921.

Gases Produced in the Use of Carbon Tetrachloride and Foamite Fire Extinguishers in Mines. A. C. FIELDNER AND S. H. KATZ. Reports of Investigations. Serial No. 2262. 6 pp. Issued June, 1921. A summary of results is included giving the important constituents of the atmospheres produced in the use of carbon tetrachloride and foamite extinguishers in the wood fire experiments.

Monthly Statement of Coal-Mine Fatalities in the United States, April, 1921. W. W. ADAMS. 9 pp. Issued June, 1921. Paper, 5 cents.

DEPARTMENT OF AGRICULTURE

Waterproofing and Mildewproofing of Cotton Duck. H. P. HOLMAN, B. S. LEVINE AND T. D. JARRELL. Farmers' Bulletin 1157. 13 pp. Paper, 5 cents. Reprinted with slight changes, June 1921.

COMMERCE REPORTS—JULY 1921

Conditions in the Belgian zinc industry are described. (P. 38.)

An article describing the Chinese oil resources in great detail may be obtained from the Far East Division of the Bureau of Foreign and Domestic Commerce. (P. 54.)

The oil-bearing nuts of the Guatemalan palm tree are sad to contain 65 per cent of oil, in comparison with 42 per cent for African nuts, and the yield of kernels per ton of nuts in Guatemala is about 18 per cent. (P. 56.)

The exportation of oil by American companies in Tampico stopped on July 2, 1921. (P. 65.)

Japan has recently completed a contract with a British company whereby her fuel oil tanks will be filled to capacity. (P. 84.)

The copra trade in the Dutch East Indies is reviewed. (P. 85.)

The government of Ecuador has drawn up a contract with an American company which provides for the exploitation of oil deposits in the province of El Oriente for a period of 34 years. (P. 95.)

One of the effects of the coal famine in England has been to fix attention to the possibilities of liquid fuel. Possibilities of steam raising by means of oil installations are looked upon as of more immediate concern than anything else. (Pp. 107-9.)

Great interest is shown at Sydney in the manner in which the phosphates from Nauru Island are to be divided among manufacturers of fertilizers. (Pp. 116-7.)

Forty carloads of mineral fertilizer destined for Soviet Russia were passed through Yamburg from Germany up to the end of April 1921. (P. 120.)

Announcement comes from Moscow of the success of experiments for the production of paper from flax waste, which has hitherto remained unused. (P. 120.)

The curtailment of the use of electricity for light and power has led to an interesting development in Liverpool in the installation of oil fuel apparatus for light and heat by kinema houses and other places of amusement. (P. 123.)

A new plant and buildings, costing $1,250,000, are in the course of erection by the Cape Explosives Works (Ltd.), Somerset West, Cape Province. They plan to supply every kind of fertilizer used in the country and expect to be able within a few months to produce fertilizers at the rate of 100,000 tons per annum. (P. 128.)

The stagnation of the nitrate market continues to be the principal item of interest in Chile. (P. 143.)

For the greater part of the year a prohibition on import of synthetic dyes was maintained in Bombay, India, in the interest of the British manufacturer. Licenses were, however, freely issued for foreign dyes which Great Britain was unable to produce in sufficient quantities. (P. 154.)

The new Italian import duties, effective July 1, 1921, are quoted on cottonseed oil and gasoline. (P. 165.)

It is reported that several tons of high-grade **tin ore** have been extracted near Sao Paulo, Brazil. (P. 167.)

Phosphate production in Egypt is reviewed and it is stated that the industry has rapidly advanced since the signing of the armistice until the 1920 exports were double those of 1919. (P. 183.)

The production of **petroleum** in Mexico from 1901 to 1920 was 563,523,752 bbls. of 42 gal. each. The quantity increased yearly from 10,345 bbls. in 1901 to 163,540,000 bbls. in 1920. It was estimated that in January 1921 the supply of oil in the Tampico-Tuxpam fields was 450,000,000 bbls. This would last 2.5 yrs. at the rate of production in 1920. It appears that there is no ground for anxiety about the future oil supply, though there is some difference of opinion on this subject. (P. 230.)

The British **Cast Iron Research** Association has been formed, its object being to conduct scientific and experimental work in connection with the cast iron trade. (P. 234.)

A new French company has been formed with a capital of 100 million francs to market **oil** in France and the French colonies. Of the capital the French syndicate guarantees the subscription of 55 per cent and the Anglo-Persian Oil Company the remaining 45 per cent. (P. 234.)

Statistics are given showing the total production of **petroleum** for Mexico for the years 1901-1920, inclusive; also the figures for production, exportation, and consumption in 1921, up to and including May. (P. 271.)

The future export tendencies of German **coal-tar colors** are described and the following table is included showing the quantity of aniline and coal-tar dyestuffs exported to various countries in 1920 as compared with the quantity exported to these countries in 1913:

Countries of Destination	1913 Tons	1920 Tons	Countries of Destination	1913 Tons	1920 Tons
United States	13,855	338	Sweden	900	893
Great Britain	11,000	970	Switzerland	784	464
Austria-Hungary	5,800	741	Spain	656	447
Czechoslovakia	...	2,335	Brazil	627	...
Italy	4,100	1,257	Mexico	543	...
China	8,500	....	Canada	443	...
Japan	3,500	....	Turkey	437	195
India	3,800	....	Portugal	418	...
Belgium	2,500	790	Norway	270	220
Russia	1,100	....	Denmark	237	216
Holland	1,400	1,047	Finland	236	194
France	1,400	670			

(Pp. 279-80.)

The **petroleum** industry in Soviet Russia in 1920 is reviewed. In 1920 there was produced 10,000,000 lbs. of crude petroleum more than in 1919. (Pp. 284-5.)

The possibilities of the sale of American **drugs** and medicines in India warrant a careful study of the market. (P. 289.)

According to an Indian expert, **oil** may soon be discovered in Bihar and Orissa, in the Central Provinces, and in the Peninsula. There are also indications of a fairly well-defined oil belt between Assam and Burma, passing through Chittagong. (P. 289.)

Word comes from England that the North Staffordshire Railway has, in common with many other companies, adopted **oil-burning** for **locomotives.** An interesting feature of the change is that both coal and oil can be used as fuel at the same time on these locomotives. (P. 317.)

Near-Eastern markets for **paints** and **varnishes,** including Palestine, Smyrna, Syria and Turkey, are reviewed. (Pp. 318-20.)

British trade in **chemicals, drugs** and **dyes** is reviewed. (Pp. 330-3.)

The British **palm-kernel** and **edible-oil** industry is described and in comparing the 1920 with the 1913 status it is noted that the United Kingdom and Germany have exchanged positions in the palm-kernel crushing industry. (Pp. 338-42.)

The **vegetable-oil** industry of Belgium is reviewed. The four years of war had a disastrous effect on the industry from which it has not yet recovered. (Pp. 363-5.)

The production of **salt** in the Fukien Province, China, during 1920 amounted to 40,103 tons. (P. 376.)

A market for **aniline dyes** is said to exist in the Chungking District, China. (P. 376.)

Statistics are given showing the production of **minerals** and metals in the United Kingdom during 1918 and 1919. (Pp. 378-9.)

The Havre trade in **oleaginous nuts** is reviewed. (Pp. 384-5.)

Cellulose of a good quality, capable of being used in the manufacture of fine grades of paper and gunpowder, is manufactured in Jugoslavia. (P. 416.)

Trade in **dyestuffs** in Japan has become more active. (P. 452.)

There were exported 13,901,524 metric quintals of **nitrate** from Chilean ports during the first four months of the present year. (P. 471.)

The Secretary of the Scientific and Industrial Nitrate Institute states that at the present rate of production of nitrate it is possible to extract only 700 tons of **iodine** annually in Chile; that in normal times the production may be estimated at double that figure. (P. 471.)

The slump in exchange during 1920 has completely upset all Chinese business in the **dye** trade. (P. 485.)

STATISTICS OF EXPORTS OF THE UNITED STATES—JUNE 1921

Shanghai—(Pp. 1248-9)
Antimony
  Crude
  Oxide
Albumin
Camphor
Tungsten ore

Cuba—(Pp. 1270-1)
Gold, silver and platinum
Iron and steel
Copper and alloys
Paints and varnishes
Chemical products
Oils
Hides and skins

Jamaica—(P. 1294)
Orange oils
Tanning materials
Copra

London—(P. 1785)
Rubber
Tin
Leather, hides
Drugs and chemicals
Gums

France—(P. 1307)
Chemicals

Colors
Copper
Hides and skins

Leghorn—(P. 1330)
Sienna earth
Umber earth

Palermo, Italy—P. 1549)
Olive oil
Sulfur oil
Bergamot
Manna
Oil of lemon
Oil of orange
Dyeing and tanning materials
Citrate of lime
Citric acid
Tartaric acid

Glasgow, Scotland—(P. 1627)
Creosote oil acids
Fertilizers
Magnesite
Manganese oxide and ore
Sulfate of ammonia

Aleppo, Syria—(P. 1616)
Gum tragacanth

Mexico City—(P. 1738)
Jalap root
Ipomea orizabensis
Indigo
Valerian
Copper
Hides and skins
Linaloa oil
Sesame oil
Quicksilver
Silver
Turpentine

Kalamata, Greece—(P. 1791)
Hides and skins
Resin

Curacao, West Indies—(P. 1807)
Copaiba balsam
Chicle
Gasoline

Algeria—(P. 1869)
Essence of geranium
Glue stock
Iron ore

STATISTICS OF EXPORTS OF THE UNITED STATES—JULY 1921

Indo-China—(P. 15)
Gums, gamboge
Plumbago or graphite
Rubber, India, crude
Sticklac

Brazil—(P. 41)
Carnauba wax
Cottonseed
Manganese
Monazite sand
Rubber

Capetown—(P. 74)
Buchu leaves
Lead and copper
Vanadium
Wax

Liverpool—(P. 123)
Tin
Ferromanganese
Palm oil

Vigo, Spain—(P. 147)
Arsenic
Olive oil

Hankow, China—(P. 495)
Antimony
Cottonseed oil
Sesamum seed
Tallow, vegetable

Birmingham, England—(P. 240)
Aluminium
Chemicals and drugs
Acid, citric
Ammonium carbonate
Ammonium muriate
Soda tartrate
Gelatin

Bombay, India—(Pp. 156-8)
Linseed
Sesamum
Rape seed
Bone meal
Copra
Drugs
Gums
Oil
Coconut
Rose
Ore, manganese
Seeds
  Castor
  Poppy
  Mustard

Calcutta, India—(P. 253)
Lac
Linseed
Rapeseed
Castor seed

Greece—(P. 343)
Attar of roses
Chrome ore
Magnesite ore
Opium
Rosin
Saffron
Tartrate of lime

Egypt—(P. 201)
Alcohol
Medical preparations
Oils, mineral

London, England—(P. 510)
Rubber
Tin
Drugs and chemicals

Austria—(Pp. 360-1)
Oils, fats
Paints and tanning materials
Gums and resins
Mineral oils, charcoal and slate tar
Chemical products and chemical materials
Acid tartaric
Fusel oil
Mineral wax

Mexico—(Pp. 579-91)
Citrate of lime
Oil of lime
Oil cake
Coconut
Sesame seed
Silver and lead ore
Copper ore
Manganese ore
Silver ore
Zinc ore
Glycerol, crude
Oils, essential
Molybdenum ore
Tungsten ore
Arsenic
Cottonseed oil
Rosin
Rubber
Turpentine
Wax
Bark
Cinchona
Sarsaparilla
Chicle, crude
Nitrate of potash
Quicksilver

Tampico, Mexico—(Pp. 180-1)
Petroleum

BOOK REVIEWS

Metallography, Part II. The Metals and Common Alloys. By SAMUEL L. HOYT, E. M., Ph. D. 1st Edition. x+462 pages. McGraw-Hill Book Co., Inc., New York. 1921. Price, $5.00.

To the general reader the subtitle of this book gives little idea of the valuable material contained in it. While the aluminium alloys, the brasses and bronzes, the bearing metals, steels and cast irons are strictly speaking common alloys they are so important both from a scientific and technical point of view they deserve a better adjective to describe them. In his preface the author refers to them as "the more important metals and alloys" which is much more appropriate. This volume describes the constitution and microstructure, the physical and mechanical properties, the heat treatment, effects of impurities, and the uses of (1) pure metals, (2) white metal alloys, (3) light metal alloys, (4) brasses and bronzes, (5) steel and cast iron, and (6) special steels. The introduction into a book on metallography of a discussion of the properties of the individual metals is a welcome and entirely proper addition, and under this heading the author has collected from the most reliable sources, and discussed the data concerning the more important properties of the metals. Naturally copper and iron receive the greatest attention. For the sake of completeness and on account of its importance, data on nickel should have been included, but unfortunately the author gives none and refers to another publication which may be available to a comparative few. The discussion of the properties of the metals is interesting, concise, accurate, and with abundant reference to the original data.

The author has departed from the usual practice of treating the nonferrous alloys. Instead of classifying them as copper, lead, or zinc base alloys he has grouped them under the headings of bearing metals, light metal alloys, and brasses and bronzes. This scheme has advantages in that under these general headings there can be the older classification according to metals. Under the simple bearing metals, the author discusses the equilibrium diagrams and the properties of the binary alloys, lead-tin, lead-antimony, tin-antimony, etc., and then a few of the ternary alloys.

Under the light metal alloys are discussed the alloys of aluminium with copper, zinc, iron, manganese, silicon, alloys which may be cast, forged, or heat treated. Duralumin, on account of its increasing importance in airplane construction and its unusual change of properties brought about by heat treatment and "ageing," receives fuller discussion.

Although the brasses and bronzes are commercially old and important, it is only comparatively recently that they have received adequate scientific attention. The author traces the development of this work from Charpy's first paper in 1896 to the most recent, and discusses comprehensively the equilibrium diagrams of each group, the mechanical and physical properties, microstructure, effect of impurities. One would naturally expect a discussion of the important phenomena of corrosion and season cracking at this point, but the author is probably reserving it for the volume to follow on "Technical Practice."

The author devotes about two-thirds of the volume to steel, cast iron, and special steels. His statement in beginning the discussion of the iron-carbon constitution diagram that the diagram may be regarded as orthodox has a

certain grim humor about it when one considers that it is the foundation stone of all the discussion that follows. The diagram is, however, discussed fully, clearly, and with good judgment. In regard to the austenite-pearlite transformation taking place on slow cooling the author uses excellent judgment, and the logic of the phase rule in dismissing the conception held by some that martensite and troostite are intermediate phases in this transmission. Again he shows discrimination in not being misled by propaganda in favor of certain alloying elements in special steels, or as to the harmless effects of certain impurities such as phosphorus and sulfur in ordinary steels. Indeed, one of the features of the book is the good judgment not only as to choice of material but also as to its relative importance. Nickel, chromium, manganese, silicon, tungsten, molybdenum, chrome-nickel, chrome-vanadium, and high speed steels are discussed with abundant reference to the literature. The collection of data in regard to the physical properties, constitution, critical temperatures, microstructure, and uses of all these steels will be welcomed most heartily. In his discussion of the uses of manganese steel, the author makes the statement that manganese steel containing below 1.5 per cent manganese is used in Europe, especially in Germany, evidently forgetting the recent extensive manufacture of rifles in this country. Such omissions are extremely rare, and on the whole the book is excellent, being clear, concise, accurate, and well balanced.

HENRY FAY

Rubber, Resins, Paints and Varnishes. By R. S. MORRELL, Ph.D., and A. DE WAELE, A.T.C. xii + 236 pages. D. Van Nostrand Co., New York, 1920. Price, $4.00 net.

This is one of a series of volumes giving a comprehensive survey of the chemical industries, under the editorship of Dr. Samuel Rideal. As is said in the preface, the object of the books is to "give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture."

The volume will be useful to the nontechnical as well as to the chemical reader, as it gives a brief, but withal an eminently satisfactory, review of the subjects in question, the space devoted to each being as follows: Rubber, 35 pages; drying oils, 42; resins and pitches, 31; pigments and paint, 55; linoleum, 15; varnishes, 51.

Stress is laid upon the chemistry involved—in the case of synthetic rubber, for example—and the action of driers in paints is carefully explained.

Statistics are not included, nor are analytical data or methods, except briefly in the case of varnishes.

It would have been instructive in connection with paints to have given the results of the extensive and practical tests on paint made in the United States by Holley and Ladd and Gardner, and by the American Society for Testing Materials.

A well-selected bibliograph with each chapter is a useful feature.

The book may be recommended cheerfully to all who have occasion to deal with the subjects in question as an interesting and authoritative treatise on their occurrence, the chemistry of their manufacture, and their uses.

A. H. GILL.

American Chemistry. By Harrison Hale.   vii + 215 pages. D. Van Nostrand Co., New York, 1921. Price, $2.00.

Here is a little book with a most attractive title, written with an excellent purpose: "It seeks to be of service both to the general reader and to the reader still in school. For the student, it is intended for use either as collateral reading along with a course in General Chemistry, or as a short separate course."

Essentially then, this is to be a popular instructive treatment of a great subject. It is eminently true that the treatment of a subject such as chemistry in simple language, suited to the layman, requires greater care than its presentation to those conversant with the rudiments of the science. In the former case, statements must either be entirely comprehensible to one with a good general education, or must convey the impression to such a reader that the meaning is clear to him. He must encounter few words with which he is not familiar, even though he may not be aware of their full meaning. Too many unknown words soon cause him to lose interest, and to feel that the subject is beyond his understanding. It must be said that, unfortunately, in this book, the author has failed to meet this requirement. For example, how can the unprepared reader gain any pleasure from statements such as these:

More recently by treating cottonseed oil with hydrogen in the presence of a catalyzer, the melting point is raised due to an increase in the molecular weight of certain constituents, and so a larger amount of solid fat can be obtained.

At higher temperatures the heavy oils with the heavier molecule tend to break up into oils with a lower boiling point and smaller molecular weight. This process is called "cracking."

Hence all drying oils are chemically unsaturated compounds, that is all of their valency bonds are not satisfied, and these bonds are filled by the oxygen upon exposure to the air.

The book contains chapters on a number of subjects of very live interest, subjects which should be brought to the attention of the public from a chemist's point of view, but these are handled here in a haphazard, careless fashion which does not give any proper sequence to the facts, or make them stand out in their true relation to each other. The book reads, in fact, as though it were a collection of verbatim notes taken at lectures given by one who had prepared only by reading a number of descriptive articles such as those quoted as references.

It must be said that this carelessness goes even beyond the mere construction of the chapters. It is to be found in the English used and in the inaccuracy of the proofreading. Those who write as members of the class of educators, should be careful to use pure, clear English. Here we read:

The advantages of the American system, now in very general use in this country, are lower construction cost, greatly lessened requirement of land for the buildings and the ease of washing the filter, which is generally carried out daily by the use of compressed air followed by filtered wash water forced up from below and allowed to run to waste.

In addition to this, certain substances, not all of which are clearly understood, are necessary to control and regulate body processes.

The increased use of paint materials has without doubt made, not only for improved sanitary conditions and more beautiful surroundings, but also for economy on account of the protection from rot and rust resulting from the action of the atmosphere and of moisture.

In addition, the pit-falls of "as to" and of split infinitives are not avoided.

It would be foolish to take space in such a Journal to point out short-comings of this kind, were it not that they are characteristic of a great deal of the simplified science writings of today. Would it be too much to ask of those about to publish matters of this kind to have someone accustomed to criticize English pass upon their manuscript? There are some surprising statements in consequence of careless wording in this little book. We read that nitrogen is used (!) as "a diluent for the more active oxygen of the air," and again, that "one of the uses (!) of nitrogen in the air is to dilute the more active oxygen." Presumably, this should have been mentioned in the first chapter of Genesis. Again, cellulose is "named from the plant cells of which it is made," and finally, the North American Indians in 1659 sold crude oil as an "external and internal medicine, frequently being sold as Seneca oil."

It is a pity that this book is not better. Its faults overshadow its virtues, chief among which is that of listing numerous references which are likely to prove of interest and benefit to students beginning their study of chemistry.

R. E. Rose

Copper Refining. By Lawrence Addicks, Consulting Engineer. ix + 211 pp. McGraw-Hill Book Co., Inc., New York, 1921. Price, $3.00.

The volume is a timely and valuable addition to a library on the metallurgy of copper. As the title indicates, the text is strictly limited to the purification of blister copper. The thirteen chapters discuss the following general subjects: metal losses, metals in process, tank resistance, current density, current efficiency, impurities, by-products, furnace refining, the requirements of refined copper, copper from secondary material, the power problem, elements of design, and applications to other fields. The discussions under the general headings are well designed, the subdivisions being clearly stated and well developed in order. This is one of the many strong points in the book and helps to make it thoroughly readable and easily grasped. The flow sheets of a copper refining plant, and those dealing with the different phases of the refining process are admirably worked out in clear detail and add greatly to the descriptive matter which they accompany. The whole work appears to be well up-to-date and offers many suggestions for investigation of new processes for improved efficiency and for the prevention of waste. Very little theory is developed in the book, though the results of modern theories are used wherever applicable. One may summarize the text by saying that it is a clear description of modern copper refining practice together with the application of the principles upon which the practice is based.

As is common in first imprints of a book there are a number of typographical errors, some rather glaring, and occasionally there is a poor English sentence. Only one serious error was noticed in applying principles. This is in the discussion of the order of oxidation of the metals based upon the heats of formation of the oxides. The author makes his comparison with molar heats, rather than with equivalents, and thus wrongly concludes that tin would be oxidized to the dioxide in preference to zinc. From the thermochemical data given, however, zinc would reduce stannic oxide with the evolution of heat, and thus would become oxidized in preference to tin.

Since both the series and multiple arrangements of the electrodes in the tanks are in commercial use, the reviewer would have welcomed a discussion of the relative efficiencies of the two types of connection under varying conditions. On the whole, the text rather exceeds one's expectations regarding a subject on which so little had been compiled.

J. H. Ransom

NEW PUBLICATIONS

Flotation: Concentration by Flotation. Compiled and edited by T. A. RICKARD. 692 pp., Illustrated. Price, $7.00 postpaid. John Wiley & Sons, Inc., New York.

Metallurgy of the Common Metals. LEONARD S. AUSTIN. 5th edition, revised and enlarged. 615 pp. Illustrated. Price, $7.00. John Wiley & Sons, Inc., New York.

RECENT JOURNAL ARTICLES

Aluminum: Losses in Aluminum and Aluminum Alloy Melting. ROBERT J. ANDERSON. BRASS WORLD, Vol. 17 (1921), No. 6, pp. 154-56.

Aluminum: Metodo Gasvolumetrico per la Determinazione dell' Alluminio. L. LOSANA. GIORNALE DI CHIMICA INDUSTRIALE ED APPLICATA, Vol. 3 (1921), No. 6, pp. 239-41.

Catalysis: Le Mecanisme de l'Action Catalytique. CH. MATIGNON. CHIMIE ET INDUSTRIE, Vol. 6 (1921), No. 1, pp. 7-10.

Cement: Relation between Tensile and Compressive Strengths of Cement Mortars. J. R. DWYER. CONCRETE, Vol. 18 (1921), No. 6, pp. 123-25.

Cement: The Relation of Carbon Dioxide and Moisture to the Setting Time of Cement. S. L. MEYERS. CONCRETE, Vol. 19 (1921), No. 1, pp. 128-30.

Coal: The Use of Oil in Cleaning Coal. G. ST. J. PERROTT and S. P. KINNEY. COAL AGE, Vol. 20 (1921), No. 4, pp. 132-134; CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 182-88.

Coal: The Scope of Pulverized Coal. F. P. COFFIN. COMBUSTION. Vol. 5 (1921), No. 2, pp. 62-65, 82.

Coal: Les Matières Volatile de la Houille. ACHILLE DELCLÈVE. CHIMIE ET INDUSTRIE, Vol. 6 (1921), No. 1, pp. 33-40.

Coal: Some of the Many Problems in the Cleaning of Coal. EDWARD O'TOOLE. COAL AGE, Vol. 20 (1921), No. 1, pp. 3-6.

Colloids: In Relation to Clarification in Sugar Manufacture. STUART M. LITTLEMORE. CHEMICAL ENNGINEERING AND MINING REVIEW, Vol. 13 (1921), No. 153, pp. 319-22.

Copper: Principles of Leaching and Precipitation of Copper. FRANK A. LATHE. CANADIAN CHEMISTRY AND METALLURGY, Vol. 5 (1921), No. 7, pp. 202, 203.

Corrosion: Les Corrosion du Fer et leur Suppression par le Degazage de l'Eau. G. PARIS. CHIMIE ET INDUSTRIE, Vol. 6 (1921), No. 1, pp. 11-32.

Cottonseed: Chemical Changes in Cottonseed during Heat and Storage. JOHN MALOWAN. THE COTTON OIL PRESS, Vol. 5 (1921), No. 4, pp. 40-43.

Dyeing: A Study of the Variations in Hematine Dyeings with Different Methods of Chrome Mordanting. CARL W. STAPLES. TEXTILE COLORIST, Vol. 43 (1921), No. 511, pp. 463-466; No. 512, pp. 528-31.

Dyeing: Dyestuff Testing in the Textile Industry. EDW. WALLACE PIERCE. CANADIAN DYER AND COLOR USER, Vol. 1 (1921), No. 7, pp. 132-36.

Dyeing: The Mechanical Ventilation of Dyehouses. J. E. BRIERLEY. JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS, Vol. 37 (1921), No. 7, pp. 187-90.

Explosion Hazard and its Prevention. JOSEPH F. SHADGEN.. THE IRON AGE, Vol. 108 (1921), No. 3, pp. 127-30; No. 4, pp. 205-06, 239-40.

Gasoline: Problems of Motor Gasoline. E. W. DEAN. PETROLEUM, Vol. 11 (1921), No. 4, pp. 40, 45.

Gelatin: Les Propriétés de la Gélatine. L. MEUNIER. CHIMIE ET INDSTRIE, Vol. 5 (1921), No. 6, pp. 642-50.

Glass. The Manufacture of Constructional Glass in the United States. E. WARD TILLOTSON, JR. JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY, Vol. 40 (1921), No. 13, pp. 155t-59t.

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Heat Waste: Stopping Wastes in the Boiler Plant. LOREN L. HEBBERD. SUGAR, Vol. 23 (1921), No. 7, pp. 384-86.

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Iron: Electric Reduction of Iron Ores. H. A. de FRIES. CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 193-94.

Lead: Notes on the So-called Action of Water on Lead. JOHN C. THRESH. THE ANALYST Vol. 46 (1921), No. 544, pp. 270-79.

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Petroleum: The Colloid Chemistry of Petroleum. FRED. W. PADGETT. CHEMICAL AND METALLURGICAL ENGINEERING, Vol. 25 (1921), No. 5, pp. 189-92.

Phosgene: Azione del Fosgene sulla Ricinoleina. ARNOLDO PIUTTI and A. CURZIO. GIORNALE DI CHIMICA INDUSTRIALE ED APPLICATA, Vol. 3 (1921), No. 6, pp. 242-44.

Pulp: Dyeing of Straw Pulp. CLARENCE J. WEST. PAPER, Vol. 28 (1921), No. 16, pp. 23-24.

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Rubber: Pitch Hydrocarbons used in the Rubber Industry. FREDERIC DANNERTH. THE INDIA RUBBER WORLD, Vol. 64 (1921), No. 5, pp. 821-24.

Steel: An Occurrence of Nitrogen in Steel. A. A. BLUE. THE IRON

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Starch: The Manufacture of Starch, Glucose and By-Products. R. H. WILLIAMS. CANADIAN CHEMISTRY AND METALLURGY, Vol. 5 (1921), No. 7, pp. 195-96. AGE Vol. 108 (1921), No. 1, pp. 1-5.

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Sugar: Water Concentration: A Neglected Factor in Polariscopic Methods of Sugar Analysis. C. A. BROWNE. LOUISIANA PLANTER AND SUGAR MANUFACTURER, Vol. 67 (1921), No 3, pp. 44-46.

Sulfite Liquor: L'Utilization des Lessives Residuaires de Fabrication des Celluloses à Papier. H. BRAIDY. REVUE GÉNERALE DES MATIÈRES COLORANTES DE LA TEINTURE, DE L'IMPRESSION ET DES APPRÊTS, Vol. 25 (1921), No. 923, pp. 65-70.

Textiles: Faults in Fabrics Due to Chemical Causes. D. K. COLLEDGE. AMERICAN DYESTUFF REPORTER, Vol. 9 (1921), No. 1, pp. 18-20.

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Textiles: The Uses of Copper Salts in Textile Treatment. A. J. HALL. AMERICAN DYESTUFF REPORTER, Vol. 9 (1921), No. 5, pp. 21, 24; No. 5, pp. 20, 25, 26. From DYER AND CALICO PRINTER.

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Varnish: Progrés Réalisés dans la Fabrication des Vernis à la Colophane. CH. COFFIGNIER. CHIMIE ET INDUSTRIE Vol. 5 (1921), No. 5, pp. 495-99.

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Vitamines: Methods of Extracting and Concentrating Vitamines A, B, and C, together with an Apparatus for Reducing Milk, Fruit Juices, and Other Fluids to a Powder without Destruction of Vitamines. J. F. McCLENDON. JOURNAL OF BIOLOGICAL CHEMISTRY Vol. 47 (1921), No. 2 pp. 411-20.

Waste: Disposal of Industrial Wastes and Stream Pollution. .C. A. EMERSON, JR. JOURNAL OF THE FRANKLIN INSTITUTE, Vol. 191 (1921), No. 6, pp. 807-18.

MARKET REPORT—AUGUST, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

	August 1	August 15
Acid, Boric, cryst., bbls........lb.	.13¼	.12¾
Hydrochloric, com'l, 200....lb.	.01½	.01½
Hydriodic ....oz.	.19	.19
Nitric, 420.................lb.	.07¼	.07¼
Phosphoric, 50% tech......lb.	.13	.12
Sulfuric, C. P............lb.	.07	.07
Chamber, 660..........ton	18.00	18.00
Oleum 20%............ton	22.00	22.00
Alum, ammonia, lump.........lb.	.03½	.03½
Aluminium Sulfate (iron-free)..lb.	.03	.03
Ammonium Carbonate, pwd.....lb.	*.07	*.07
Ammonium Chloride, gran.....lb.	*.06¾	*.06¾
Ammonia Water, carboys, 260..lb.	.08	.08
Arsenic, white.................lb.	.06½	.06¼
Barium, Chloride..............ton	*57.50	*52.00
Nitrate ....lb.	*.08¼	*.08¼
Barytes, white.................ton	30.00	30.00
Bleaching Pwd.,35%, works, 100 lbs.	2.25	2.25
Borax, cryst., bbls.............lb.	.06	.05¾
Bromine, pure.................lb.	.27	.27
Calcium Chloride, fused.......ton	28.75	28.75
Chalk, precipitated, light......lb.	.04	.04
China, Clay, imported.........ton	18.00	18.00
Copper Sulfate............100 lbs.	5.62½	5.62½
Feldspar ....ton	8.00	8.00
Fuller's Earth..............100 lbs.	1.00	1.00
Iodine, resublimed.............lb.	3.50	3.50
Lead Acetate, white crystals....lb.	.13	.12
Nitrate ....lb.	.15	.15
Red American........100 lbs.	.11¼	.11½
White American.......100 lbs.	.09½	.09½
Lime Acetate..............100 lbs.	2.00	2.00
Lithium Carbonate.............lb.	*1.40	*1.40
Magnesium Carbonate, tech.....lb.	.10	.10
Magnesite ....ton	72.00	72.00
Mercury flask.............75 lbs.	*46.00	*45.00
Phosphorus, yellow.............lb.	.30	.30
Plaster of Paris...........100 lbs.	1.50	1.50
Potassium Bichromate..........lb.	.11½	.11½
Bromide, imported.......lb.	*.18	*.18
Carbonate, calc., 80-85%....lb.	.05	.05
Chlorate, cryst...........lb.	*.08	*.08
Hydroxide, 88-92%.........lb.	.04¾	.04½
Iodide, bulk...............lb.	2.75	*2.65
Nitrate ....lb.	.10	.10
Permanganate, U. S. P....lb.	*.27	*.25
Salt Cake, bulk.................ton	25.00	25.00
Silver Nitrate.................oz.	.41½	.42
Soapstone, in bags............ton	12.00	12.00
Soda Ash, 58%, bags......100 lbs.	2.10	2.10
Caustic, 76%.........100 lbs.	3.80	3.80
Sodium Acetate.................lb.	.06	.06
Bicarbonate ....100 lbs.	2.25	2.25
Bichromate ....lb.	.08	.08
Chlorate ....lb.	.07½	.07½
Cyanide ....lb.	.20	.20
Fluoride, technical..........lb.	*.10½	*.10
Hyposulfite, bbls........100 lbs.	3.50	3.50
Nitrate, 95%.........100 lbs.	2.20	2.20
Silicate, 400.............lb.	.01½	.01¼
Sulfide ....lb.	.06	.06
Bisulfite, powdered.........lb.	.06	.06
Strontium Nitrate.............lb.	.12	.12
Sulfur, flowers...........100 lbs.	3.00	3.00
Crude ....long ton	20.00	20.00
Talc, American, white.........ton	18.00	18.00
Tin Bichloride.................lb.	.18	.18
Oxide ....lb.	.40	.40
Zinc Chloride, U. S. P.........lb.	.35	.35
Oxide, bbls.................lb,	.09	.09

ORGANIC CHEMICALS

	August 1	August 15
Acetanilide ....lb.	*.27	*.28
Acid, Acetic, 28 p. c........100 lbs.	2.50	2.50
Glacial ....lb.	.10	.10
Acetylsalicylic ....lb.	*.60	*.60
Benzoic, U.S.P., ex-toluene..lb.	.65	.65
Carbolic, cryst., U.S.P., drs..lb.	10	.10
50- to 110-lb. tins.......lb.	.21	.21
Citric, crystals, bbls.........lb.	*.45	*.45

Acid (Concluded)	August 1	August 15
Oxalic, cryst., bbls..........lb.	.17	.16½
Pyrogallic, resublimed.......lb.	1.75	1.75
Salicylic, bulk, U. S. P.....lb.	*.20	*.19
Tartaric, crystals, U. S. P...lb.	*.28	*.27
Trichloroacetic, U. S. P....lb.	4.40	4.40
Acetone, drums.................lb.	.12½	.12½
Alcohol, denatured, complete...gal.	.37	.35
Ethyl, 190 proof...........gal.	4.75	4.75
Amyl Acetate.................gal.	2.15	2.15
Camphor, Jap, refined.........lb.	.77	.72
Carbon Bisulfide...............lb.	.06	.06
Tetrachloride ....lb.	10½	.10½
Chloroform, U. S. P...........lb.	*.38	*.38
Creosote, U. S. P..............lb.	.40	.40
Cresol, U. S. P................lb.	.17	.17
Dextrin, corn............100 lbs.	2.85	2.85
Imported Potato...........lb.	.07	.07
Ether, U. S. P., conc., 100 lbs...lb.	.16	.16
Formaldehyde ....lb.	*.13	*.12½
Glycerol, dynamite, drums......lb.	.12½	.13
Methanol, pure, bbls..........gal.	1.25	1.25
Pyridine ....gal.	2.75	2.75
Starch, corn............100 lbs.	2.28	2.28
Potato, Jap...............lb.	.05	.05
Rice ....lb.	.18	.18
Sago ....lb.	.04½	.04½

OILS, WAXES, ETC.

	August 1	August 15
Beeswax, pure, white.........lb.	.40	.37
Black Mineral Oil, 29 gravity..gal.	.22	.22
Castor Oil, No. 3..............lb.	.08½	.09
Ceresin, yellow...............lb.	.10	.08½
Corn Oil, crude, tanks, mills...lb.	.06¼	.06¾
Cottonseed Oil, crude, f.o.b. mill.lb.	.06¾	.07
Linseed Oil, raw (car lots)....gal.	.78	.73
Menhaden Oil, crude (south'n).gal.	.30	.30
Neat's-foot Oil, 200...........gal.	1.00	1.00
Paraffin, 128-130 m. p., ref......lb.	.06	.06
Paraffin Oil, high viscosity....gal.	.45	.45
Rosin, "F" Grade, 280 lbs......bbl.	5.40	5.40
Rosin Oil, first run...........gal.	.35	.35
Shellac, T. N..................lb.	.52	.44
Spermaceti, cake...............lb.	.30	.30
Sperm Oil, bleached winter,380.gal.	1.73	1.73
Stearic Acid, double-pressed....lb.	.09¼	.09*
Tallow, Oil, acidless..........gal.	.65	.65
Tar Oil, distilled.............gal.	.60	.60
Turpentine, spirits of.........gal.	.59	.65

METALS

	August 1	August 15
Aluminium, No. 1, ingots........lb.	.21	.21
Antimony, ordinary........100 lbs.	4.87½	4.87½
Bismuth ....lb.	1.50	1.50
Copper, electrolytic............lb.	.12	.11¾
Lake ....lb.	.12¼	.12
Lead, N. Y...................lb.	.04½	.04½
Nickel, electrolytic...........lb.	.41	.41
Platinum, refined, soft.........oz.	72.00	72.00
Quicksilver, flask.......75 lbs. ea.	46.00	45.00
Silver, foreign...............oz.	.61	.61⅞
Tin ....lb.	.27	.27
Tungsten Wolframite......per unit	3.25	3.25
Zinc, N. Y................100 lbs.	4.50	4.50

FERTILIZER MATERIALS

	August 1	August 15
Ammonium Sulfate, export.100 lbs.	2.15	2.15
Blood, dried, f. o. b. N. Y......unit	3.00	3.00
Bone, 3 and 50, ground, raw...ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia	4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works ....unit	2.90 & .10	2.90 & .10
Phosphate Rock, f. o. b. mine:		
Florida Pebble, 68%.......ton	5.00	5.00
Tennessee, 78-80%.........ton	8.00	8.00
Potassium Muriate, 80%.......unit	.90	.90
Pyrites, furnace size, imp'ted..unit	.14	.14
Tankage, high-grade, f. o. b. Chicago ....unit	2.25 & .10	2.25 & .10

* Resale or Imported (not an American Maker's price).

COAL-TAR CHEMICALS

Crudes		August 1	August 15
Anthracene, 80-85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.18	.17
Cresylic Acid, 97-99%	gal.	.90	.80
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.10	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	gal.	.60	.45

Intermediates

Acids:

		August 1	August 15
Anthranilic	lb.	1.50	1.50
Benzoic tech.	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.30	1.30
Gamma	lb.	3.00	3.00
H.	lb.	1.15	1.15
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.75	2.75
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.29	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.18	.18
For Red		.42	.42
Aniline Salt	lb.	.26	.26
Anthraquinone	lb.	1.75	1.75
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech.	lb.	.50	.50
U. S. P.	lb.	1.50	1.50
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	5.00	5.00
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.45
Dinitrobenzene	lb.	.25	.25
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.65
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.50	1.50
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.14	.14
Monoethylaniline	lb.	2.00	2.00
a-Naphthylamine	lb.	.38	.38
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist.	lb.	.32	.32
m-Nitroaniline	lb.	.95	.95
p-Nitroaniline	lb.	.80	.80
Nitrobenzene, crude	lb.	.12	.12
Rectified (Oil Mirbane)	lb.	.13¾	.13¾
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.85	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.70	1.70
Phthalic Anhydride	lb.	.40	.40
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.65	.60
Resorcinol, tech.	lb.	1.50	1.50
U. S. P.	lb.	1.75	1.75
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.42	.42
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.45	.45
o-Toluidine	lb.	.25	.25
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		August 1	August 15
Black	lb.	.80	.80

Acid Colors (Concluded)

		August 1	August 15
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III.	lb.	.50	.50
Red	lb.	1.00	1.00
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Brythrosin	lb.	7.50	7.50
Indigotin, conc.	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.70	.70

Direct Colors

		August 1	August 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc.	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		August 1	August 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III.	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

		August 1	August 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90

Chrome Colors

		August 1	August 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.75	.75
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		August 1	August 15
Auramine, O, domestic	lb.	2.25	2.25
Auramine, OO	lb.	4.15	4.15
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	3.50	3.50
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	2.00	2.00
Methylene Blue, tech.	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol.	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	7.00	7.00
Rhodamine B, extra conc.	lb.	10.00	10.00
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00